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SINGAPORE

**UTILIZING ELECTRONIC, IONIC AND PHOTONIC
COUPLING FOR NEUROMORPHIC DEVICES**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2019

UTILIZING ELECTRONIC, IONIC AND PHOTONIC COUPLING FOR NEUROMORPHIC DEVICES

JOHN ROHIT ABRAHAM

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

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A handwritten signature in blue ink, appearing to read 'Rohit', with three horizontal lines underneath.

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John Rohit Abraham

Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

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Nripan Mathews

Authorship Attribution Statement

This thesis contains material from papers published in the following peer-reviewed journals where I was the first author.

Chapter 4 is published as R. A. John, N. Yantara, Y. F. Ng, G. Narasimman, E. Mosconi, D. Meggiolaro, M. R. Kulkarni, P. K. Gopalakrishnan, C. A. Nguyen, F. De Angelis, S. G. Mhaisalkar, A. Basu, N. Mathews. “Ionotronic Halide Perovskite Drift-Diffusive Synapses for Low-Power Neuromorphic Computation”. *Advanced Materials*, 2018, 1805454. DOI:10.1002/adma.201805454.

The contributions of the co-authors are as follows:

- I conceived the idea with guidance from Prof N. Mathews and performed all the laboratory work and analysis at the School of Materials Science and Engineering, NTU.
- Dr. N. Yantara and Y.F. Ng helped with the device fabrication, x-ray diffraction and scanning electron microscopy.
- G. Narasimman performed the neural network simulations under the supervision of Prof. A. Basu.
- Dr. E. Mosconi and D. Meggiolaro carried out the DFT calculations under the supervision of Prof F. De Angelis.
- M. R. Kulkarni and P. K. Gopalakrishnan assisted with the array-level arduino integration experiment.
- I prepared the manuscript drafts. The manuscript was revised by Dr. C. A. Nguyen, Prof. F. De Angelis, Prof. S. G. Mhaisalkar, Prof. A. Basu and Prof. N. Mathews.

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The contributions of the co-authors are as follows:

- I conceived the idea with guidance from Prof. A. Basu and Prof. N. Mathews and performed all the laboratory work and analysis at the School of Materials Science and Engineering, NTU.
- Dr. N Tiwari and M. Kulkarni helped fabricate the thin-film transistors.
- C. Yaoyi, Ankit and N. Tiwari fabricated the solid-state ionic dielectric and also carried out the dielectric spectroscopy, Fourier transform infrared spectroscopy, thermogravimetric analysis and differential scanning calorimetry experiments.
- I prepared the manuscript drafts. The manuscript was revised by Dr. A. Nirmal, Dr. A. C. Nguyen, Prof. A. Basu and Prof. N. Mathews.

Chapter 6 is published as R. A. John, F. Liu, N. A. Chien, M. R. Kulkarni, C. Zhu, Q. Fu, A. Basu, Z. Liu, N. Mathews. “Synergistic Gating of Electro-Iono-Photoactive 2D Chalcogenide Neuristors: Coexistence of Hebbian and Homeostatic Synaptic Metaplasticity”. *Advanced Materials*. 2018, 30, 1800220. DOI:10.1002/adma.201800220.

The contributions of the co-authors are as follows:

- I conceived the idea with guidance from Prof N. Mathews and performed all the laboratory work and analysis at the School of Materials Science and Engineering, NTU.
- Dr. F. Liu contributed equally to the manuscript and helped fabricate the field-effect transistors with C. Zhu and Q. Fu, under the supervision of Prof. Z. Liu.
- Dr. N. A. Chien and M. R. Kulkarni assisted with the data collection and analysis.
- I prepared the manuscript drafts. The manuscript was revised by Dr. N. A. Chien, Prof. Z. Liu, Prof. A. Basu and Prof. N. Mathews.

Chapter 7 is currently being prepared as a manuscript- R. A. John, Ankit, C. Zhu, S. K. Bose, N. S. E. Timothy, N. A. Chien, J. Y. Chan, A. Nirmal, A. Chaturvedi, K. K. Zhang, X. Manzhang, Z. Liu, A. Basu, N. Mathews. “A Dummy Optogenetic Toolkit with Photosensitive Neuristors and Soft Robots”.

The contributions of the co-authors are as follows:

- I conceived the idea with guidance from Prof N. Mathews and Prof. A. Basu and performed all the laboratory work and analysis at the School of Materials Science and Engineering, NTU.
- Ankit fabricated the soft dielectric elastomeric actuators and conducted the actuation experiments along with J. Y. Chan.
- C. Zhu fabricated the field-effect transistors under the supervision of Prof. Z. Liu.
- S. K. Bose configured the neuron circuit with guidance from Prof. A. Basu.
- N. S. E. Timothy, Dr. N. A. Chien, Dr. A. Nirmal and X. Manzhong helped prepare the manuscript.
- A. Chaturvedi and K. K. Zhang provided the ReS₂ crystals.
- I prepared the manuscript drafts. The manuscript was revised by N. S. E. Timothy, Dr. N. A. Chien, Dr. A. Nirmal, Prof. Z. Liu, Prof. A. Basu and Prof. N. Mathews.

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Abstract

Inspired by neural computing, the pursuit of ultralow power neuromorphic architectures with highly distributed memory and parallel processing capability has recently gained more traction. Memristive devices emulating brain-like signal processing forms the foundation for development of efficient learning circuitry, but few devices offer analog-like switching transitions, symmetry, linearity and wide range of dynamic conductance states, necessary for efficient computation. Conventional drift-based memristors relying on stochastic metallic/defect filament formation fall behind in this regard due to their abrupt switching transitions. Very recently, diffusive memristors and second-order drift memristors have been engineered to approximate the biological synaptic dynamics based on metal atom diffusion, thermal dissipation, mobility decay and spontaneous nanoparticle formation. A common feature in all these systems is the insertion/extraction of mobile ions, directly or indirectly altering the electronic conductivity in a continuous analog-like manner. Hence, a hybrid ionic-electronic (ionotronic) conduction mechanism could be considered vital to mimic the biological neural dynamics. This calls for the need of material systems and device configurations where ionic and electronic conductivities co-exists intimately and which could be synergistically controlled in a manner, temporally similar to neural dynamics.

Drawing inspiration from this, the dissertation tackles the hardware switching requirements for bio-inspired computations by adopting novel memristive device configurations encompassing ionically and optically-active semiconductors and dielectrics. Ionic semiconducting properties of halide perovskites are initially investigated in a two-terminal memristive configuration, followed by ionic gating of metal oxide and two-dimensional (2D) transition metal di-chalcogenides (TMDCs) in a three-terminal field-effect configuration. Finally, optical modulation of carrier concentration is exploited to create optoelectronic synapses with multi-modal programmability and higher plasticity. All material sets and device configurations are investigated and compared based on the degree of achievable plasticity -specifically short and long-term plasticity, conductance linearity, symmetry of weight changes and energy consumption.

An ionic semiconductor which couples fast electronic transitions with slow drift-diffusive ionic kinetics would enable energy-efficient analog-like switching of metastable conductance states. Here, the intimate ionic-electronic (ionotronic) coupling in halide perovskite semiconductors is utilized to create memristive synapses with a dynamic continuous transition of conductance states. Co-existence of carrier injection barriers and ion migration in the perovskite films defines the degree of synaptic plasticity, more notable for the larger organic ammonium and formamidinium cations than the inorganic cesium counterpart. Optimized pulsing schemes facilitate a balanced interplay of short and long-term plasticity rules like paired-pulse facilitation and spike time dependent plasticity, cardinal for learning and computing. Trained as a memory array, halide perovskite synapses demonstrate reconfigurability, learning, forgetting and fault tolerance analogous to the human brain. Network-level simulations of unsupervised learning of handwritten digit images utilizing experimentally-derived device parameters, validates the utility of these memristors for energy-efficient neuromorphic computations, paving way for novel ionotronic neuromorphic architectures with halide perovskites as the active material.

In contrast to the abrupt switching transitions in a conventional two-terminal memristor configuration, a three-terminal field-effect transistor (FET) configuration exhibiting time-dependent hysteresis would result in much smoother conductance transitions. A gated control harnessing slow ion diffusive kinetics would enable precise modulation of electronic transitions and an analog programming of channel conductance. Combining multiple gating controls that can induce temporally distinct modulations on the carrier concentration would increase the weight plasticity and memory storage capacity, enabling emulation of more complex neuronal behaviour. Herein, artificial synapses with intimate electronic-ionic (ionotronic) coupling are realized in a dual-gated electric-double-layer neuristor configuration with high-mobility amorphous metal oxide semiconducting channels, a solid-state ionic top dielectric and a bottom electronic insulator. This multi-gated architecture allows one gate to capture the effect of local activity correlations and the second gate to represent global neuromodulations, enabling higher-order temporal correlations like heterosynaptic plasticity, homeostasis and association at a unitary level. The dual-gate operation extends the available dynamic range of synaptic conductance while maintaining symmetry in the weight-update operation, expanding the number of accessible memory states. Finally, operating

neuristors in the sub-threshold regime enables synaptic weight changes with high gain, while maintaining ultralow power consumption of the order of femto-Joules.

Information transmission via light-pulses as opposed to voltage-packets could unlock exceptionally fast transmission speeds with less cross-talk, high parallelism, low noise and nearly unlimited bandwidth. Neuromorphic transistors programmable via multimodal electrical and optical pulses would pave way for novel synergistic architectures encompassing advantages of both electron and photon-based computing platforms. Here, temporal plasticity of 2D TMDC-based neuristors are investigated via synergistic electronic, ionotronic and photoactive gating controls, addressing different charge-trapping probabilities to finely modulate the synaptic weights. The slow recombination of photo-generated carriers augments the ionotronic modulation of channel conductance in such configurations, resulting in orthogonally programmable (electrical + optical) artificial synapses with enhanced plasticity. Synergistic gating controls amalgamate neuromodulation schemes to achieve “plasticity of plasticity-metaplasticity” via dynamic control of Hebbian spike-time dependent plasticity and homeostatic regulation. The optoelectronic gating approach facilitates precise programming of conductance states with high temporal plasticity, wide dynamic conductance range and high linearity, compatible with both spiking and deep neural networks. Photons pulses are utilized for potentiation and electrical pulses for depression of weights, allowing facile emulation of basic arithmetic operations like an abacus, in addition to the bio-inspired plasticity models. Finally, photons are utilized as global, virtual interconnects in an array composed of light sensitive and insensitive elements to selectively modulate plasticity. Global neuromodulations are encompassed as photon packets, regulating the network dynamics. Drawing inspiration from optogenetics, these devices are portrayed as optogenetic actuators in combination with dielectric elastomeric actuators to create an optogenetic toolbox for artificially intelligent behavioural soft robotics.

Lay Summary

The present-day computers are built on a stored-program computer concept or in other words a von Neumann architecture. In this configuration, both instruction and program data are stored in the same memory, and a central processing unit (CPU) manages the process flow and execution of data and program into and out of the memory- one at a time in a serial manner. This architecture limits the performance of the system, especially for data-heavy applications like artificial intelligence (AI) and machine learning (ML) algorithms, since the memory pathway for the data operation and execution cycle is shared, referred to as the von Neumann bottleneck. Although smart software tweaks can be optimized to improve the performance, it is still fundamentally limited by the lack of efficient hardware. This calls for the need of developing hardware circuitry that can overcome this von Neumann bottleneck or in other words have coexisting processing and memory units. Such an in-memory computing would increase the system's efficiency and also save energy.

Unsurprisingly, nature provides a solution to this problem-the brain. The human brain follows a non von Neumann architecture with highly parallel in-memory computations at a low power consumption of ~ 20 W, utilizing the massive interconnectivity achieved between 10^{12} neurons and 10^{15} synapses. Neurons can be considered as nano-processors and synapses as adaptive memory elements responsible for both computing and storing information. Recently, hardware circuitry that seeks to emulate these biological neurons and synapses with comparable performance and power consumption has been defined as a research target to create artificially intelligent machines with computational power matching the human brain. Hardware implementation of physical devices emulating synaptic functionalities thus becomes the foremost challenge in realizing a truly artificially intelligent network in future.

In contrast to the conventional digital logic and memory technology, such brain-inspired or in other words neuromorphic applications demand unique properties from their hardware. Smooth analog-like conductance transitions and memory of the device history that enables learning abilities are necessities for such intelligent circuitry. Conventional silicon-based implementations although efficient, lack the necessary

learning abilities in hardware and instead rely on software algorithms to do the job. The hardware primarily falls behind in terms of the switching requirements, footprint and energy consumption, necessary to match the human brain. In this context, memristive devices that remember the amount of charge that previously flowed through it and retains this memory even without power, promise a great potential. Nonetheless, most memristive implementations depict abrupt switching transitions and lag in terms of true analog-like conductance transitions, adversely affecting the computational efficiency.

This dissertation tackles the hardware switching requirements for bio-inspired computations by adopting novel memristive materials and device configurations that encompass ionically and optically-active semiconductors and dielectrics, directly or indirectly tuning the electronic conductivity on demand. Novel devices exploiting the advantages of electrons, ions and photons are proposed and realized with concurrent compute and store capabilities.

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Table Captions

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Table 4.2 Comparison of energy consumption of our devices with literature. © “From R. A. John, N. Yantara, Y. F. Ng, G. Narasimman, E. Mosconi, D. Meggiolaro, M. R. Kulkarni, P. K. Gopalakrishnan, C. A. Nguyen, F. De Angelis, *Adv. Mater.* 2018, 1805454. Reprinted with permission from John Wiley and Sons.”

Table 4.3 Average values of the current states used for long-term plasticity analysis. © “From R. A. John, N. Yantara, Y. F. Ng, G. Narasimman, E. Mosconi, D. Meggiolaro, M. R. Kulkarni, P. K. Gopalakrishnan, C. A. Nguyen, F. De Angelis, *Adv. Mater.* 2018, 1805454. Reprinted with permission from John Wiley and Sons.”

Table 4.4 The calculated ionic, electronic, and total conductivities of halide perovskite thin films with different cations. © “From R. A. John, N. Yantara, Y. F. Ng, G. Narasimman, E. Mosconi, D. Meggiolaro, M. R. Kulkarni, P. K. Gopalakrishnan, C. A. Nguyen, F. De Angelis, *Adv. Mater.* 2018, 1805454. Reprinted with permission from John Wiley and Sons.”

Table 4.5 Calculated vacancy migration energy barriers (eV) for MAPbBr₃, FAPbBr₃ and CsPbBr₃ using the experimental cell parameters. © “From R. A. John, N. Yantara, Y. F. Ng, G. Narasimman, E. Mosconi, D. Meggiolaro, M. R. Kulkarni, P. K. Gopalakrishnan, C. A. Nguyen, F. De Angelis, *Adv. Mater.* 2018, 1805454. Reprinted with permission from John Wiley and Sons.”

Table 4.6 Calculated defect formation energies (DFE) for A-cation vacancies. © “From R. A. John, N. Yantara, Y. F. Ng, G. Narasimman, E. Mosconi, D. Meggiolaro, M. R. Kulkarni, P. K. Gopalakrishnan, C. A. Nguyen, F. De Angelis, *Adv. Mater.* 2018, 1805454. Reprinted with permission from John Wiley and Sons.”

Table 5.1 Best fit values of PPF decay as a function of pulse interval. "Reprinted with permission from R. A. John, N. Tiwari, C. Yaoyi, * Ankit, N. Tiwari, M. Kulkarni, A. Nirmal, A. C. Nguyen, A. Basu, N. Mathews, *ACS Nano* **2018**. © [2018] American Chemical Society."

Table 5.2 Comparison of Energy Consumption with state of the art. "Reprinted with permission from R. A. John, N. Tiwari, C. Yaoyi, * Ankit, N. Tiwari, M. Kulkarni, A. Nirmal, A. C. Nguyen, A. Basu, N. Mathews, *ACS Nano* **2018**. © [2018] American Chemical Society."

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Figure Captions

Figure 2.1^[1] Computation, communication, and memory. (A) The parallel, distributed architecture of the brain is different from the sequential, centralized von Neumann architecture of today's computers. The trend of increasing power densities and clock frequencies of processors^[2] is headed away from the brain's operating point. Number and POWER processors are from IBM, Incorporated; AMD, Advanced Micro Devices, Incorporated; Pentium, Itanium, and Core 2 Duo, Intel, Incorporated. (B) In terms of computation, a single processor has to simulate both a large number of neurons as well as the inter-neuron communication infrastructure. In terms of memory, the von Neumann bottleneck^[3], which is caused by separation between the external memory and processor, leads to energy-hungry data movement when updating neuron states and when retrieving synapse states. In terms of communication, interprocessor messaging^[4] explodes when simulating highly interconnected networks that do not fit on a single processor. (C) Conceptual blueprint of an architecture that, like the brain, tightly integrates memory, computation, and communication in distributed modules that operate in parallel and communicate via an event-driven network. © "From P. A. Merolla, J. V Arthur, R. Alvarez-Icaza, A. S. Cassidy, J. Sawada, F. Akopyan, B. L. Jackson, N. Imam, C. Guo, Y. Nakamura, *Science*. **2014**, 345, 668. Reprinted with permission from AAAS."

Figure 2.2^[15] Spiking neural network overview using CMOS. The 1.72mm² 10nm FinFET SNN combines sparse connectivity, stochastic operation, voltage scaling, and power gating to achieve 4.8× throughput and 6.8× energy improvements over previously reported SNNs. © [2018] IEEE. "From G. K. Chen, R. Kumar, H. E. Sumbul, P. C. Knag, R. K. Krishnamurthy, in *2018 IEEE Symp. VLSI Circuits*, IEEE, **2018**, pp. 255–256. Reproduced with permission from IEEE."

Figure 2.3^[22–24] Deep Convolutional Neural Networks with Resistive Cross-Point Devices. (A) Schematics of a convolutional layer showing the input volume, kernels, and the output volume. (B) Schematics of a mapped convolutional layer to a Resistive Processing Unit (RPU) array showing the input and output matrixes and their propagation through the kernel matrix during the forward, backward and the update

cycles. (C) shows the typical horizontal and vertical structure of a RPU/RRAM. Morphology and component of conductive filaments (CF) observed in Ag/SiO₂/Pt planar structure after electroforming with various compliance current (I_{CC}). (D) As-prepared fresh device without any electrical treatment. (E-G) Morphologies of the CF with $I_{CC} = 5$ nA, $I_{CC} = 100$ nA and $I_{CC} = 100$ μ A, respectively. © “From T. Gokmen, M. Onen, W. Haensch, *Front. Neurosci.* **2017**, *11*, 538. Reproduced as per the Creative Commons License Deed.”; “Reprinted from Monolithic 3D neuromorphic computing system with hybrid CMOS and memristor-based synapses and neurons. H. An, M. A. Ehsan, Z. Zhou, F. Shen, Y. Yi, *Integr. VLSI J.* **2017**. © (2017), with permission from Elsevier.”; © “From H. Sun, Q. Liu, C. Li, S. Long, H. Lv, C. Bi, Z. Huo, L. Li, M. Liu, *Adv. Funct. Mater.* **2014**, *24*, 5679. Reprinted with permission from John Wiley and Sons.”

Figure 2.4^[45] The multistore model and the human-memory forgetting curve. (A) The psychological model of human memory proposed by Atkinson and Shiffrin. This multistore model provides for three types of memory, that is, sensory memory (SM), short-term memory (STM) and long-term memory (LTM). (B) Simplified memorization model in the inorganic synapse, which was inspired by the multistore model. After storing new information as SM, information is stored in STM for short periods of time, whereas repeated rehearsal events result in LTM. At a higher repetition rate, rehearsal before complete decay in memorization level forms LTM, as shown by the red line. Rehearsal at lower repetition rate cannot form LTM, as shown by the blue line. (C) Typical change of memory retention in the inorganic synapse for the decay in STM mode. A power function, used to analyse psychological behaviour such as STM^[46], $y = b \times t^{-m}$, was used to fit the conductance curves, where y is the memory retention, b is the fit constant for scaling, t is the time from the n^{th} rehearsal and m is the power function rate. Memory retention was normalized using a conductance value of 77.5 μ S. The conditions of the input pulse were $V = 80$ mV, $W = 0.5$ s and $T = 4$ s. **Inorganic synapse showing STP and LTP, depending on input-pulse repetition time.** (D) Schematics of a Ag₂S inorganic synapse and the signal transmission of a biological synapse. Application of input pulses causes the precipitation of Ag atoms from the Ag₂S electrode, resulting in the formation of a Ag atomic bridge between the Ag₂S electrode and a counter metal electrode. When the precipitated Ag atoms do not

form a bridge, the inorganic synapse works as STP. After an atomic bridge is formed, it works as LTP. In the case of a biological synapse, the release of neurotransmitters is caused by the arrival of action potentials generated by firing, and then a signal is transmitted as a synaptic potential. Frequent stimulation causes long-term enhancement in the strength of the synaptic connection. **(E,F)** Change in the conductance of the inorganic synapse when the input pulses ($V = 80$ mV, $W = 0.5$ s) were applied with intervals of $T = 20$ s **(E)** and 2 s **(F)**. The conductance of the inorganic synapse with a single atomic contact is $2e^2/h$ ($=77.5$ μ S), where e is the elementary charge, and h is Planck's constant. Reprinted by permission from Springer Nature [Nature Materials], "From T. Ohno, T. Hasegawa, T. Tsuruoka, K. Terabe, J. K. Gimzewski, M. Aono, *Nat. Mater.* 2011, 10, 591. © 2011."

Figure 2.5^[62] The mechanisms of Ag nanowire growth and shrinkage; **(A)** the activation energies for reduction (E_R) and oxidation (E_O) are equal in the equilibrium condition without any bias application. **(B)** Application of positive bias to the Ag₂S electrode causes the diffusion of Ag⁺ cations towards the surface of the Ag₂S electrode, making E_R smaller than E_O , which enhances the reduction of Ag⁺ cations into Ag atoms. **(C)** Application of negative bias to the Ag₂S electrode causes a diffusion of Ag⁺ cations towards the bottom of the Ag₂S electrode, making E_O smaller than E_R , which enhances the oxidation of the precipitated Ag atoms into Ag⁺ cations, re-dissolving into the Ag₂S electrode. © "From T. Hasegawa, K. Terabe, T. Tsuruoka, M. Aono, *Adv. Mater.* 2012, 24, 252. Reprinted with permission from John Wiley and Sons."

Figure 2.6^[73] **Schematic illustration of the growth of a conductive filament during electroforming.** In device type A, having two inert electrodes – filament grows from the cathode towards the anode **(A)** and **(B)**. In device type B with an OEL – filament grows from the OEL regardless of the polarity: **(C)** filament grows from the OEL anode towards the cathode or **(D)** filament grows from the cathode, when the anode is inert. © "Republished with permission of RSC Pub from E. Yalon, I. Karpov, V. Karpov, I. Riess, D. Kalaev, D. Ritter, *Nanoscale* 2015, 7, 15434; permission conveyed through Copyright Clearance Center, Inc."

Figure 2.7^[77] Three types of RRAM and the corresponding characteristics comparison. (A) Filamentary analog RRAM with multiple-weak-filaments; (B) conventional strong-filament based RRAM; (C) non-filamentary RRAM; (D) comparison of five specifications. © [2017] IEEE. “From M. Zhao, H. Wu, B. Gao, Q. Zhang, W. Wu, S. Wang, Y. Xi, D. Wu, N. Deng, S. Yu, in *Electron Devices Meet. (IEDM), 2017 IEEE Int.*, IEEE, 2017, pp. 34–39. Reproduced with permission from IEEE.”

Figure 2.8^[102] The structure of a CNT synapse and a post-synaptic current triggered by a pre-synaptic spike. (A) A schematic diagram showing the transistor-like structure of a CNT synapse with an electrochemical cell containing hydrogen ions in a polymer electrolyte integrated in its gate. The inset is an atomic force microscopy (AFM) image of a random CNT network. The average density of the single-wall CNTs is $\sim 8/\mu\text{m}^2$, and the average density of the CNT bundles is $\sim 2/\mu\text{m}^2$. (B) A scheme showing a biological synapse between a pre-synaptic neuron and a post-synaptic neuron. (C) A symbol represents the CNT synapse within a scheme showing that a pre-synaptic potential spike applied on its top gate triggers an excitatory post-synaptic current (EPSC) on its drain. (D) A pre-synaptic spike (top) applied on a CNT synapse and EPSC (bottom) triggered by the spikes are shown versus time. The superimposed grey lines represent the EPSCs measured from 20 independent tests, and the red line represents the average EPSC. The insets illustrate the distributions of the mobile hydrogen ions (red balls) in the polymer layer and free electrons (blue balls) in the CNT before (left), during (middle), and after (right) the pre-synaptic spike is applied. © “From K. Kim, C. Chen, Q. Truong, A. M. Shen, Y. Chen, *Adv. Mater.* **2013**, 25, 1693. Reprinted with permission from John Wiley and Sons.”

Figure 2.9^[121] Comparison of typical bipolar-curves of two different types of memristive devices. (A–B) I – V curves and schematic drawings of a class of memristive devices, where the resistance switching is based on ionic motion. (C) Emulation of synaptic plasticity with an individual $\text{TiN}/\text{Al}_2\text{O}_3/\text{TiO}_{2-x}/\text{TiN}$ cell. A sequence of potentiation pulses of + 2 V and depression pulses of - 2 V. The pulse width for the measurements was $t_{\text{set}} = 10$ ms. (D) Emulation of synaptic plasticity with an $\text{Al}/\text{Al}_2\text{O}_3/\text{TiO}_{2-x}/\text{Al}$ cell. A sequence of potentiation pulses of + 3.4 V followed by a sequence of depression pulses of - 3.4 V. The pulse width for the measurements was t_{set}

= 10 ms. © [2015] IEEE. “From M. Ziegler, C. Riggert, M. Hansen, T. Bartsch, H. Kohlstedt, *IEEE Trans. Biomed. Circuits Syst.* **2015**, 9, 197. Reproduced with permission from IEEE.”

Figure 3.1^[15] Device architecture. Architecture of an artificial synapse with halide perovskites as the active switching materials. © “From R. A. John, N. Yantara, Y. F. Ng, G. Narasimman, E. Mosconi, D. Meggiolaro, M. R. Kulkarni, P. K. Gopalakrishnan, C. A. Nguyen, F. De Angelis, S. G. Mhaisalkar, A. Basu, N. Mathews, *Adv. Mater.* **2018**, 1805454. Reprinted with permission from John Wiley and Sons.”

Figure 3.2^[16] Device architecture. Chemical structures of the [EMIM][TFSI] ionic liquid (top) and the P(VDF-HFP) copolymer (bottom) which are cured to obtain free-standing ion gels (*left*). The proposed dual-gated architecture of oxide neuristors (*right*). "Reprinted with permission from R. A. John, N. Tiwari, C. Yaoyi, * Ankit, N. Tiwari, M. Kulkarni, A. Nirmal, A. C. Nguyen, A. Basu, N. Mathews, *ACS Nano* **2018**. © [2018] American Chemical Society."

Figure 3.3^[17] Device architecture. The proposed multi-gated architecture of MoS₂ neuristors. © “From R. A. John, F. Liu, N. A. Chien, M. R. Kulkarni, C. Zhu, Q. Fu, A. Basu, Z. Liu, N. Mathews, *Adv. Mater.* **2018**, 1800220. Reprinted with permission from John Wiley and Sons.”

Figure 3.4 Device architecture. The proposed architecture of ReS₂ neuristors.

Figure 3.5 DEA Fabrication. The figure depicts various stages of the actuator fabrication.

Figure 4.1 Biological and Artificial Synapses. (A) Schematic of the biological synaptic transmission. Arrival of an action-potential causes selective endocytosis and exocytosis of Na⁺, K⁺ and Ca²⁺ deciding the extent of membrane polarization. (B) Architecture of an artificial synapse with halide perovskites as the active switching materials. Three different materials namely MAPbBr₃, FAPbBr₃ and CsPbBr₃ are investigated as switching matrices. The memristive/hysteretic electrical effects in

halide perovskites are utilized to create and modulate plasticity in these devices. © “From R. A. John, N. Yantara, Y. F. Ng, G. Narasimman, E. Mosconi, D. Meggiolaro, M. R. Kulkarni, P. K. Gopalakrishnan, C. A. Nguyen, F. De Angelis, S. G. Mhaisalkar, A. Basu, N. Mathews, *Adv. Mater.* **2018**, 1805454. Reprinted with permission from John Wiley and Sons.”

Figure 4.2 Physical Characterization of halide perovskites and their DC I-V memristive characteristics. (A) XRD spectra of MAPbBr₃, FAPbBr₃, and CsPbBr₃ films respectively, (B) Cross-sectional SEM images of the halide perovskite films deposited on ITO-PEDOT: PSS. (C) Energy band diagram of the device architecture used. (D-F) Standard memristor characteristics for MAPbBr₃, FAPbBr₃ and CsPbBr₃-based thin film devices [Device structure: Au/perovskite/ITO]. © “From R. A. John, N. Yantara, Y. F. Ng, G. Narasimman, E. Mosconi, D. Meggiolaro, M. R. Kulkarni, P. K. Gopalakrishnan, C. A. Nguyen, F. De Angelis, S. G. Mhaisalkar, A. Basu, N. Mathews, *Adv. Mater.* **2018**, 1805454. Reprinted with permission from John Wiley and Sons.”

Figure 4.3 Short-term plasticity in halide perovskite memristors. (A) PPF index comparison between MAPbBr₃, FAPbBr₃ and CsPbBr₃. PPF index is defined as the amplitude ratio between the second (A₂) and the first (A₁) postsynaptic current [$PPF = \left(\frac{A_2}{A_1}\right) * 100\%$)]^[19]. (B) PPF index variation with increasing pulse interval: comparison of MAPbBr₃, FAPbBr₃ and CsPbBr₃. An exponential decay fit is applied to obtain two characteristic timescales as shown in Table 4.1. All the devices under test depicted diode characteristics with the threshold (V_{th}) for sharp current increase varying from 2 to 2.5 V. Hence for a fair comparison between the three systems and not compromising on the energy consumption per spike, pre-conditioning pulses of + 3 V (> V_{th}) were chosen to simulate short-term plasticity. (C) Temporal high-pass filters enabled by frequency-dependent short-term plasticity of halide perovskite memristors. EPSCs in response to presynaptic stimuli trains of different frequencies (2-95 Hz) for MA-based memristors. The stimulus train at each frequency consisted of 10 stimulus spikes of amplitude + 3 V. (D) Filter gain (B₁₀/B₁) plotted as a function of pre-synaptic spike frequency. Note: B₁₀ and B₁ are amplitudes of the 1st and 10th EPSC for each frequency as shown in (C). © “From R. A. John, N. Yantara, Y. F. Ng, G. Narasimman, E.

Mosconi, D. Meggiolaro, M. R. Kulkarni, P. K. Gopalakrishnan, C. A. Nguyen, F. De Angelis, S. G. Mhaisalkar, A. Basu, N. Mathews, *Adv. Mater.* **2018**, 1805454. Reprinted with permission from John Wiley and Sons.”

Figure 4.4 Short-term plasticity-extended and variations. (A) Spike-duration-dependent plasticity (SDDP): Postsynaptic current in the artificial synapse as a function of presynaptic spike width. (B) PPF index variation with pulse interval of MA devices for increasing pulse widths of presynaptic spikes. Variation in (C) EPSCs of MAPbBr₃-based devices and PPF indices of (D) MAPbBr₃, (E) FAPbBr₃, (F) CsPbBr₃-based devices fabricated in a single batch consisting of 32 devices. © “From R. A. John, N. Yantara, Y. F. Ng, G. Narasimman, E. Mosconi, D. Meggiolaro, M. R. Kulkarni, P. K. Gopalakrishnan, C. A. Nguyen, F. De Angelis, S. G. Mhaisalkar, A. Basu, N. Mathews, *Adv. Mater.* **2018**, 1805454. Reprinted with permission from John Wiley and Sons.”

Figure 4.5 Energy Consumption. (A) Comparison of the ON-state energy consumption per spike (E_{on}) of the halide perovskite synapses. (B) Energy scaling of halide perovskite synapses with device area. © “From R. A. John, N. Yantara, Y. F. Ng, G. Narasimman, E. Mosconi, D. Meggiolaro, M. R. Kulkarni, P. K. Gopalakrishnan, C. A. Nguyen, F. De Angelis, S. G. Mhaisalkar, A. Basu, N. Mathews, *Adv. Mater.* **2018**, 1805454. Reprinted with permission from John Wiley and Sons.”

Figure 4.6 Long-term plasticity in halide perovskite synapses. (A) Classification of human memory based on the time scale of retention. The metastable conductance-states consolidated to a permanent state on application of > 10 training pulses of width 500 ms and amplitude + 3 V. (*Left side*) Depicts short-term memory (STM) on application of 2 pulses of amplitude + 3 V, pulse width = 10.5 ms and interval = 5 ms. The current returns back to the original state on removal of the pulse, i.e. volatile change. (*Right side*) Depicts long-term memory (LTM) on application of 40 pulses of amplitude + 3 V, pulse width = 500 ms and interval = 5 ms. The current does not return back to the original state on removal of the pulse, i.e. non-volatile change. This depicts the STM-LTM transition in our devices. Training (B) MAPbBr₃, (C) FAPbBr₃ and (D) CsPbBr₃ synapses with large number of rehearsals resulted in higher weight changes, higher

retention and slower decay of memory. Increasing presynaptic pulse amplitudes also resulted in higher weight changes, higher retention and slower decay of memory as indicated by (E-G). © “From R. A. John, N. Yantara, Y. F. Ng, G. Narasimman, E. Mosconi, D. Meggiolaro, M. R. Kulkarni, P. K. Gopalakrishnan, C. A. Nguyen, F. De Angelis, S. G. Mhaisalkar, A. Basu, N. Mathews, *Adv. Mater.* **2018**, 1805454. Reprinted with permission from John Wiley and Sons.”

Figure 4.7 Long-term plasticity-continued. For weight analysis, the conductance state was allowed to reach a stable steady state and the final conductance state was read by a reading pulse of + 0.5 V. Comparison of the long-term potentiation achieved in (A) MAPbBr₃, FAPbBr₃ and CsPbBr₃-based synapses trained with 40 pulses of amplitude + 3 V, width 500 ms and interval 5 ms. The graph depicts the decay of current 5 seconds after the application of these pulses. (B) The Ebbinghaus forgetting curve depicts the decline of memory retention with time. Highest numerical value of the long-term weight changes were normalized to compare the retention characteristics. Repetitive learning softened the forgetting behaviour. (C) Controlled LTP and LTD were achieved in our devices by applying a series of potentiating and depressing presynaptic spikes. Potentiating spikes were of amplitude + 3 V, while depressing pulses were – 3 V. The degree (slope) of potentiation and depression was dependent on the active material composition and could be further modulated with the amplitude and number of training pulses. Note: Samples with similar initial conductance states were taken for fair analysis. © “From R. A. John, N. Yantara, Y. F. Ng, G. Narasimman, E. Mosconi, D. Meggiolaro, M. R. Kulkarni, P. K. Gopalakrishnan, C. A. Nguyen, F. De Angelis, S. G. Mhaisalkar, A. Basu, N. Mathews, *Adv. Mater.* **2018**, 1805454. Reprinted with permission from John Wiley and Sons.”

Figure 4.8. Hebbian spike-time-dependent plasticity (STDP) variants realized in halide perovskite synapses. (A) Difference in timing of the pre- and post-synaptic pulses (Δt) lead to potentiation (pre before post) or depression (post before pre). In circuit realizations, these differences in timing can be translated into voltage amplitude differences in various ways inducing weight changes (ΔW) in the system and hence, facilitating different types of STDP. The graph on the right side shows the commonly observed STDP curves in biology. Input waveforms (*left side*) applied at the pre and

post-synaptic terminals to realize **(B)** antisymmetric anti-Hebbian, **(C)** antisymmetric Hebbian, **(D)** symmetric Hebbian, **(E)** symmetric anti-Hebbian learning rules (*right side*) in halide perovskite synapses. © “From R. A. John, N. Yantara, Y. F. Ng, G. Narasimman, E. Mosconi, D. Meggiolaro, M. R. Kulkarni, P. K. Gopalakrishnan, C. A. Nguyen, F. De Angelis, S. G. Mhaisalkar, A. Basu, N. Mathews, *Adv. Mater.* **2018**, 1805454. Reprinted with permission from John Wiley and Sons.”

Figure 4.9 Neuromorphic halide perovskite memory array for pattern recognition.

(A) A 4x4 array of halide perovskite synapses was implemented as a reconfigurable and trainable memory unit with fault tolerance. The image of “N” was programmed into the array using an external microcontroller biasing (5 V, 10 seconds) individual pixels on demand with others in a floating-mode. With time, these synapses exhibited extinction of memory analogous to forgetting but could be retrained faster to reach the same conductance levels. **(B)** After complete erasing of the image of “N”, “T” and “U” were also programmed and erased. **(C)** The memory array also exhibits good fault tolerance and robustness to spurious inputs. Spurious inputs of + 1.5 V, 10 ms did not affect the conductance state on a long time-scale and the pixels could be read successfully. **(D)** The proposed two-layer neural network that is trained in simulations to recognize handwritten digits selected from the MNIST database. All input pixels connect to each excitatory neuron in layer 1 through synapses equipped with STDP behavior. Each excitatory neuron connects to an inhibitory neuron in layer 2 through fixed weight excitatory synapses. Each inhibitory neuron connects to all layer 1 neurons using fixed weight inhibitory synapses inducing winner-take-all based competition among layer 1 neurons. The receptive fields of 100 neurons in the excitatory layer obtained after training on 6000 images are shown here. © “From R. A. John, N. Yantara, Y. F. Ng, G. Narasimman, E. Mosconi, D. Meggiolaro, M. R. Kulkarni, P. K. Gopalakrishnan, C. A. Nguyen, F. De Angelis, S. G. Mhaisalkar, A. Basu, N. Mathews, *Adv. Mater.* **2018**, 1805454. Reprinted with permission from John Wiley and Sons.”

Figure 4.10 Proposed ionic and electronic conduction in halide perovskites. (A) Galvanostatic measurement setup for ion migration kinetics. Electronic resistance of the films extracted from **(B)** was used to decouple ionic resistance from the total resistance (ionic- blue region and electronic- yellow region) **(C)** for a constant current

level. Al_2O_3 (2 nm) was used as an ion blocking layer for this measurement. **(D)** Vacancy-mediated migration-pathways for A-site cations and bromide anions with the calculated activation energies obtained from density functional theory (DFT) calculations. **(E)** Schematic of ion migration in halide perovskite synapses. Pulse induced ion redistribution in halide perovskites causes self p- and n-doping and defect passivation, resulting in better carrier injection into the devices. Removal of the bias causes the ions to relax back. This ion migration-relaxation (drift-diffusion) kinetics is modulated by the pre- and post-synaptic training pulse characteristics like amplitude and frequency, to create short and long-term plasticity. © “From R. A. John, N. Yantara, Y. F. Ng, G. Narasimman, E. Mosconi, D. Meggiolaro, M. R. Kulkarni, P. K. Gopalakrishnan, C. A. Nguyen, F. De Angelis, S. G. Mhaisalkar, A. Basu, N. Mathews, *Adv. Mater.* **2018**, 1805454. Reprinted with permission from John Wiley and Sons.”

Figure 5.1 **(A)** Synaptic transmission steps (left) and the proposed multi-gated architecture of analogous artificial oxide neuristors (right). Transfer and Output characteristics of IWO TFTs in the **(B-C)** electronic global-gated mode **(D-E)** ionotronic local-gated mode. While SiO_2 serves as the back-gate dielectric in the global-gated mode, ion gel serves as the top-gate dielectric in the local-gated mode. "Reprinted with permission from R. A. John, N. Tiwari, C. Yaoyi, * Ankit, N. Tiwari, M. Kulkarni, A. Nirmal, A. C. Nguyen, A. Basu, N. Mathews, *ACS Nano* **2018**. © [2018] American Chemical Society."

Figure 5.2 Physical Characterization of the solid-state ionic dielectric. **(A)** Frequency dependence of specific capacitance for the free-standing ion gel dielectric. Inset shows scanning electron microscopy image of the ion gel. **(B)** FTIR, **(C)** DSC and **(D)** TGA spectra of the (PVDF-HFP) polymer, Ionic liquid (EMITFSI) and ((PVDF-HFP) +EMITFSI) ion gel.

Figure 5.3 A pair of presynaptic action potentials (pulse width = 20 ms, interval = 10 ms, input waveforms are shown as inset) triggered a pair of excitatory postsynaptic currents (EPSCs) with increasing amplitude due to hysteresis. This phenomenon known as paired pulse facilitation (PPF) reflects the number of residual carriers during trapping-detrapping mechanisms in the global-gated mode **(A)** and ion migration

relaxation kinetics in the local-gated mode **(B)**. **(C)** PPF index, defined as [$PPF = \left(\frac{A_2}{A_1}\right) * 100\%$] is plotted as a function of inter-spike interval to demonstrate the decay process. It quantifies the degree of facilitation and indicates the vesicular release probability, in agreement with the residual Ca^{2+} hypothesis by Katz and Miledi.^[21] **(D-F)** Reversal of polarity of presynaptic action potentials result in short-term depression or paired pulse depression, with the indices dependent on pulse width and interval of the presynaptic action potentials, similar to facilitation. Frequency dependent volatile changes in conductivity/weights create high-pass filtering of signals in the **(G)** global-gated and **(H)** local-gated modes of operation. **(I)** Frequency of presynaptic action potentials determine the gain of temporal filters. "Reprinted with permission from R. A. John, N. Tiwari, C. Yaoyi, * Ankit, N. Tiwari, M. Kulkarni, A. Nirmal, A. C. Nguyen, A. Basu, N. Mathews, *ACS Nano* **2018**. © [2018] American Chemical Society."

Figure 5.4 Energy Consumption. **(A)** Comparison of the ON-state energy consumption per spike (E_{on}) of oxide neuristors in the global and local-gated modes of operation. E_{on} was calculated from the equation $E_{on} = I_{peak,first} \times t \times V_{ds}$; where I_{peak} is the peak value of 1st generated EPSC, t is the spike duration, and V_{ds} is the applied drain voltage.^[29] Scaling down of device dimensions and reducing spike durations to sub-millisecond levels could be also utilized as strategies to decrease the energy consumption per event even further. The values reported are for the best performing devices. **(B)** Variation of energy consumption with device scaling. "Reprinted with permission from R. A. John, N. Tiwari, C. Yaoyi, * Ankit, N. Tiwari, M. Kulkarni, A. Nirmal, A. C. Nguyen, A. Basu, N. Mathews, *ACS Nano* **2018**. © [2018] American Chemical Society."

Figure 5.5 Long-term Plasticity. Representative Long-term potentiation (LTP) **(A)** and depression (LTD) **(B)** in global-gated mode. LTP **(C)** and LTD **(D)** in the local-gated mode. The devices were pre-programmed to a common initial conductance state prior to these measurements for a fair analysis. "Reprinted with permission from R. A. John, N. Tiwari, C. Yaoyi, * Ankit, N. Tiwari, M. Kulkarni, A. Nirmal, A. C. Nguyen, A. Basu, N. Mathews, *ACS Nano* **2018**. © [2018] American Chemical Society."

Figure 5.6 Long-term Plasticity-continued. (A) The forgetting curve depicts the decline of memory retention with time. Highest numerical value of the long-term weight changes in the two operational modes were normalized to compare the retention characteristics. Repetitive learning softened the forgetting behaviour in both modes as shown. Input waveforms used for STDP measurements in the (B) global-gated and (C) local-gated modes respectively. A read pulse of + 0.1 V is applied at the drain terminal to read the memconductance states before and after the STDP write operations. (D) Relative timing between pre- and postsynaptic spikes created voltage differences across the neuristors, permanently strengthening and weakening the synaptic connections, also called Spike-timing-dependent plasticity (STDP). While the weight change pattern in the global-gated mode followed a STDP rule, a “reverse” STDP (rSTDP) rule was exhibited in the local-gated mode. "Reprinted with permission from R. A. John, N. Tiwari, C. Yaoyi, * Ankit, N. Tiwari, M. Kulkarni, A. Nirmal, A. C. Nguyen, A. Basu, N. Mathews, *ACS Nano* **2018**. © [2018] American Chemical Society."

Figure 5.7 Dual-gated configuration enables multi-level memory in neuristors. Linear variation of channel conductance with write operations featuring 8 (3-bit storage) distinct conductance levels for all 3 operational modes but spanning different conductance ranges. Symmetric presynaptic voltage write-pulses of constant magnitude + 1.5 V (local-gated), +20 V (global-gated) and number (10) were applied to generate the conductance linearity curve. The memconductance states were addressed using a drain bias of + 0.1 V. "Reprinted with permission from R. A. John, N. Tiwari, C. Yaoyi, * Ankit, N. Tiwari, M. Kulkarni, A. Nirmal, A. C. Nguyen, A. Basu, N. Mathews, *ACS Nano* 2018. © [2018] American Chemical Society."

Figure 5.8 Modulations of strength of LTP-LTD realized via multiple gating. (A) Controlled facilitation and depression were achieved in our devices by applying a series of potentiating and depressing presynaptic spikes. Potentiating spikes for the global-gated mode involved spikes of amplitude - 20 V and pulse width 500 ms, and + 1.5 V for the local-gated mode. The dual-gated mode allowed weight modulations with improved strength. For the dual-gated mode, both global and local presynaptic spikes were applied simultaneously. (B) Long-term potentiation achieved in the global-gated mode is regulated by depression in the global, local and dual-gated modes via selective

gating. The slopes of depression depend on the operation mode activated to homeostatically stabilize the runaway synaptic potentiation. Long-term potentiation in the local (**C**) and dual-gated modes (**D**) are regulated by depression in the other modes. Potentiating spikes for the global-gated mode involved spikes of amplitude - 20 V and pulse width 500 ms, and + 1.5 V for the local-gated mode. For the dual-gated mode, both global and local presynaptic spikes were applied simultaneously. "Reprinted with permission from R. A. John, N. Tiwari, C. Yaoyi, * Ankit, N. Tiwari, M. Kulkarni, A. Nirmal, A. C. Nguyen, A. Basu, N. Mathews, *ACS Nano* **2018**. © [2018] American Chemical Society."

Figure 5.9 Dual-gated configuration enables higher order temporal correlations in neuristors. Modulation of temporal filter characteristics with additional gating. Level shifting was achieved with the second control gate and without any additional circuitry. "Reprinted with permission from R. A. John, N. Tiwari, C. Yaoyi, * Ankit, N. Tiwari, M. Kulkarni, A. Nirmal, A. C. Nguyen, A. Basu, N. Mathews, *ACS Nano* **2018**. © [2018] American Chemical Society."

Figure 5.10 Heterosynaptic Plasticity. (A) depicts the input waveforms applied at the pre and post-synaptic terminals. Higher order temporal correlations were achieved *via* interaction between two different presynaptic action potentials and the postsynaptic action potential, creating real-time modulations of the standard STDP behaviour. (B) The dual gating approach allowed the second gate terminal to modulate the weight changes caused by the first gate, augmenting the plasticity and enabling higher order temporal correlations. The nature and degree of the effective conductance/weight change depended on temporal correlations between the postsynaptic sequence and two different input sequences (pre-synaptic and modulatory), resulting in heterosynaptic plasticity. "Reprinted with permission from R. A. John, N. Tiwari, C. Yaoyi, * Ankit, N. Tiwari, M. Kulkarni, A. Nirmal, A. C. Nguyen, A. Basu, N. Mathews, *ACS Nano* **2018**. © [2018] American Chemical Society."

Figure 5.11 Schematic of the concept of Pavlov's dog experiment for associative memory. Prior to conditioning, the Pavlov's dog salivated to unconditioned stimuli alone (stage: i). Here, 12 μ A was set as the threshold for salivation. Persistent training

with simultaneous application of unconditioned and conditioned stimuli created association between them, after which the Pavlov's dog salivated to independent application of conditioned stimuli (stages: ii-iii). The association was weakened and became extinct with time on training with conditioned stimuli alone (stage: iv). However, retraining helped recover this association within a shorter time scale (stage: v-vi). "Reprinted with permission from R. A. John, N. Tiwari, C. Yaoyi, * Ankit, N. Tiwari, M. Kulkarni, A. Nirmal, A. C. Nguyen, A. Basu, N. Mathews, *ACS Nano* **2018**. © [2018] American Chemical Society."

Figure 5.12 Coincidence Detection. (A) Schematic of the neuronal basis underlying interaural time difference (ITD) based audio signal-processing, (B) Spikes applied at two physically separate local and global gates. The depicted waveforms represent an example of the above-threshold region of operation. (C) Input spikes applied with a delay at two physically separate gate terminals, akin to ITD as proposed by Jeffress model, created symmetric weight changes or coincidence. Coincidence detectors operating in the sub-threshold region depicted a wider weight change window, reflecting higher sensitivity. "Reprinted with permission from R. A. John, N. Tiwari, C. Yaoyi, * Ankit, N. Tiwari, M. Kulkarni, A. Nirmal, A. C. Nguyen, A. Basu, N. Mathews, *ACS Nano* **2018**. © [2018] American Chemical Society."

Figure 5.13 Sub-threshold operation of neuristors. Long-term weight changes and STDP learning rules programmed in the sub-threshold region yielded higher conductance changes when compared to above-threshold region. (A) depicts symmetric potentiation and depression weight changes achieved as a function of the gate voltage. Input waveforms corresponding to (B) was used for STDP measurements at each step of gate voltage corresponding to the transfer characteristics of the neuristor. Weight changes were defined by effective write voltages ($V_{\text{write}} = V_{\text{max}} - V_{\text{min}}$) and read voltages equivalent to V_{min} were used to read the memconductance states (C). (D-E) Programming of neuristors create long-term weight changes in channel conductance (weight), reflected as threshold voltage (V_{th}) shifts of neuristors as a function of the programming gate voltage. "Reprinted with permission from R. A. John, N. Tiwari, C. Yaoyi, * Ankit, N. Tiwari, M. Kulkarni, A. Nirmal, A. C. Nguyen, A. Basu, N. Mathews, *ACS Nano* **2018**. © [2018] American Chemical Society."

Figure 6.1 (A) Raman-spectra of multilayer MoS₂ flake depicting the in-plane E_{12g} mode and the out-of-plane A_{1g} mode. (B) PL spectra indicating transition from direct to indirect bandgap with increasing number of MoS₂ layers. (C) AFM image at the MoS₂ flake edge. (D) Optical image of the MoS₂ flake. © “From R. A. John, F. Liu, N. A. Chien, M. R. Kulkarni, C. Zhu, Q. Fu, A. Basu, Z. Liu, N. Mathews, *Adv. Mater.* **2018**, 1800220. Reprinted with permission from John Wiley and Sons.”

Figure 6.2 Biological and Artificial Synapse. (A) Schematic of biological synaptic transmission. (B) The proposed multi-gated architecture of analogous artificial MoS₂ synapses. © “From R. A. John, F. Liu, N. A. Chien, M. R. Kulkarni, C. Zhu, Q. Fu, A. Basu, Z. Liu, N. Mathews, *Adv. Mater.* **2018**, 1800220. Reprinted with permission from John Wiley and Sons.”

Figure 6.3 Transistor Characteristics. Transfer characteristics of (A) Back-gated MoS₂ – SiO₂ architecture (electronic-mode) (B) Top gated MoS₂ – IL configuration (ionotronic-mode). Output characteristics of devices in (C) electronic-mode and (D) ionotronic-mode. (E) Working principle of ionotronic MoS₂ electric-double-layer (EDL) transistors. (i) initial state of the ions in the ionic liquid dielectric before voltage is applied. (ii) on application of positive gate voltage pulse, cations (DEME) in the ionic liquid-polymer dielectric migrate and accumulate at the dielectric-semiconductor interface inducing a channel current in the MoS₂ semiconducting layer. (iii) on removal of gate voltage pulse, the DEME cations gradually relax back to their initial positions, reducing channel conductivity and the drain current gradually decreases back to the resting current. © “From R. A. John, F. Liu, N. A. Chien, M. R. Kulkarni, C. Zhu, Q. Fu, A. Basu, Z. Liu, N. Mathews, *Adv. Mater.* **2018**, 1800220. Reprinted with permission from John Wiley and Sons.”

Figure 6.4 Short-term Plasticity. A single presynaptic spike input induces an excitatory postsynaptic current (EPSC) response in (A) electronic-mode, (B) ionotronic-mode. The current abruptly increases on application of the voltage spike and decays back to the resting current on removal of the voltage spike. A pair of presynaptic spikes (pulse width = 22 ms, interval = 5.3 ms) triggered a pair of EPSCs, with amplitude of the 2nd (A2) higher than the 1st (A1). This indicated facilitation due to

carrier trapping / ionic retention in (C) electronic-mode, (D) ionotronic-mode respectively. (E) PPF index, defined as the ratio of A_2/A_1 , that is $[PPF = \left(\frac{A_2}{A_1}\right) * 100\%]$ is plotted as a function of inter-spike interval to demonstrate the facilitation decay. It quantifies the degree of facilitation and reflects the synaptic vesicular release probability. It also gives an indication of the amount of residual and active Ca^{2+} according to the residual Ca^{2+} hypothesis by Katz and Miledi.^[27] In neuroscience, PPF is responsible for cognitive abilities involving temporal processes and determines the degree of associative learning. (F) Short-term depression emulated in electronic-mode synapses. © “From R. A. John, F. Liu, N. A. Chien, M. R. Kulkarni, C. Zhu, Q. Fu, A. Basu, Z. Liu, N. Mathews, *Adv. Mater.* **2018**, 1800220. Reprinted with permission from John Wiley and Sons.”

Figure 6.5 Short-term Plasticity-continued. EPSCs in response to presynaptic trains of different frequencies. The stimulus train at each frequency consisted of 10 spikes (A) + 50 V (electronic-mode) / (B) + 2 V (ionotronic-mode). (C) Filter gain = A_{10}/A_1 plotted as a function of presynaptic spike frequency. (D) SDDP: EPSC modulation with presynaptic pulse width. (E) Comparison of the ON-state energy consumption per spike (E_{on}) of the MoS_2 synapses as a function of presynaptic pulse width in the electronic and ionotronic-modes. E_{on} was calculated from the equation^[36] $E_{on} = I_{peak} \times t \times V$; where I_{peak} is the maximum value of generated EPSC, t is the spike duration, and V is the applied drain voltage. Further scaling down of device dimensions and reducing spike durations to sub-millisecond levels could be utilized as strategies to bring down the energy consumption per event. © “From R. A. John, F. Liu, N. A. Chien, M. R. Kulkarni, C. Zhu, Q. Fu, A. Basu, Z. Liu, N. Mathews, *Adv. Mater.* **2018**, 1800220. Reprinted with permission from John Wiley and Sons.”

Figure 6.6 Long-term Plasticity (LTP). Increment in LTP strength as a function of persistent training in (A) electronic-mode (magnified view), (B) ionotronic-mode. © “From R. A. John, F. Liu, N. A. Chien, M. R. Kulkarni, C. Zhu, Q. Fu, A. Basu, Z. Liu, N. Mathews, *Adv. Mater.* **2018**, 1800220. Reprinted with permission from John Wiley and Sons.”

Figure 6.7 Long-term Plasticity (LTP)-continued. Increment in LTP strength as a function of persistent training in (A) photoactive-mode (variation with increment in light intensity ($\lambda = 445$ nm, 5.25 mW/mm²). (B) Magnified view of the transient post synaptic conductance change on optical illumination ($\lambda = 445$ nm, 5.25 mW/mm²). (C) Variation in decay / relaxation time as a function of the percentage of incident optical power. © “From R. A. John, F. Liu, N. A. Chien, M. R. Kulkarni, C. Zhu, Q. Fu, A. Basu, Z. Liu, N. Mathews, *Adv. Mater.* **2018**, 1800220. Reprinted with permission from John Wiley and Sons.”

Figure 6.8 Ebbinghaus Forgetting Curve. The graph depicts the retention of memory states in each mode of activation, namely- electronic, ionotronic and phototronic. The maximum current levels are normalized for a fair comparison of the retention properties.

Figure 6.9 Interplay of Hebbian Metaplasticity and Homeostatic Regulation. (A) Input waveforms used to generate STDP data in the ionotronic and electronic-modes respectively. The pulse width used for this measurement = 500 ms. (B) Spike-timing-dependent plasticity (STDP) and “reverse” STDP (rSTDP) achieved with the electronic and ionotronic-modes respectively. Differences in trapping probabilities modulated the PSCs and relative timing between the output and input spikes modified the strength of synaptic weights through facilitation and depression. Reversal of pre- and post-synaptic terminals resulted in reversal of the STDP protocols, as indicated by the dotted lines. (C) Controlled facilitation and depression achieved in our devices with the multi-gated architecture. STDP modulation and homeostatic regulation in the (D) electronic (Asymmetric Hebbian) and (E) ionotronic-mode (Asymmetric anti-Hebbian) of operation. (F) Symmetric Hebbian STDP protocol observed in the photoactive-mode of operation. © “From R. A. John, F. Liu, N. A. Chien, M. R. Kulkarni, C. Zhu, Q. Fu, A. Basu, Z. Liu, N. Mathews, *Adv. Mater.* **2018**, 1800220. Reprinted with permission from John Wiley and Sons.”

Figure 6.10 Classical conditioning Pavlov’s dog experiment. (A) Schematic representing outline of Pavlov’s dog experiment. (B) Voltage pulses/ conditioned stimulus (CS), (C) Optical pulses/unconditioned stimulus (US) and their responses. (D)

Classical conditioning demonstrated by Pavlov's dog experiment. Initially, light pulses (unconditioned stimulus) led to an efficient unconditioned response (salivation) (state a). However, voltage pulses to the back gate (conditioned stimulus) did not lead to an efficient conditioned response before training (current < 500 nA, no salivation). Initial training sequences with conditioned and unconditioned stimuli did not result in effective association as depicted by state b. Repeated training led to strong association, after which conditioned stimulus alone could trigger salivation (states c-f, current > 500 nA). However, the PSCs decreased below the salivation threshold when triggered by conditioned stimulus alone without accompanying unconditioned stimulus for ~ 2 hours, indicating extinction of associative memory (state g). Finally, the association was recovered back faster with simultaneous conditioned and unconditioned stimuli (state h). © "From R. A. John, F. Liu, N. A. Chien, M. R. Kulkarni, C. Zhu, Q. Fu, A. Basu, Z. Liu, N. Mathews, *Adv. Mater.* **2018**, 1800220. Reprinted with permission from John Wiley and Sons."

Figure 7.1 Physical and TFT Characterization of ReS₂ devices. (A-C) AFM and optical images of a ReS₂ sample, respectively. (B) Height profile of ReS₂ flake along the red line in (A), depicting a thickness of ~ 5 nm. (D) Raman spectra of ReS₂. (E-F) Transfer and Output characteristics of ReS₂ neuristors. Inset shows the device architecture.

Figure 7.2 Electrical asymmetric Hebbian STDP rules in ReS₂ neuristors. (A-B) Input waveforms used for STDP measurements. (C-D) Conductance variations corresponding to LTP and LTD without and with optical illumination. (E) STDP: Long-term weight changes as a function of the interval between pre- and post-synaptic spikes (Time_{post-pre}) (dark).

Figure 7.3 photo-modulated Spike Timing Dependent Plasticity (pSTDP) learning rules in ReS₂ neuristors. The devices were subjected to optical stimulations during the STDP measurements. This resulted in a modulation of the STDP window as a function of the wavelength and intensity of photo-dosage and exposure, akin to optogenetic measurements. The graphs (read row-wise) depict the modulations of STDP upon illumination with (A) red (623 nm), (B) green (525 nm) and (C) blue (445 nm) light, as

a function of the intensity of photo-dosage. (D) compares the modulations as a function of the wavelength of illumination for intensities 65, 130, 200 and 230 mW/cm².

Figure 7.4 photo-modulated Spike Timing Dependent Plasticity (pSTDP) learning rule and recovery of the original STDP function. Removal of the optical stimulation resulted in retrieval of the original STDP function as shown above.

Figure 7.5 Optically addressable multi-level memory for DNNs. (A) An input optical pulse train of constant pulse width and interval (10 s, 65 mW/cm² intensity (inset) resulted in a precise stepped increase in conductance equivalent to 1024 distinct conductance states or 10-bit equivalent. (B-D) shows a magnified version of the conductance states (1-16) depicted in (A). During these measurements, the devices were electrically biased at a constant voltage of – 40 V to ensure a low initial conductance state. The switching transitions depended solely on the accumulation and retention of photo-generated carriers. Inset in each graph shows the conductance states (1009-1024). As expected, increased photo-dosage increased the slope further extending the dynamic range, while maintaining linearity as shown in (E-G). The graphs depict states 1-16 as an example.

Figure 7.6 Analysis of endurance during “write”-“erase” operations. Application of synergistic optoelectronic pulses (A) result in precisely controlled near-symmetric bidirectional weight changes via optical potentiation and electrical depression as shown in (B-D). Higher erasing electrical voltages were applied at the back gate to counteract the higher degree of potentiation induced by shorter wavelength optical stimulation. (E-G) Magnified view of the conductance response during the first 128 voltage-controlled cycling tests. (H-M) ΔG vs G plots – a measure of endurance and write noise during cycling tests. Plots (H, J, L) depict the variation in the changes in conductance during “write” operations, while (I, K, M) depict the variations during the “erase” operations for red, green and blue wavelengths of optical stimuli.

Figure 7.7 Retention of the non-volatile states. The devices were switched between the 1st and 16th conductance state and the conductance states were read by a reading voltage of 0.1V. The neuristors depicted excellent retention characteristics (tested up

10^4 seconds) for all the three wavelengths of optical stimulation, namely (A) red, (B) green and (C) blue.

Figure 7.8 Optical Abacus Operation. Precise optical potentiation and electrical depression enabled facile emulation of arithmetic operations, analogous to an abacus. Multiple neuristors were employed to represent the unit's (blue bead), ten's (red bead) and counter's (green bead) place and programming steps were designed as per the arithmetic operation under calculation. Optical stimulations resulting in potentiation represented rightward sliding of the beads, while electrical stimulations causing depression represented leftward sliding of the beads. The modus operandi of the operations are indicated with necessary illustrations as insets.

Figure 7.9 Photon pulses as a global neuromodulatory scheme. (A) Input optical pulse and electrical bias applied on the neuristors. (B) Spatial conductance map of the devices in the initial state. Spatial conductance maps of the neuristors when subjected to (C) red ($\lambda = 623$ nm), (D) green ($\lambda = 525$ nm) and (E) blue ($\lambda = 445$ nm) optical stimuli for intensities varying from 65 to 230 mW/cm².

Figure 7.10 Specificity of the photon-based write pulses. (A) A 36-element array comprising of 16 light sensitive ReS₂ and 20 insensitive IWO neuristors were assembled and initially programmed to a common low conductance state (5 nS). Spatial conductance maps of the neuristors when subjected to (B) red ($\lambda = 623$ nm), (C) green ($\lambda = 525$ nm) and (D) blue ($\lambda = 445$ nm) optical stimuli (intensity = 65 mW/cm²). Illumination with optical stimuli selectively activated the light sensitive low band-gap ReS₂ neuristors without affecting the light insensitive high band-gap IWO neuristors. A spatial conductance map readout of the array resembled the images of “N”, “T” and “U”, with the light sensitive ReS₂ neuristors spatially arranged to resemble these alphabets. These results demonstrate the specificity of a photon-based “write” operation, globally capable of addressing light-sensitive neural elements on demand with high specificity.

Figure 7.11 Selective neuronal firing with optical stimuli. (A) Application of sinusoidal global optical clock signals to the ReS₂ neuristors resulted in a long-term

weight modulation as depicted by the graph on the right. An electrical bias of - 40 V was applied during these measurements to enable a common low initial conductance state of ~ 5 nS. **(B)** A 36-element array comprising of 36 ReS₂ neuristors was assembled and initially programmed to a common low conductance state (5 nS). Selective illumination with optical sinusoidal optical clock stimuli (red and blue) activated the neuristors with each device depicting a non-volatile weight change corresponding to the wavelength. Some of the devices were manually blocked during this illumination experiment (as depicted by the black bars) to realize selectivity. The blue wavelength of irradiation triggered weight changes in the devices as expected, resulting in a final spatial conductance map ~ 102 nS, crossing the pre-set firing threshold of 80 nS. On the other hand, the red wavelength stimulation triggered weight changes to a final value of ~ 13 nS, inactivating neuronal firing.

Figure 7.12 A comprehensive optogenetic toolkit. The photoreceptive neuristors were integrated with soft dielectric elastomeric actuators to comprehensively emulate the biological optogenetic toolkit. The photoreceptive neuristors mimicked the role of opsins and synapses, monitoring the channel conductance/ synaptic weight, akin to optogenetic sensors and the DEA embodied an artificial eye, completing the optogenetic toolkit. Figure shows the flowchart **(A)** and photograph **(B)** of the setup utilized for this experiment.

Figure 8.1 depicts some examples of numerous halide perovskites that differ in their composition and dimensionality. The low-dimensionality perovskites possess highly localized electronic states with strong quantum confinement effects, which could unravel unique memristive switching properties.

Figure 8.2^[19] Circuit diagram of a biomimetic active memristor neuron and active memristor device characteristics. **(A)** Schematic structure of a biological neuron, showing that an action potential is fired near the axon hillock (under sufficient input stimulus) and propagates along the cell axon towards the output synapses. **(B)** Mechanism of voltage-gated Na⁺ and K⁺ ion flows across the cell membrane that accounts for the action potential generation and repetition across the nodes of Ranvier (myelin-sheath gaps). A similar mechanism exists in neurons that lack a myelin sheath.

(C) Basic circuit topology of a two- channel active memristor neuron to emulate the neuronal dynamics in (B). A voltage-gated Na^+ (K^+) channel is emulated by a negatively (positively) d.c. biased active memristor device, which is closely coupled with a local membrane capacitor C_1 (C_2) and a series load resistor R_{L1} (R_{L2}). (D) Schematic structure and a scanning electron micrograph of a typical VO_2 active memristor nano-crossbar device (X_1 or X_2 in (C)). Scale bar: 100 nm. (E) Typical two-terminal quasi d.c. voltage-controlled (force V) and current-controlled (force I) I–V characteristics of a VO_2 active memristor device. A wide hysteresis loop exists in the voltage-controlled mode due to the Mott transitions (blue arrows). The same Mott transitions are manifested by an “S” shaped negative differential resistance (NDR) regime (highlighted by cyan color) with a much narrower hysteresis (red arrows) in the current-controlled mode. In its resting state, the resistor load line for memristor X_1 (or X_2) intersects with its I–V loci outside the NDR regime (green dotted line). An input current or voltage stimulus can shift the load line into the NDR regime (green dashed line) and elicit an action potential generation (spiking). © “From W. Yi, K. K. Tsang, S. K. Lam, X. Bai, J. A. Crowell, E. A. Flores, *Nat. Commun.* **2018**, 9, 4661. Reproduced as per the Creative Commons License Deed.”

Abbreviations

2D	two-dimensional
TMDCs	transition metal di-chalcogenides
FET	field-effect transistor
CPU	central processing unit
AI	artificial intelligence
ML	machine learning
FLOPS	floating point operations per second
CMOS	complementary metal oxide semiconductor
RAMs	random access memories
DAC	digital-to-analog converter
SNN	spiking neural network
DNN	deep neural network
STDP	spike-timing dependent plasticity
AI	artificial intelligence
LEDs	light-emitting diodes
MAPbBr ₃	methylammonium lead bromide (CH ₃ NH ₃ PbBr ₃)
FAPbBr ₃	formamidinium lead bromide (CH(NH ₂) ₂ PbBr ₃)
CsPbBr ₃	cesium lead bromide
TFT	thin film transistor
EDL	electric-double-layer
IWO	indium tungsten oxide
EMIM TFSI	1-ethyl-3-methylimidazoliumbis(trifluoromethylsulfonyl) imide
P(VDF-HFP)	poly (vinylidene fluoride- co -hexafluoropropylene)
SiO ₂	silicon dioxide
MoS ₂	Molybdenum disulphide
ReS ₂	Rhenium disulphide
I	current
V	voltage
NVM	non-volatile memory
CBRAMs	conductive-bridging random access memories
PCMs	phase change memories
RRAMs	resistive random access memories

3D	three-dimensional
I&F	integrate-and-fire
LTP	long-term potentiation
LTD	long-term depression
LIF	leaky-integrate-and-fire
SRAMs	static random access memories
DRAM	dynamic random access memories
T	transistor
R	resistor
CL	conductance linearity
RPU	Resistive Processing Unit
CF	conductive filaments
WTA	winner-take-all
MNIST	Modified National Institute of Standards and Technology
GPU	graphics processing unit
RNG	Random Number Generation
MTJ	Magnetic Tunnel Junction
STP	short-term potentiation
LTP	long-term potentiation
PPF	paired-pulse facilitation
PTP	post-tetanic potentiation
SM	sensory memory
STM	short-term memory
LTM	long-term memory
SRDP	spike-rate dependent plasticity
ANNs	artificial neural networks
CMOL	Cmos + MOLEcular scale device hybrids
HfO ₂	hafnium oxide
GST	Germanium-Antimony-Telluride (Ge ₂ Sb ₂ Te ₅)
Ag ₂ S	silver sulphide
TiO _x	titanium oxide
TaO _x	tantalum oxide
WO _x	tungsten oxide
AlO _x	aluminium oxide

VRRAM	vertical resistive random access memory
MoO _x	molybdenum oxide
Nb _x O _y	niobium oxide
CNT	carbon nanotube
IZO	Indium zinc oxide
NOMFET	nanoparticle organic memory FET
AFM	atomic force microscopy
EPSC	excitatory post-synaptic current
PEDOT:PSS	poly(3,4-ethylenedioxythiophene) polystyrene sulfonate
ENODE	electrochemical neuromorphic organic device
NVRC	non-volatile redox cell
MTJs	magnetic tunnel junctions
NPs	nanoparticles
NiO _x	nickel oxide
FeO _x	iron oxide
DWM	domain wall magnets
IMT	insulator-metal transition
VCM	valence change memory
V _{os}	oxygen vacancies
ECM	electrochemical metallization
ITO	Indium tin oxide
HTL	hole transporting layer
ETL	Electron Transporting Layer
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
Bphen	Bathophenanthroline
UV	ultraviolet
RF	radio frequency
DEMETFSI	[N, N-diethyl-N-(2-methoxyethyl)-N-methyl ammonium bis (trifluoromethylsulfonyl) imide
DEA	dielectric elastomer actuator
TTL	transistor–transistor logic
FESEM	Field emission scanning electron microscopy
XRD	X-ray diffraction

λ	wavelength
θ	angle of diffraction
DFT	density functional theory
SVR	scalar relativistic approach
FTIR	Fourier transform infrared
IR	infrared
DSC	differential scanning calorimetry
TGA	thermogravimetric analysis
DTG	differential thermogravimetry
PL	photoluminescence
PSPD	position-sensitive photo diode
PPF	paired-pulse facilitation
EPSC	excitatory post-synaptic current
SDDP	Spike-Duration-Dependent Plasticity
E_{on}	ON-state energy consumption per spike
LTP	Long-Term Potentiation
LTD	Long-Term Depression
ALD	atomic layer deposition
DFE	defect formation energy
V_{bi}	Built-in voltage
TFT	thin-film transistor
IPSC	inhibitory post synaptic current
PSC	post-synaptic current
MLC	multi-level cell characteristics
DPEs	Dot product engines
ITD	interaural time differences
SNR	signal-to-noise ratio
IL	ionic liquid
STD	short-term depression
V_{ap}	action potential
hBN	hexagonal boron nitride
NMDA	N-methyl-D-aspartate
AMPA	α -amino-3-hydroxy-5-methyl-4-isoxazolepropionic acid
PPC	Persistent photoconductivity

RLPF	random local potential fluctuation
US	unconditioned stimulus
UR	unconditioned response
CS	conditioned stimulus
CR	conditioned response
GECIs	genetically encoded calcium indicators
pSTDP	photo-modulated spike-timing dependent plasticity
ΔG	conductance change
G	absolute conductance
ΔG_{avg}	average conductance change
σ	standard deviation
LDR	light-dependent resistor
TLs	transport layers
IoT	Internet of Things

Chapter 1

Introduction

This chapter introduces the field of neuromorphic electronics with focus on materials research and device configurations. The issues that limit the performance of current devices are identified. General strategies to realize analog switching properties are discussed, followed by research objectives and motivation. In short, it is identified that a hybrid conduction mechanism is necessary to achieve analog switching properties with highly modulatable plasticity, wide dynamic range, good conductance linearity and low programming energy. The research objective of this work is to investigate and compare novel material sets and device configurations that couple electronic, ionic and photonic modes of charge transport to comprehensively emulate complex neuronal characteristics. The motivation is to elucidate the effect of this hybrid charge transport on emulation of synaptic properties in a memristive/ field-effect transistor configuration. Subsequently, the research hypotheses and approaches are detailed. The last section of this chapter provides an overview of the thesis organization with a short introduction of each chapter that follows and the major findings and outcomes.

1.1 Overview

The present digital computing paradigm works on two fundamental attributes: Boolean logic and von Neumann architecture. While these traditional systems are ideal for solving structured problems that involve precisely defined data sets, they lag their biological counterpart- the human brain, in problems involving real-world unstructured data such as images and real-time audio-video recordings. The fundamental difference between these two processors is the way in which memory and processing is organized^[1]. In conventional von Neumann computers, the information storage and processing unit is physically separated, thus requiring a multitude of data transfer exchanges between the processor and memory during computation. In contrast to this conventional serial processing, the human brain utilizes highly parallel, energy-efficient, compute and store architectures comprising of a multitude of neurons (nano-processors) connected via synapses (adaptive memory elements) to achieve 10^{18} floating point operations per second (FLOPS- a measure of computational performance) at a power consumption of ~ 20 W^[2]. With ~ 86 billion neurons in synaptic communication making 10 quadrillion calculations every second, the human brain possesses an unmatched parallel processing power with 17.2 trillion action potentials per second^[3]. Hence, such bio-inspired circuitry that can overcome the von Neumann bottleneck (limitation of throughput due to the inadequate rate of data transfer between memory and the processor) has attracted considerable attention.

Most solutions relying on traditional complementary metal oxide semiconductor (CMOS) devices based on silicon^[4], lack inherent hardware learning abilities and rely on software programming^[5] to implement complex neural networking tasks, restricting their usage. Information packets, generally represented by the device conductance aka synaptic weights, are typically stored in leaky, noisy, power and area-inefficient capacitors and conventional random access memories (RAMs)^[6] and often require post-processing with additional digital-to-analog (DAC) converters. With memory of operational history, atomic-level scalability, non-volatility, low energy consumption and ultrafast switching speeds, nanoscale memristive devices are touted as potential building blocks for brain-inspired computing architectures and have been extensively investigated in recent years^[7,8]. However despite their excellent properties, they fall behind in terms of reliable analog switching properties – a prerequisite for the emulation of brain-like functions. Contrary to mass storage and conventional logic

operations, neuromorphic applications set unique requirements on the hardware switching devices, namely- non-abrupt switching transitions and continuously distributed conductance states. Furthermore, different computational schemes demand unique switching properties from devices. While spiking neural networks (SNNs) following a spike-timing dependent plasticity (STDP)-based local learning rule demand bidirectional temporal plasticity of conductances/weights, deep neural networks (DNNs) emphasize more on wide dynamic conductance range and conductance linearity for machine learning algorithms and vector matrix multiplications^[9].

With regards to the analog-like switching requirement, most device prototypes like those based on electrochemical metallization or filamentary switching are handicapped since the switching mechanisms are based on inherently stochastic processes like the formation and rupture of conductive filaments^[5]. Randomness in the location and direction of filamentary growth, migration and degradation rates and uncontrollable diffusion pathways like grain boundaries or dislocations, adversely influence their effectiveness for neural emulation^[10–12]. This calls for the need of investigation into switching modalities that portray gradual modulation of conductance states for effective neural emulation^[13].

1.2 Problem Statement

Emulation of brain-inspired functions in hardware places unique and stringent switching and storage requirements on nanoscale memristive devices- fundamental building blocks of the electronic circuitry. In contrast to the conventional digital logic and memory storage technology, neuromorphic circuitry demands analog-like switching transitions, continuously distributed conductance states, wide dynamic range, good linearity, low programming energy and a threshold-driven accumulative non-volatility. Most of the current memristive solutions fall behind with regards to these requirements, calling for systematic investigation into switching modalities, novel material properties and device configurations that can portray gradual modulation of conductance states with spatiotemporal plasticity, akin to biological synapses and neurons.

1.3 Objectives and Scope

Incorporating slow charge-coupling kinetics with fast electronic transitions would

result in a smooth analog-like switching of conductance states. Ionic modulation and conductance is often disparaged in nanoelectronics devices, but its slow diffusive nature could help with this requirement. Furthermore, trap-assisted slow recombination of photo-generated carriers could enable additional gradual modulations of conductance via optical inputs. The primary goal of this dissertation is to investigate novel material sets and device configurations that intimately couple multiple charge modulation effects- namely electronic, ionic and photonic, to realize artificial synaptic weight-change elements with unparalleled plasticity. Ionic semiconductors in halide perovskites are initially investigated in a two-terminal memristive configuration. The mixed ionic-electronic conduction is harnessed to realize artificial synapses with programmable plasticity. With respect to the achievable weight-plasticity, the three-terminal field-effect configuration is identified as a better alternative because of the additional modulatory gate terminal, that can precisely control switching transitions in the channel conductance. Ion gel transistors are hence investigated with ultra-thin metal oxide semiconducting channels encoding the memconductance states. To further incorporate additional modulations via optical inputs, low band-gap 2D TMDCs are next investigated as semiconducting channels for artificial synapses. The importance of gating is realized over the course of these studies and hence, approaches to encompass multiple types of gating control are undertaken throughout to enrich the degree of achievable plasticity. On a general note, the material sets and device configurations are benchmarked primarily on the degree of plasticity, energy consumption, conductance linearity and dynamic range.

Specific objectives of this dissertation include:

1. Evaluate ionic semiconductors as suitable active materials for low-power efficient artificial synapses. Investigate drift-diffusive ion migration-relaxation kinetics in halide perovskites and harness these effects to achieve analog-like memristive effects. Investigate and compare the effects of halide perovskite composition on the degree of achievable short and long-term plasticity features and energy consumption. Simulate large-scale neural networks based on experimentally-derived device parameters to project utility of these devices for complex computations, pattern recognition and classification.
2. Evaluate ion gels as stable solid-state ionic dielectrics and high-mobility amorphous

oxide thin-films as semiconducting channels for synaptic transistors. Investigate hysteretic transistors as gated memristive channels with intimate integration of ionic and electronic charge coupling modes for neuromorphic computations. Compare the plasticity features and power consumption of the two modes of operation- electronic and ionotronic. Evaluate the degree of plasticity achieved with synergistic dual-gated operation.

3. Incorporate photonic charge coupling to orthogonally program optical analog conductance states in neuromorphic transistors through investigation of low band-gap 2D TMDC-based semiconducting channels. Evaluate synergistic fusion of the three gating controls and compare the achievable plasticity and programming energy in various modes of operation- electronic, ionotronic and photonic, and combinations thereof.

4. Optimize the input pulsing schemes for such optoelectronic neuristors to demonstrate compatibility of the same device with both SNNs and DNNs. Investigate the wavelength and photo-dosage dependence of weight plasticity. Demonstrate basic arithmetic operations analogous to an abacus. Evaluate optical stimuli as global neuromodulatory signals for selective neuronal firing of light-sensitive neuristors.

Note: This dissertation addresses the challenges of hardware switching devices primarily from a fundamental material-design perspective with focus on emulation of synapses. Although this is a principal step towards realizing efficient hardware for artificial intelligence (AI) and machine learning algorithms, engineering challenges like scalability, design and integration with CMOS circuitry, etc are not addressed in this dissertation. Individual chapters of this thesis addresses specific scientific hypotheses, as detailed below.

1.4 Hypotheses and Approaches

1.4.1 Ionic-Electronic Drift-Diffusive Halide Perovskite Memristive Synapses

Hypothesis: An ionic semiconductor which intimately combines slow drift-diffusive ionic kinetics with rapid electronic transitions would enable dynamic tuning of memconductance states, facilitating comprehensive emulation of synaptic characteristics and catering for novel low-power architectures that exploit electronic

properties of the semiconductor.

Approach: Halide perovskites are facilely processable ionic semiconductors which have revolutionized the field of photovoltaics and light-emitting diodes (LEDs) with their superior electronic properties, such as long carrier-diffusion lengths and low defect-densities. Ionic effects have been accounted for the origin of hysteresis, slow photocurrent decay as well as above bandgap photo-voltages in these devices. These hysteretic effects considered deleterious in the photovoltaic community, are harnessed here to induce memristive effects emulating synaptic signatures. Investigations are carried out on halide perovskites containing both organic and inorganic cations, namely methylammonium lead bromide ($\text{CH}_3\text{NH}_3\text{PbBr}_3/\text{MAPbBr}_3$), formamidinium lead bromide ($\text{CH}(\text{NH}_2)_2\text{PbBr}_3/\text{FAPbBr}_3$) and cesium lead bromide (CsPbBr_3), and the plasticity features and energy consumption are compared comprehensively. Network-level simulations of unsupervised learning based on experimentally-measured device properties are conducted to illustrate the computational capability of these drift-diffusive memristors for pattern recognition and image classification algorithms.

1.4.2 Dual Gated Ionic-Electronic Synaptic Transistors

Hypothesis: A gated control harnessing slow ion diffusive kinetics would enable dynamic modulation of electronic transitions and an analog programming of channel conductance. Combining multiple gating controls that can induce temporally distinct modulations on the carrier concentration would increase the weight plasticity and memory storage capacity, enabling emulation of more complex neuronal behaviour.

Approach: With a gated control of channel conductance exploiting time-dependent hysteresis, the thin film transistor (TFT) configuration is promising in achieving dynamic and linear temporal plasticity of synaptic weights. Electrolyte gating has been previously reported for ultra-low voltage operation of transistors and results in an unavoidable hysteresis. This smooth transition of channel conductance would enable storage of synaptic weights and the switching characteristics of transistors would facilitate simultaneous signal-processing, alleviating need for additional selectors in the circuitry. Herein, artificial synapses with intimate electronic-ionic coupling are realized in a dual-gated electric-double-layer (EDL) neuristor configuration with indium-tungsten oxide (IWO) semiconducting channels, a solid-state ionic dielectric [1-ethyl-

3-methylimidazolium bis(trifluoromethylsulfonyl)imide- poly(vinylidene fluoride-co-hexafluoropropylene){[EMIM][TFSI]-P(VDF-HFP)}} serving as the top-gate insulator and silicon dioxide (SiO_2) as the electronic back gate dielectric. The multi-gated architecture enables independent operation in a pristine top gated ionotronic mode, bottom-gated electronic mode and synergistic operations in a dual-gated additive/subtractive mode. The degree of weight plasticity and energy consumption are first compared across the two independent modes of operation. The dual-gating approach is then employed to demonstrate more complex neuronal behaviours like heterosynaptic plasticity and association- all in a single synaptic transistor. The ionotronic mode is configured to capture the effect of local activity correlations and the electronic mode represents global neuromodulations, to address the immense interplay between local and global neuromodulations, often overlooked in the electrical circuitry. Finally, these synaptic transistors or neuristors are operated in their sub-threshold regime to demonstrate high-gain conductance/weight changes at ultra-low power of the order of femto-Joules.

1.4.3 Optoelectronic Synaptic Transistors- Utilizing Electrons, Ions and Photons for Computing

Hypothesis: Information transmission via light-pulses as opposed to voltage-packets could unlock exceptionally fast transmission speeds with less cross-talk, high parallelism, low noise and nearly unlimited bandwidth. Neuromorphic transistors programmable via multimodal electrical and optical pulses would pave way for novel synergistic architectures encompassing advantages of both electron and photon-based computing platforms. Such artificial synapses with augmented plasticity would enable the design of robust neuromorphic circuitry with drastically lesser neural elements, overcoming the stringent circuit density requirements and fabrication challenges necessary to match the computational capability of the human brain. Utilizing photons as global virtual interconnects would help overcome electrical interconnect limitations, mitigate thermal loss and decrease the footprint and circuit density requirements at the system level.

Approach: In the first sub-project, charge carrier concentration across molybdenum disulphide (MoS_2) semiconducting channels is modulated via synergistic electronic, ionotronic and photoactive modes of operation. Low bandgap of the semiconducting

channel enables optical pulses to be utilized as an additional gating control, augmenting the achievable plasticity. Synergistic operation of these three modes enables co-existence of Hebbian and Homeostatic metaplasticity rules, and associative learning within a single device. Next, wavelength tunability of these bio-inspired functions are demonstrated with rhenium disulphide (ReS_2) semiconducting channels. The optoelectronic gating approach is harnessed to facilitate precise programming of conductance states with temporal plasticity, wide dynamic conductance range and high linearity, compatible with SNNs and DNNs. Photons pulses are utilized for potentiation and electrical pulses for depression of weights, allowing facile emulation of basic arithmetic operations like abacus, in addition to the bioinspired plasticity models. Finally, photons are utilized as global virtual interconnects in an array composed of light sensitive ReS_2 and insensitive IWO elements to selectively modulate plasticity. Global neuromodulations are encompassed as photon packets, regulating the network dynamics. Drawing inspiration from optogenetics, these devices are portrayed as optogenetic actuators in combination with dielectric elastomers to create an optogenetic toolbox for artificially intelligent soft robots.

1.5 Dissertation Overview

- *Chapter 1* provides a brief introduction to the problem statement and motivation for this work. The hypotheses and approaches are put forth. A brief structure of the rest of the thesis is provided and the major findings and novelties are listed.
- *Chapter 2* reviews the literature concerning recent advances in the application of memristive switching devices to neuromorphic computing paradigms. The relevant merits and demerits of these devices are assessed and strategies for regulating adaptive memristive characteristics are discussed. The research gap entailing the development of materials and devices with analog switching properties is finally provided to justify the motivation of this work-the need for coupled electronic, ionic and photonic charge transport.
- *Chapter 3* discusses the rationale behind the selection of materials and device configurations and details the various fabrication processes and characterization techniques employed.

- *Chapter 4* probes ionic migration in halide perovskite semiconductors and utilizes this as a proxy to enable dynamic tuning of metastable memconductance states, allowing efficient emulation of synaptic characteristics. A drift-diffusive model is proposed to account for these electrical memristive effects, more notable for organic cation containing halide perovskites. Network-level simulations of unsupervised learning are performed to illustrate the computational power of these drift-diffusive memristors for pattern recognition and image classification algorithms.
- *Chapter 5* investigates the weight plasticity features in a FET configuration by dynamic modulation of electronic transitions achieved via gated controls harnessing slow ion migration-relaxation kinetics and carrier trapping-detrapping mechanisms at the semiconductor-dielectric interface. Multiple gates (ionic and electronic) are employed on amorphous oxide semiconducting channels concurrently to induce temporally distinct modulations of the carrier concentration, enabling emulation of a higher form of plasticity. With one gate capturing the effect of local activity correlations and the other representing global neuromodulations, this dual-gated configuration addresses the effect of immense interplay between local and global neuromodulations on synaptic weight modulations, often overlooked in previous reports.
- *Chapter 6 and 7* examines photonic gating as an additional modulatory control to realize optoelectronically programmable neuromorphic transistors, encompassing advantages of both electron and photon-based computing platforms. Synergistic gating techniques are employed on photoactive 2D TMDC semiconductors (MoS₂ and ReS₂) to unravel a richer vein of higher-order plasticity features relevant for both SNNs and DNNs. Photons are proposed as global virtual interconnects to help overcome limitations of electrical interconnects, mitigating thermal loss and circuit density requirements. Drawing inspiration from optogenetics, these devices are portrayed as optogenetic actuators in combination with dielectric elastomers to create an optogenetic toolbox for artificially intelligent soft robots.
- *Chapter 8* finally summarizes and draws conclusions that validate the hypotheses put forth. A brief outlook on the future directions is provided with insights into the

potential applications of this technology.

1.6 Findings and Outcomes/Originality

This research addresses important issues related to hardware realization of artificial synapses using memristive switching devices, yielding novel and fundamental insights. They include (chapter-wise) :

1. *Ionotronic halide perovskite memristors*^[14]: Utilization of the unique ionotronic conduction in halide perovskites as a proxy to realize memristive synapses with programmable plasticity. Halide perovskites were utilized till date solely for applications like solar cells and LEDs. Its unique ionotronic conduction was often overlooked and considered deleterious because of the resultant hysteretic current (I)-voltage (V) curves. In this study, these hysteretic effects were harnessed to realize drift-diffusive electrical memristors and artificial synapses, first of its kind. Three active material compositions were investigated thoroughly and the weight plasticity features and power consumption were compared for all the compositions under investigation. Memristive effects were observed to be more prominent in the organic cation containing perovskites, shining light onto the material design rules for efficient halide perovskite-based computing elements.

2. *Electronic-Ionotronic dual-gated synaptic transistors*^[15]: A systematic analysis was carried out to investigate the effects of ionic and electronic gating on the weight modulation capability of synaptic transistors. An ion gel was employed as the gate dielectric instead of the previously reported chemically-volatile ionic liquids. The concept of utilizing multiple (ionic and electronic) gating controls to induce temporally distinct modulations of the carrier concentration is novel. This facilitated emulation of a higher order of weight plasticity rules (heterosynaptic plasticity) based on interaction between the gating controls, pertinent for both SNNs and DNNs, which is again breaking new ground. Operating synaptic transistors in the sub-threshold region resulted in weight changes with higher gain at ultra-low power. This observation is again novel with regards to the field of neuromorphic devices. With one gate capturing the effect of local activity correlations and the other representing global neuromodulations, this dual-gated configuration addressed the effect of immense interplay between local and global neuromodulations on synaptic weight modulations, often overlooked in previous reports.

3. *Opto-iono-electronic neuristors*^[16]: The concept of employing light as a gating control to realize optoelectronically programmable synapses is the first of its kind in the field of neuromorphic computing. Synergistic electronic, ionic and photonic gating empowered emulation of complex neuronal phenomena like Hebbian plasticity, homeostatic regulation and associative learning at an elemental level, paving way for novel metaplastic computing architectures. To the best of our knowledge, this is the first demonstration of interplay between Hebbian and Homeostatic plasticity in a single artificial neural element. Such neuromorphic transistors programmable via multimodal electrical and optical pulses paves way for novel synergistic architectures, encompassing advantages of both electron and photon-based computing platforms.

4. *Inspiration from optogenetics*: Inspired from optogenetics, the strategy of utilizing light to tune the learning and memory behaviours in artificial neural circuitry is novel and remains unexplored till date. This would allow optical stimuli to be utilized as an *ex situ* behavioural manipulator for AI circuitry, controlling the learning rates on demand, and would also open up possibilities as a non-contact debugging tool to diagnose and fix faulty electrical circuitry. Here, photo-receptive neuristors with optoelectronically modulatable plasticity were demonstrated to be compatible with both SNN and DNN algorithms using optimized pulsing schemes. Multi-level memories with 1024 addressable levels (8-bit storage) were programmed with optical pulses demonstrating high conductance linearity, as demanded by on-line machine learning algorithms. Precise control over the weight changes were utilized to implement basic arithmetic operations analogous to an abacus, highlighting the memcomputing capability of these devices. Finally, these neuristors were integrated with soft dielectric elastomeric actuators to realize an artificial eye, with learning and memory behaviours that resemble a human eye.

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Chapter 2

Literature Review

This chapter critically reviews the literature concerning recent advances in the application of memristive switching devices for neuromorphic computing paradigms. A brief overview of the computing paradigms is first provided. Next, recent research employing different types of memristive devices as artificial synapses and neurons for neuromorphic computations is surveyed. The pertinent merits and demerits of these approaches are evaluated in detail with focus on the smoothness, linearity and symmetry of conductance transitions, dynamic range, retention, switching power, endurance and device variability. Vital insights into the strategies adopted to achieve smooth conductance transitions are discussed. The research gap entailing development of novel materials and device configurations with analog switching properties is finally provided to justify the motivation of this work-the need for coupled electronic, ionic and photonic charge transport. The following chapters embark on the hypotheses and objectives to fill the research gaps identified in this chapter.

2.1 Overview

With systematic device scaling breakthroughs following Moore's law, von Neumann architectures have driven exponential improvements in computing performance till date. However, with the near end of Moore and Dennard scaling laws, the energy and time spent transporting data across the so-called 'von-Neumann bottleneck' has become particularly problematic for data-centric applications. While von Neumann computers attempt to mitigate this by utilizing a hierarchy of caches, the human brain follows a non-von Neumann architecture performing in-memory computations. With a massively parallel architecture interconnecting an infinitely large ocean of neurons (ultralow-power computing elements) via synapses (adaptive memory elements), the human brain outperforms even the fastest supercomputers on many tasks involving unstructured data classification and pattern recognition (Figure 2.1).

Figure 2.1^[1] Computation, communication, and memory. (A) The parallel, distributed architecture of the brain is different from the sequential, centralized von Neumann architecture of today's computers. The trend of increasing power densities and clock frequencies of processors^[2] is headed away from the brain's operating point. Number and POWER processors are from IBM, Incorporated; AMD, Advanced Micro Devices, Incorporated; Pentium, Itanium, and Core 2 Duo, Intel, Incorporated. (B) In terms of computation, a single processor has to simulate both a large number of neurons as well as the inter-neuron communication infrastructure. In terms of memory, the von Neumann bottleneck^[3], which is caused by separation between the external memory and processor, leads to energy-hungry data movement when updating neuron states and when retrieving synapse states. In terms of communication, interprocessor messaging^[4] explodes when simulating highly interconnected networks that do

not fit on a single processor. (C) Conceptual blueprint of an architecture that, like the brain, tightly integrates memory, computation, and communication in distributed modules that operate in parallel and communicate via an event-driven network. © “From P. A. Merolla, J. V. Arthur, R. Alvarez-Icaza, A. S. Cassidy, J. Sawada, F. Akopyan, B. L. Jackson, N. Imam, C. Guo, Y. Nakamura, *Science*. **2014**, 345, 668. Reprinted with permission from AAAS.”

The atomic-level scalability of dense non-volatile memory (NVM) arrays provide an opportunity to emulate the human brain’s connectivity in hardware, but are limited at the neural-network level by lack of a robust computational scheme, selector devices and peripheral circuitry, and other inherent device limitations like finite dynamic range, programming energy, non-ideal device reliability and variability. The significantly different switching mechanisms of various types of NVMs necessitates development of *computational schemes* tailored to the corresponding device physics^[5]. For example while conductive-bridging random access memories (CBRAMs) are more suitable for a binary ‘on/off’ response representing presence or absence of a synaptic connection^[6], phase change memories (PCMs)^[7] and resistive-RAMs (RRAMs)^[8] fit better for applications requiring analog weight updates. Complete exploitation of the density of nanoscale crossbar NVM arrays require development of compact, efficient *CMOS peripheral circuitry* that can support massively parallel access schemes, like the ‘CrossNet’ concept which employs a three-dimensional (3D) integration technology^[9]. A dense crossbar implementation also requires development and integration of *selector devices* in series with the memristive elements to prevent parasitic ‘sneak path’ currents and incorrect sensing of the NVM conductance^[5]. The incredibly low power consumption (< 20 W) of the human brain makes *programming energy efficiency* one of the benchmarking criteria, but remains unmatched till date^[10]. Other inherent *NVM device issues*^[5] like the *dynamic range and retention of conductance, and device variability* also pose several challenges towards developing large-scale neural networks. For example, variability among devices may cause significantly different read currents into an integrate-and-fire (I&F) circuit model, unnecessarily firing neurons and triggering other synaptic runaway dynamics. Asymmetric response of such memristive devices during programming also causes weight preferences of one sign over the other, adversely affecting the network efficiency.

In this chapter, the current status of neuromorphic computing is reviewed with focus on materials and electronic devices employed as artificial neural elements. Computational schemes like spiking neural networks (SNNs), Deep Neural Networks (DNNs) and other ‘memcomputing’ applications are first discussed. Next, biological synaptic functions are briefly introduced, followed by survey of the various types of electronic devices employed as artificial synapses and neurons including PCMs, CBRAMs, filamentary RRAMs, non-filamentary RRAMs and synaptic transistors. Desirable properties and switching dynamics of these devices in the context of neuromorphic applications are discussed in detail. The research gap is identified and how this dissertation fits into the literature is introduced, before concluding the chapter.

2.2 Computational schemes

2.2.1 *Spike-timing dependent plasticity for Spiking Neural Networks*

Learning in the human brain occurs via temporary and permanent strengthening and weakening of synaptic connections, interconnecting each neuron to up to 10^4 other neurons^[11]. *Spike-timing dependent plasticity (STDP)* is a biological process that adjusts the strength of synaptic connections based on the relative timing between the pre-synaptic (input) and post-synaptic (output) neuronal ‘action potentials’^[12]. Causal spiking result in persistent strengthening or *long-term potentiation (LTP)*, while acausal spiking decreases synaptic strength or *long-term depression (LTD)*. An implementation of Hebbian learning, STDP is considered to be the first law of synaptic plasticity and forms the basis of associative learning.

Artificial implementations of this spike-based synaptic weight plasticity using asynchronous spikes of identical amplitude and duration, are referred to as spiking neural networks [SNNs]^[13]. Information is encoded in the timing and frequency of the spikes. Spiking of the pre-synaptic neuron modifies the post-synaptic neuron membrane potential by an amount determined by the ‘synaptic weight’ (electrical conductance), eventually leading to a post-synaptic spike through a leaky-integrate-and-fire (LIF) or other similar neuron model^[5]. Mapping of STDP-based local learning rules with memristive switches utilizes one terminal to represent pre-synaptic and the other to represent post-synaptic neurons. The applied voltage represents membrane potential and device conductance the synaptic weight. Delay in timing of the spikes at the pre- and post-synaptic neurons creates effective voltage differences across these devices,

which if crosses a pre-set threshold conceives non-volatile changes in the device conductance.

In pristine CMOS-based implementations, device conductances/synaptic weights are typically stored in analog or digital devices such as capacitors, static RAMs (SRAMs) or dynamic RAMs (DRAMs)^[1] (Figure 2.2). These avoid reliability issues and other vagaries of emerging NVMs, but at the cost of a larger overall system size^[14]. Incorporating more biologically realistic functions such as short-term plasticity further increases the complexity and footprint. Capacitors can store analog weight values, but are leaky and subject to noise. SRAMs are area-inefficient and subject to high leakage power. DRAMs require frequent refreshing and most of these implementations often require additional digital-to-analog converters (DACs) which adds to the footprint and energy consumption further.

Figure 2.2^[15] Spiking neural network overview using CMOS. The 1.72mm² 10nm FinFET SNN combines sparse connectivity, stochastic operation, voltage scaling, and power gating to achieve 4.8× throughput and 6.8× energy improvements over previously reported SNNs. © [2018] IEEE. “From G. K. Chen, R. Kumar, H. E. Sumbul, P. C. Knag, R. K. Krishnamurthy, in *2018 IEEE Symp. VLSI Circuits*, IEEE, **2018**, pp. 255–256. Reproduced with permission from IEEE.”

In context of the device footprint, memristive devices promise a great potential when compared to CMOS-based implementations^[16]. Based on the device physics, programming pulses can be designed to implement STDP with either overlapping or non-overlapping pulses. Each memristor can potentially replace multiple digital bits by

storing analog synaptic weights, but suffers from increased susceptibility to noise. In practice, ideal memristor device models were utilized to simulate a small-scale sequence STDP-based learning problem on a 25×25 array^[17]. A homeostatic control over the average neuron firing rate was proposed as a method to improve network resilience to device variability^[17]. A 2T1R (T-transistor, R-resistor) synaptic unit cell design^[18], with one transistor specifically allocated for I&F and the second responsible for programming STDP was introduced to avoid sneak-path effects. An event-based simulator called ‘Xnet’, for modelling the effect of device vagaries on STDP was also proposed^[19]. In general, since many forms of biologically plausible spike-based learning rules bear resemblance to STDP, this serves as a good starting point to qualify novel material systems and device configurations as artificial synapses for bio-inspired computations.

2.2.2 Vector-matrix multiplication for Deep Neural Networks

In contrast to the SNN's asynchronous, uni-valued spikes, the neuron outputs in a DNN^[20] are real-valued numbers, processed on synchronous time-steps. With objective function minimizations implemented via backpropagation algorithms, massive labelled datasets, and highly-parallel matrix-multiplications, DNNs demonstrate tremendous potential for online machine learning weight updates^[21] (Figure 2.3). Such networks require devices with a wide dynamic conductance range and excellent conductance linearity (CL) characteristics.

Memristive devices again hold great promise for such multiply-accumulate operations for forward-inference and training, but fall behind in terms of dynamic conductance range and linearity. Crossbar-compatible weight-update schemes were proposed with independent firing of upstream and downstream neurons accumulating at the shared cross-points, updating the weight. Test accuracies remained unaffected and different learning rules such as winner-take-all (WTA)^[22] were implemented for applications such as image compression and reconstruction of images.

Figure 2.3^[23–25] **Deep Convolutional Neural Networks with Resistive Cross-Point Devices.**

(A) Schematics of a convolutional layer showing the input volume, kernels, and the output volume. (B) Schematics of a mapped convolutional layer to a Resistive Processing Unit (RPU) array showing the input and output matrixes and their propagation through the kernel matrix during the forward, backward and the update cycles. (C) shows the typical horizontal and vertical structure of a RPU/RRAM. Morphology and component of conductive filaments (CF) observed in Ag/SiO₂/Pt planar structure after electroforming with various compliance current (I_{CC}). (D) As-prepared fresh device without any electrical treatment. (E–G) Morphologies of the CF with $I_{CC} = 5$ nA, $I_{CC} = 100$ nA and $I_{CC} = 100$ μA, respectively. © “From T. Gokmen, M. Onen, W. Haensch, *Front. Neurosci.* **2017**, *11*, 538. Reproduced as per the Creative Commons License Deed.”; “Reprinted from Monolithic 3D neuromorphic computing system with hybrid CMOS and memristor-based synapses and neurons. H. An, M. A. Ehsan, Z. Zhou, F. Shen, Y. Yi, *Integr. VLSI J.* **2017**. © (2017), with permission from Elsevier.”; © “From H. Sun, Q. Liu, C. Li, S. Long, H. Lv, C. Bi, Z. Huo, L. Li, M. Liu, *Adv. Funct. Mater.* **2014**, *24*, 5679. Reprinted with permission from John Wiley and Sons.”

The deterioration of recognition accuracy with non-linearity was studied for a sparse-coding algorithm and the tolerance for non-linearity was identified as 10 % of the overall conductance range^[26]. With respect to dynamic range, Burr et al.^[26] proposed up to 6-bit resolution between the minimum and maximum conductance with a conductance pair representing a single weight. ‘Spike-coding’ schemes employed with

pre-trained weights demonstrated competitive performance on the Modified National Institute of Standards and Technology (MNIST) database and a parallel combination of RRAM devices were observed to offer higher robustness to device variability^[27]. Modelling based on the programming dynamics of oxide memristors^[28] depicted high accuracies for MNIST digit classification^[29]. Such NVM-based DNN implementations also depicted a 25x speedup and orders of magnitude lower power with respect to graphics processing units (GPUs) for DNN training^[30].

2.2.3 Memcomputing (non-neuromorphic applications)

The internal state dynamics of emerging memristive elements have also been utilized for memcomputations. NAND operation and other Boolean logic was implemented using three memristive devices connected to a load resistor by utilizing a ‘material implication’ gate $q \leftarrow p \text{IMP} q$ (equivalent to $(\text{NOT} p) \text{OR} q$)^[31]. Such IMP logic was later realized on a shared bit-line crossbar architecture^[32], followed by NOR implementations^[33]. Other incarnations of memristive device physics to logic-in-memory operations include exploitation of the accumulation property of phase-change materials for basic arithmetic processes of addition, multiplication, division and subtraction with simultaneous storage^[34] and factoring capabilities^[35].

The stochasticity associated with many memristive devices finds suitable applications in the area of random number generation (RNG) for stochastic computing and cryptography^[36]. Spin-torque switching in magnetic tunnel junctions (MTJs)^[37] and the random formation and rupture of conductive filaments within CBRAMs and RRAMs^[38] have been utilized to generate sequences of random numbers. The randomness associated with the atomic configurations of the amorphous phase created *via* the melt-quench process after PCM RESET operations has also been harnessed for RNG^[39].

2.3 Synaptic Functions

Mimicking synaptic signal transmission through nanoelectronic circuits is the cardinal research target in the field of neuromorphic engineering. However, hardware implementation of neural networks emulating synaptic functionalities with comparable complexity and feasible power dissipation remain exceptionally challenging. Very recently, several ideas have been proposed to emulate elementary neuroplasticity in

memristive devices, including short- and long-term potentiation and depression, paired-pulse facilitation, spike-rate dependent plasticity, and spike-timing dependent plasticity.

To tailor the switching properties of artificial synapses and neurons, first necessitates primary understanding of the mechanism of biological signal transmission. In biological synapses, the synaptic weight, i.e., the strength of synaptic connections is determined by intracellular ionic concentrations (e.g., Ca^{2+} , Na^+ , Mg^{2+} and K^+) which activate/inhibit the release of neurotransmitters with certain timing constraints^[40]. The change of synaptic weight or plasticity is governed by many parameters including pre- and post-synaptic voltage, spiking rate, spiking interval, dendritic location and synaptic depolarization. Such an activity-dependent plasticity is considered fundamental for learning and memory in neuronal systems involving information processing and storage.

Short and long-term potentiation (STP and LTP) are the most prominent forms of plasticity observed at excitatory synapses in the human brain^[41] (Figure 2.4). A filter for biological signal transmission^[42], STP is a temporal strengthening of synaptic connections which lasts for tens of milliseconds to a few minutes. **Paired-pulse facilitation (PPF)** and **post-tetanic potentiation (PTP)** are the two most common forms of STP, activated by frequency-dependent spike pair protocols. Biologically, STP has been very recently identified as cardinal for pattern recognition, sound localization and associative learning^[43], but widespread utilization in computational algorithms still demands further research efforts. In contrast, LTP^[44] represents a permanent increase of synaptic strength lasting from minutes to several weeks. Cardinal for weight storage, this forms the basis for majority of the computational schemes.

Figure 2.4^[45] The multistore model and the human-memory forgetting curve. (A) The psychological model of human memory proposed by Atkinson and Shiffrin. This multistore model provides for three types of memory, that is, sensory memory (SM), short-term memory (STM) and long-term memory (LTM). (B) Simplified memorization model in the inorganic synapse, which was inspired by the multistore model. After storing new information as SM, information is stored in STM for short periods of time, whereas repeated rehearsal events result

in LTM. At a higher repetition rate, rehearsal before complete decay in memorization level forms LTM, as shown by the red line. Rehearsal at lower repetition rate cannot form LTM, as shown by the blue line. (C) Typical change of memory retention in the inorganic synapse for the decay in STM mode. A power function, used to analyse psychological behaviour such as STM^[46], $y = b \times t^{-m}$, was used to fit the conductance curves, where y is the memory retention, b is the fit constant for scaling, t is the time from the n^{th} rehearsal and m is the power function rate. Memory retention was normalized using a conductance value of 77.5 μS . The conditions of the input pulse were $V = 80 \text{ mV}$, $W = 0.5 \text{ s}$ and $T = 4 \text{ s}$. **Inorganic synapse showing STP and LTP, depending on input-pulse repetition time.** (D) Schematics of a Ag_2S inorganic synapse and the signal transmission of a biological synapse. Application of input pulses causes the precipitation of Ag atoms from the Ag_2S electrode, resulting in the formation of a Ag atomic bridge between the Ag_2S electrode and a counter metal electrode. When the precipitated Ag atoms do not form a bridge, the inorganic synapse works as STP. After an atomic bridge is formed, it works as LTP. In the case of a biological synapse, the release of neurotransmitters is caused by the arrival of action potentials generated by firing, and then a signal is transmitted as a synaptic potential. Frequent stimulation causes long-term enhancement in the strength of the synaptic connection. (E,F) Change in the conductance of the inorganic synapse when the input pulses ($V = 80 \text{ mV}$, $W = 0.5 \text{ s}$) were applied with intervals of $T = 20 \text{ s}$ (E) and 2 s (F). The conductance of the inorganic synapse with a single atomic contact is $2e^2/h$ ($=77.5 \mu\text{S}$), where e is the elementary charge, and h is Planck's constant. Reprinted by permission from Springer Nature [Nature Materials], "From T. Ohno, T. Hasegawa, T. Tsuruoka, K. Terabe, J. K. Gimzewski, M. Aono, *Nat. Mater.* **2011**, *10*, 591. © 2011."

Analogously, STP can be emulated in artificial synapses by inducing volatile (meta-stable) transitions in device conductance. For memristors or resistive switches in general, this is enabled by a threshold-switching behaviour in which the conductance state returns back to its initial state upon removal of bias^[47]. For synaptic transistor configurations, this is enabled by electrostatic doping or ultrafast charge trapping dynamics at the semiconductor-dielectric interface, temporarily modulating the channel conductance^[48]. Such forms of STP often consolidate to LTP upon induction of any strong stimulus that can form (field-driven) or annihilate (thermally) non-volatile (stable) conductive channels in these devices. This transition requires overcoming internal energy barriers dependent on the device history and hence, can be modulated by the amplitude and frequency of input stimuli. Higher frequency or energy stimulation often helps overcome the programming energy barrier resulting in the transition from short- to long-term memory (STM-LTM)^[45].

As the “first law” of synaptic plasticity, ***spike-timing dependent plasticity (STDP)*** is an important synaptic modification rule for competitive Hebbian learning. It refers to the observation that the precise timing of pre and post-synaptic spikes significantly affects the sign and magnitude of synaptic plasticity, establishing temporal correlations^[28]. Pre-synaptic spikes preceding post-synaptic spikes within a narrow time window often leads to LTP, and if the order is reversed results in LTD. The degree of weight change in either case is a function of the delay between the pre- and post-synaptic spikes, with larger changes induced by shorter time intervals. Employing a hybrid synapse/neuron circuit composed of CMOS neurons and nanoscale memristor devices, STDP was first emulated by Jo et al.^[49] Li et al. later implemented four forms of STDP in a chalcogenide memristor by careful design of spike pairing protocols^[50]. A number of other excellent studies subsequently reported STDP behaviour. ***Spike-rate dependent plasticity (SRDP)*** reflects the influence of the synaptic activation frequency on the long-lasting modification. Alibart et al. first reported SRDP in their organic nanoparticle transistors based on frequency-dependent trapping and detrapping of charge carriers^[51]. Studies emulating PPF and PTP indirectly supported the same phenomenon, with modulations dependent on the shape of input waveforms, total number of stimuli and the stimulation rate^[47].

To match the computational prowess of the human brain, its intrinsically massive ***parallel information processing*** ability and ***connectivity*** must also be emulated. Most implementations focus on emulating basic synaptic properties as discussed above, but fail to address this issue. In this context, a hybrid CMOS/memristor concept was proposed to map the structure of artificial neural networks (ANNs) and emulate the connectivity of the human brain. Such CMOLs (Cmos + MOlecular scale device hybrids)^[9] combine the reliability and high functionality of the CMOS circuitry with the scalability of 3D stacked nanoscale thin film memristors, connected via synaptic connections on the top layer grid^[52]. “Axons” and “Dendrites” formed the rows and columns of the CMOL nanowire crossbar^[53], memristive devices served as configurable analogue weight banks, and the CMOS circuitry was utilized as the summing amplifier to provide gain and signal restoration^[8]. However, despite exciting progress, the practical implementation of ANNs is still seriously challenged due to the inevitable electroforming step requirement, abrupt switching and stochasticity associated with the formation and rupture of conductive filaments in memristors. As a

result, although demonstrations of larger crossbar circuits with conventional materials and devices are becoming increasingly common, intense research efforts focusing on novel analog-switching memristive devices are still required.

2.4 Memristive device as a synapse

2.4.1 Phase Change Memory (PCM)

PCMs store data by switching between amorphous and crystalline states of the material at a microscopic level^[54]. In the amorphous disordered phase, the material exhibits high electrical resistance and switches to a low resistance crystalline ordered phase upon electrical heating. Thus, electrical currents can be switched on and off to represent digital high and low states. PCMs are considered to be 500 to 1,000 times faster than normal flash memories and are also robust, cost-effective, bit-alterable, highly scalable, CMOS-foundry compatible and demonstrate faster reading and writing speeds. However, the lifetime of these devices are affected by thermal expansion during programming and metal migration. PCMs fit well in neuromorphic applications where ‘device history’ is desirable. The ‘SET’ process, i.e. programming into the high-conductance state is usually made incremental with repetitive pulses slowly crystallizing the high-resistance amorphous state within the device. But programming into the low-conductance state (referred to as ‘RESET’) involves melt and quench processes which tend to be abrupt, not desirable for a continuous weight-change device^[5].

Bichler^[55] and Rajendran^[56] et al. used a two-PCM approach to implement STDP with separate devices for LTP and LTD. Causal firing between the pre- and post-synaptic neurons triggered a partial SET pulse at the LTP synapse, while acausal firing programmed the LTD synapse. However, this implementation demanded a refresh protocol for fully SET synapses, in which inputs were disabled, effective weights were read, and the conductance was abruptly RESET to maintain weights with low conductance values. Improved synaptic performances were obtained by introducing a thin hafnium oxide (HfO₂) layer, modifying the crystallization kinetics of Germanium-Antimony-Telluride (Ge₂Sb₂Te₅/GST)-based PCMs^[57]. The activation energies related to growth and nucleation greatly influenced the dynamic conductance range and conductance linearity, and was modified by introducing appropriate dopants^[58]. Programmable SET and RESET processes allowed different variants of STDP updates

to be emulated with a single PCM cell per synapse^[59] utilizing triangular/staircase waveforms^[60].

2.4.2 Conductive Bridging Random Access Memory (CBRAM)

CBRAMs work on the principle of electrochemical formation of conductive metallic filaments^[61] (Figure 2.5). During SET (positive bias), metal ions drift to the bottom electrode oxidizing the top electrode and reducing themselves to form a metallic filament that grows vertically until it reaches the top electrode, forming a low-resistance state. During RESET, the filament first dissolves laterally at the top of the filament due to enhanced electric fields, switching to a high-resistance state. They are promising NVMs due to its fast speed ($\sim$ ns), scalability and ultra-low power consumption ($\sim$ nW), but are disadvantaged by the inherently abrupt nature of the filament formation (SET) process and the highly conductive resulting states, leading to large overall summing currents and hence large capacitors for an I&F operation.

Figure 2.5^[62] The mechanisms of Ag nanowire growth and shrinkage; (A) the activation energies for reduction (E_R) and oxidation (E_O) are equal in the equilibrium condition without any bias application. (B) Application of positive bias to the Ag_2S electrode causes the diffusion of Ag^+ cations towards the surface of the Ag_2S electrode, making E_R smaller than E_O , which enhances the reduction of Ag^+ cations into Ag atoms. (C) Application of negative bias to the

Ag₂S electrode causes a diffusion of Ag⁺ cations towards the bottom of the Ag₂S electrode, making E_O smaller than E_R , which enhances the oxidation of the precipitated Ag atoms into Ag⁺ cations, re-dissolving into the Ag₂S electrode. © “From T. Hasegawa, K. Terabe, T. Tsuruoka, M. Aono, *Adv. Mater.* **2012**, 24, 252. Reprinted with permission from John Wiley and Sons.”

Ohno et al. implemented STDP-based synaptic operations with a silver sulphide (Ag₂S) gap-type ‘atomic switch’. Low amplitude, pulse width and number of pulses resulted in short-term memory in these devices, which then stabilized to long-term memory states upon persistent training. A 7×7 array of inorganic synapses was used to experimentally demonstrate memorization (and forgetting) of two simple patterns^[45]. Suri et al. proposed stochastic STDP-based learning rules with CBRAMs as binary synapses^[6], enabling unsupervised processing of asynchronous analog data streams for recognition and extraction of repetitive, real-time auditory and visual patterns. Yang et al. reported nanoscale memristive switches and solid-state physically evolving networks based on self-organization of Ag nanoclusters^[60].

2.4.3 Filamentary RRAM

Filamentary RRAMs are quite similar to CBRAMs, except that the filaments are composed of a chain of defects within an insulating oxide, rather than a chain of metallic atoms of one of the two electrodes through an insulating solid-electrolyte or oxide^[64] (Figure 2.6). Majorly based on metal-oxides such as titanium oxide (TiO_x), hafnium oxide (HfO_x), tantalum oxide (TaO_x), tungsten oxide (WO_x), aluminium oxide (AlO_x) and their combinations, these devices are simple, CMOS-compatible, highly scalable, and exhibit ultralow energy consumption per synaptic operation and programming currents. However like CBRAMs, the filament formation/completion process is inherently abrupt and difficult to control. And since the switching mechanism depends on moving only a handful of atomic defects, large variability through Poissonian statistics (‘shot noise’) is unavoidable. They also require compliance current control via an external circuitry to avoid over thickening of filament growth. Thick filaments are difficult to RESET and contributes higher current into a vector sum or leaky integrate-and-fire (LIF) neuron than its neighbours, adverse for neuromorphic applications. The use of compliance currents also poses several disadvantages in terms of conductance stability, synaptic behaviour and peripheral circuit design.

Yu et al. proposed a forming-free Pt/HfO_x/TiO_x/HfO_x/TiO_x/TiN multilayer oxide-based synapse^[65] with continuous resistance change observed only during the RESET operation. Short pulses of 10 ns enabled sub-pJ energy per spike operation. A stochastic compact model quantified the gradual resistance modulation and was applied to a large-scale artificial visual system simulation. A two-layer neural network was simulated based on 1024 neurons and 16,348 oxide-based synapses, depicting tolerance to resistance variations of up to 10 %. Other approaches embracing the abrupt SET operation adopted binary stochastic switching synapses^[66] to simulate a two-layer winner-take-all (WTA) neural network. Multi-level switching was demonstrated in TiN/Ti/AlO_x/TiN and TiN/HfO_x/AlO_x/Pt RRAM devices with increasing external compliance currents^[67,68]. Chua and co-workers proposed memristive cellular automata networks^[69] and a memristor bridge circuit to simplify the training of DNNs^[70]. Jeong et al. enhanced the analog switching capability and dynamic conductance range of TaO_x-based RRAM devices by 80 % by employing a multi-step ‘forming’ process with pre-heating pulses in addition to regular SET pulses^[71]. Transistors were employed as selectors and voltage-independent current sources in a 1T1R configuration with HfO₂-based RRAMs to incorporate both voltage-controlled RESET and current-controlled SET operations^[72].

Figure 2.6^[73] Schematic illustration of the growth of a conductive filament during electroforming. In device type A, having two inert electrodes – filament grows from the cathode towards the anode (A) and (B). In device type B with an OEL – filament grows from

the OEL regardless of the polarity: (C) filament grows from the OEL anode towards the cathode or (D) filament grows from the cathode, when the anode is inert. © “Republished with permission of RSC Pub from E. Yalon, I. Karpov, V. Karpov, I. Riess, D. Kalaev, D. Ritter, *Nanoscale* **2015**, 7, 15434; permission conveyed through Copyright Clearance Center, Inc.”

A HfO₂-based vertical RRAM (VRRAM) technology was recently reported by Piccolboni et al with real-time audio and video pattern extraction simulations.^[74] Each synapse was composed of a stack of VRRAMs with one common selector, exhibiting analog conductance behaviour through the parallel configuration of *N* RRAM cells. The impact of conductance-dependent STDP was investigated by Prezioso et al. in a simulation modelled on Al₂O₃/TiO₂-based memristors, which demonstrated self-adaptation capabilities^[75], suggesting that device infidelities could potentially be compensated at the system level.

2.4.4 Non-filamentary RRAM

In non-filamentary RRAMs, the switching mechanism is caused by defect migration that overcomes a Schottky or tunnelling barrier typically at an interface between two materials such as an oxide and metal^[76]. Motion of defects (dopants) towards the electrode collapses the Schottky barrier, resulting in significant resistance changes. Additionally, ionic motion can result in narrowing of the tunnelling gap, enabling gradual resistive tuning, highly suitable for implementing an analog synapse. However, these devices often require an unpleasant trade-off between programming speed (requiring a low energy barrier to defect diffusion) and retention (requiring a high energy barrier)^[5] (Figure 2.7).

Figure 2.7^[77] Three types of RRAM and the corresponding characteristics comparison. (A) Filamentary analog RRAM with multiple-weak-filaments; (B) conventional strong-filament based RRAM; (C) non-filamentary RRAM; (D) comparison of five specifications. © [2017] IEEE. “From M. Zhao, H. Wu, B. Gao, Q. Zhang, W. Wu, S. Wang, Y. Xi, D. Wu, N. Deng,

S. Yu, in *Electron Devices Meet. (IEDM), 2017 IEEE Int.*, IEEE, 2017, pp. 34–39. Reproduced with permission from IEEE.”

Bilayer memristors have attracted considerable attention in this regard owing to their simplified electroforming process, satisfactory stability, reliability and energy efficiency. Binary-oxide stacks of Al_2O_3 and TiO_{2-x} have been reported to exhibit significantly higher performance compared to its monolayer TiO_2 counterpart with a dramatic reduction of the electroforming voltage^[78]. Synaptic plasticity and STDP were emulated in a nanoscale $\text{TiO}_x/\text{TiO}_y$ bilayer RRAM system, with multilevel conductance states caused by the migration of oxygen ions between the TiO_y and the TiO_x layer^[79]. Gradual resistance tuning due to Schottky/tunnelling barrier modulation induced by oxygen ion migration explained for the observed synaptic characteristics in WO_x , TaO_x and TiO_2 based devices, including STDP and paired-pulse facilitation^[17,80]. The resistance instability in RRAM synapses was exploited to emulate frequency dependent short-term modulation in TiO_2 devices^[81]. Yang et al. reported the existence of both volatile and non-volatile switching modes within a $\text{Pt}/\text{WO}_{3-x}/\text{Pt}$ -based system^[82]. The devices exhibited volatile short-term switching characteristics at voltages below the forming voltage and switched to long-term memory beyond the forming voltage.

Incorporation of buffer layers have been shown to modify the switching behaviours drastically. Bessonov et al.^[83] sandwiched solution-processed $\text{MoO}_x/\text{MoS}_2$ heterostructures between two printed silver electrodes, with the thick MoS_2 buffer layer providing good conductance and the ultrathin molybdenum oxide (MoO_x) film dominating the resistive switching behaviour. Thickness and selection of the buffer/active layers became critical in this aspect^[84], with a higher active/buffer layer thickness ratio required for high resistivity buffer layers and vice-versa. Double-barrier memristive devices consisting of an ultra-thin memristive layer (niobium oxide- Nb_xO_y) sandwiched between a tunnel barrier (Al_2O_3) and a Schottky contact were also investigated for neuromorphic mixed-signal circuits^[85]. Oxygen diffusion and modification of the local electronic interface states within the Nb_xO_y layer modified the local Schottky barrier height, density of states and the Al_2O_3 tunnelling barrier, causing a gradual change in conductance. Reverse bias reinitialized the ionic distribution and presence of the tunnelling layer resulted in an electroforming-free switching mechanism with improved retention characteristics.

2.4.5 Other approaches

Other configurations that have been utilized majorly include synaptic transistors^[51,86–88], spin devices^[89,90], ferroelectric^[91] and Mott^[92] switches. Employing these devices as artificial synapses, several characteristics of biological synapses such as STP, LTP, LTD and STDP have been mimicked till date.

2.4.5.1 Synaptic Transistors

Besides the most commonly discussed two-terminal devices, three-terminal field-effect configurations with tunable channel conductivities have also been employed as artificial synapses^[93–95]. With an additional control terminal (gate) similar to biological dendrites, FETs based on organic^[96,97] and inorganic semiconductors^[87,88,98] seems promising in this regard, exploiting hysteresis to achieve dynamic plasticity when compared to abrupt state transitions in a memristor. To emulate synaptic functions, voltage pulses applied to the gate electrodes are typically regarded as the presynaptic spikes. The channel conductance is equivalent to the synaptic weight and the source-drain electrodes serve as postsynaptic terminals. Thus far, many such synaptic transistors have been explored for neuromorphic applications with low switching voltages, long retention times and high endurance capabilities. Most prototypes employ liquid electrolytes^[88] and rely on gate controlled electronic or ionic/protonic migration^[86,87] processes to induce temporary/permanent changes in the channel conductance. Thus, selection of an appropriate electrolyte becomes critical. Doped polymers and nanoporous materials with high ion mobility substantially improves the response time and reduces the energy consumption, finding prospective applications in this regard^[99].

In these configurations, hysteretic behaviour of the channel conductance is used to store synaptic weights (Figure 2.8). Moisture-assisted charge trapping resulted in hysteresis in carbon nanotube (CNT)-based FETs, enabling emulation of STDP using sawtooth-shaped waveforms^[100]. Zhu et al.^[87] demonstrated an in-plane lateral-coupled oxide-based artificial synapse utilizing proton migration related electrical-double-layer (EDL) effect. Indium zinc oxide (IZO) served as both the semiconducting channel and electrodes with p-doped nanogranular SiO₂ dielectric. A positive voltage pulse on the gate induced proton migration, increasing channel conductance. By controlling the pulse intervals and hence the proton migration-relaxation kinetics, short-term plasticity

features like PPF and temporal filters were demonstrated with a spatiotemporal dependence. Proton hopping via a Grotthuss mechanism was similarly utilized by Changjin et al.^[86] for laterally coupled oxide based synaptic transistors.

Alibart et al.^[51] proposed an artificial synapse based on a nanoparticle organic memory FET (NOMFET) using Au nanoparticles and pentacene as the organic semiconductor. The NOMFET was programmed to work as a facilitating or depressing synapse with short-term plasticity features. Charges stored in the nanoparticle-based nanoscale capacitors dynamically modulated transconductance of the FETs, establishing synaptic plasticity. Tian et al.^[101] demonstrated artificial synapses based on twisted bilayer graphene and AlO_x . The hysteretic migration of pulse-induced oxygen ions and vacancies in AlO_x , trapped and released carriers from graphene, tuning the drain current through graphene. The gate control influenced the carrier transport further, modulating the plasticity and synaptic dynamics.

Figure 2.8^[102] The structure of a CNT synapse and a post-synaptic current triggered by a pre-synaptic spike. (A) A schematic diagram showing the transistor-like structure of a CNT synapse

with an electrochemical cell containing hydrogen ions in a polymer electrolyte integrated in its gate. The inset is an atomic force microscopy (AFM) image of a random CNT network. The average density of the single-wall CNTs is $\sim 8/\mu\text{m}^2$, and the average density of the CNT bundles is $\sim 2/\mu\text{m}^2$. **(B)** A scheme showing a biological synapse between a pre-synaptic neuron and a post-synaptic neuron. **(C)** A symbol represents the CNT synapse within a scheme showing that a pre-synaptic potential spike applied on its top gate triggers an excitatory post-synaptic current (EPSC) on its drain. **(D)** A pre-synaptic spike (top) applied on a CNT synapse and EPSC (bottom) triggered by the spikes are shown versus time. The superimposed grey lines represent the EPSCs measured from 20 independent tests, and the red line represents the average EPSC. The insets illustrate the distributions of the mobile hydrogen ions (red balls) in the polymer layer and free electrons (blue balls) in the CNT before (left), during (middle), and after (right) the pre-synaptic spike is applied. © “From K. Kim, C. Chen, Q. Truong, A. M. Shen, Y. Chen, *Adv. Mater.* **2013**, 25, 1693. Reprinted with permission from John Wiley and Sons.”

2.4.5.2 Organic Switches

Compared to their inorganic counterparts, the solution processing capability, chemically-tailored electronic properties, biocompatibility etc. make organic materials promising candidates^[103]. With highly modulatable conductivity, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS)-based systems offer great interest in this regard. A series of synaptic behaviours such as STP, LTP, STDP and SRDP were successfully emulated in Ag/PEDOT:PSS/Ta.^[104] and Ti-based systems^[105] with a redox-based Ag migration defining the switching characteristics. Very recently, van de Burgt et al.^[106] reported a novel electrochemical neuromorphic organic device (ENODE) based on non-volatile control of the conductivity of an organic mixed ionic/electronic conductor, similar to a battery or a non-volatile redox cell (NVRC). Field driven protonation and redox reactions doped and de-doped the active electrode material (PEDOT:PSS) via an electrolyte, decoupling the barrier for state change from retention, enabling ultra-low switching voltages while maintaining reproducible states (> 500) with excellent non-volatility. Neural network simulations for training with back-propagation yielded accuracies close to 97 %, more efficient than PCMs and near the theoretical limit for this algorithm, illustrating the computational power of these devices.

2.4.5.3 Other neuronal implementations

Spintronic devices: STDP was emulated in magnetic heterostructures composed of a magnetic material exhibiting perpendicular magnetic anisotropy and a non-magnetic heavy metal with high spin–orbit coupling^[107]. Accumulation of spin-polarized electrons generated spin–orbit torque which coupled and modulated the linear function of device conductance with respect to the domain-wall position. Stochastic memristive synapses were also implemented in a winner-takes-all (WTA) architecture based on the same principle with carefully chosen programming pulses to implement controlled switching probabilities^[108]. Simulations for object recognition were carried out and the impact of device variations (minimum/maximum resistance, transient effects) were tested through Monte Carlo methods. A compound spintronic synapse and a neuron composed of multiple vertically stacked magnetic tunnel junctions (MTJs), implementing multiple resistance states and a multi-step transfer function was recently realized as an all-spin DNN^[109].

Ferroelectric devices: 3T-FeMEM ferroelectric memristors were recently used to demonstrate on-chip pattern recognition. An external CMOS selector enabled the overlap of pre- and post-synaptic spikes applied at the gate of the 3T-FeMEM, creating STDP characteristics. Associative learning and partial recall was demonstrated in a small recurrent Hopfield network fabricated with 9 CMOS neurons and 16 synapses^[110].

Nanoparticle-based devices: Nanoparticles (NPs) exhibit significantly distinct resistive switching characteristics compared to their thin film counterparts due to unbalanced charging and discharging behaviours. Nickel oxide (NiO_x) and iron oxide (FeO_x) thin films depicted digital-type unipolar switching through the formation and rupture of conducting filaments^[111], as supposed to analog memristive switching of their NP assemblies^[112]. This was attributed to the porous microstructure of NP assemblies with distributed defects providing excess charge carriers, as supposed to relatively narrow rambling grain boundaries and dislocations in thin film structures. Additionally, core-shell structures, doping, surface functionalization and dispersions in polymeric matrices provide alternate strategies to achieve analog switching behaviours^[113,114].

Artificial Neurons: In biological neurons, arrival of an action potential (electrical pulse) causes diffusion of neurotransmitters across the synaptic cleft to receptors located on a target neuron. This either causes an increase (excite) or decrease (inhibit) in the membrane potential, activating an action potential in the target neuron on exceeding a firing threshold. Emulation of these neuronal dynamics, including maintenance of the equilibrium potential, the transient dynamics and the process of neuro-transmission, are thought to be the key to the realization of biologically plausible neuromorphic computing systems^[5,115]. Wright et al. first suggested the use of PCMs for emulation of neuronal signatures^[34]. Tuma et al. experimentally demonstrated integration of post-synaptic inputs and membrane potential evolution encoded by phase configuration using PCM-based neurons^[116]. All-PCM implementations of neurons and synapses have also been reported^[117]. Stochastic neuronal dynamics-thought to play a key role in signal encoding and sensory signal transmission, were realized in PCM devices utilizing the intra-device stochasticity associated with the internal atomic configurations of the melt-quenched amorphous region. Population-based computations were implemented based on the inter-spike interval distribution. Fast signals were accurately represented by the overall neuron population despite the ‘too-slow’ firing rate of the individual neurons. Stochastic artificial neurons were also realized using TiO_x -based resistive memory^[116] and Al_2O_3 -based CBRAM^[116] using the randomness associated with filamentary formation. Integration of neuronal inputs resulted in a large voltage developed across the capacitor (representing the membrane potential of a neuronal soma), causing switching to a low-resistance state, triggering an analog spike or a digital event via an external circuitry. Neuristors built using two nanoscale Mott memristors emulated all-or-nothing spiking with signal gain and diverse periodic spiking^[118]. Transient memory effects and negative differential resistance in these devices were caused by Joule-heat driven insulating-to-conducting phase transitions, resembling Hodgkin–Huxley Na^+ and K^+ ion channels^[92]. Lateral spin valves and domain wall magnets (DWM)^[119] were implemented as neurons with a multiply-accumulate functionality. Spin-torque transfer caused soft switching of the output magnet parallel to the polarity of the input magnet, detected through an MTJ. Excitatory and inhibitory currents through DWMs were also detected by MTJs, deciding the resultant direction of current flow and hence, the magnetic polarity. Insulator-metal transitions (IMT) of NbO_2 were recently utilized as oscillatory neurons for a Hopfield network in conjunction with Mo/PCMO synapses for pattern-recognition^[120].

2.5 Discussion

As explained in the previous sections, most of the current prototypes rely on the stochastic creation and rupture of filaments, depicting a digital-type abrupt current switching behaviour. While this is apt for conventional memory storage with excellent non-volatility, endurance, speed, retention and low power consumption, it is inapposite for the emulation of synaptic plasticity akin to biological systems. In biological systems, synaptic weights are adjusted by the number and frequency of homogeneous spikes, demanding a wider dynamic range of tunable device conductance. As shown in Figure 2.9, abrupt switching characteristics yield quasi-binary potentiation/depression curves, while non-abrupt analog switching characteristics gives rise to continuously changing potentiation/depression intimately emulating biological plasticity data^[121]. It is therefore inevitable to explore analog-type current switching memristive devices with continuously tunable resistance^[122].

Figure 2.9^[121] Comparison of typical bipolar-curves of two different types of memristive devices. (A-B) I - V curves and schematic drawings of a class of memristive devices, where the resistance switching is based on ionic motion. (C) Emulation of synaptic plasticity with an

individual TiN/Al₂O₃/TiO_{2-x}/TiN cell. A sequence of potentiation pulses of + 2 V and depression pulses of - 2 V. The pulse width for the measurements was $t_{\text{set}} = 10$ ms. **(D)** Emulation of synaptic plasticity with an Al/Al₂O₃/TiO_{2-x}/Al cell. A sequence of potentiation pulses of + 3.4 V followed by a sequence of depression pulses of - 3.4 V. The pulse width for the measurements was $t_{\text{set}} = 10$ ms. © [2015] IEEE. “From M. Ziegler, C. Riggert, M. Hansen, T. Bartsch, H. Kohlstedt, *IEEE Trans. Biomed. Circuits Syst.* **2015**, 9, 197. Reproduced with permission from IEEE.”

In the case of anion-migration-based valence change memory (VCM) cells like the filamentary RRAMs, the electroforming process is prerequisite for inducing a high-density of oxygen vacancies (V_{O} s) in the insulating oxides for nucleation and subsequent growth of conductive filaments. The abrupt nature of this process can be avoided to some extent by inducing an interface-type switching behaviour modulating the Schottky barrier between the insulating oxide and the metal electrodes^[123]. Inducing a reservoir of readily available oxygen vacancies has been identified as a primary strategy for interface-type switching. Prefabrication strategies based on intentional manipulation of native point defects were employed to create electroforming-free interface-type switching^[124,125]. The aim was to create an oxygen vacancy gradient within the oxide layer forming an oxygen rich-Schottky and oxygen deficient-Ohmic contact with the bottom and top electrodes respectively. These devices were modelled with two parallel conduction paths with smooth transitions due to the redistribution of V_{O} s^[126].

In the case of cation-migration-based electrochemical metallization (ECM) cells like atomic switches and CBRAMs, metal filaments are modulated via electrochemical dissolution and re-deposition of active metal atoms. Sourcing the solid electrolyte as a metallic electrode and a vacuum nanogap insulator, a “gapless-type atomic switch” gradually modulated the metal bridge via current controlled precipitation/dissolution rates^[127]. Another strategy widely used in phase change and bidirectional inhibition devices utilizes electrical pulse trains^[128] to continuously tune the resistance states, rather than having multiple discrete levels. Incorporation of NP interlayers (e.g., Au NPs) and doping (e.g., Ag salts) has been reported to raise the formation efficiency of filaments by modifying the electric field distribution, thereby improving the device performance. Doping the solid electrolyte matrix with cations identical to the electrochemically active electrode has been utilized to facilitate continuous migration

of cations and aid the filament growth. This approach has been demonstrated to achieve gradual conductance tuning and is a feasible alternative to external modulation^[49,129,130].

Other device concepts including MTJ and synaptic transistors have also been proposed, but requires further systematic investigations with regard to speed and power efficiencies. Incorporating additional bio-realistic plasticity features like short-term plasticity, homeostasis, metaplasticity and association requires judicious design of pulsing schemes that can exploit the internal state dynamics of switching. Several studies utilizing the internal state dynamics of memristors for emulation of soma and axons of a neuron have also been proposed, but demands further systematic investigations.

Very recently, Yang et al.^[131] reported a novel diffusive Ag-in-oxide memristor utilizing spontaneous field-driven migration and interfacial energy-driven relaxation of Ag atoms. In contrast to the traditional drift dynamics, these synaptic emulators functioned primarily on the basis of diffusion, physically similar to the intracellular biological Ca^{2+} flux dynamics, enabling a direct emulation of bio-inspired plasticity rules. This provides an encouraging pathway towards designing novel materials and device configurations to physically clone biological neurotransmitter dynamics, resulting in efficient neuromorphic computing elements.

2.6 Questions to answer based on literature

As discussed in the earlier sections, current memristive solutions fall behind in terms of the smoothness of their conductance transitions, width of dynamic range, programming energy, conductance linearity and other device infidelities, crippling their employability in SNNs and DNNs. With regards to the analog-like switching requirement, most device prototypes like those based on electrochemical metallization or filamentary switching are handicapped since the switching mechanisms are based on inherently stochastic processes like formation and rupture of conductive filaments^[99]. Randomness in the location and direction of filamentary growth, the migration and degradation rates and the uncontrollable diffusion pathways like grain boundaries or dislocations, adversely influence their effectiveness for neural emulation^[84,132,133]. This calls for the need of investigation into switching modalities that portray gradual modulation of conductive states for effective neural emulation^[8].

With regards to emulation of weight plasticity, current hardware implementations mostly focus only on STDP-based learning rules. Short-term plasticity rules that depend on internal temporal state dynamics of the device are often overlooked. But STP has been very recently identified as crucial for signal processing in a fatigue STDP-based model^[134] and hence, material and device configurations emulating both short and long-term plasticity need to be identified. Computational schemes like SNNs and DNNs demanding unique plasticity requirements also entails systematic development of computational schemes tailored to the corresponding device physics^[5]. Most reports also fail to emulate more complex neuronal phenomena like homeostatic regulation, association and the massive interconnectivity observed in biology, crippling their application in large-scale neural networks^[97]. While the interconnectedness accounts for parallel processing, homeostasis^[135] regulates the neural network operation and association helps develop complex experience-dependent correlations^[136]. Emulation of the massive interconnectivity also places strict requirements on the design of CMOS neuron circuitry and peripherals to effectively address this memory array. Power consumption and speed are major concerns when implementing artificial neuronal elements, and novel systems need to offer a significant speed-up or power advantage over the existing capabilities^[10]. Moreover while emulation of synapses demand a continuum of conductance states with excellent non-volatility, emulation of neurons require volatility with an accumulative behaviour to implement leaky integrate-and-fire dynamics; demanding higher plasticity from these devices. This calls for extensive materials research and reliable device configurations, whose temporal conductance response can be tuned to demonstrate various forms of neuronal plasticity with advantages in energy, speed, cost, or other advantages when compared to the state-of-the-art.

2.7 PhD in the context of literature

Identifying the switching design requirements necessary for computationally efficient artificial synapses, this dissertation focusses on memristive device configurations that encompass ionically and optically-active semiconductors and dielectrics, directly or indirectly tuning the electronic conductivity on demand. A hybrid ionic-electronic conduction is envisaged to approximate the biological Ca^{2+} dynamics, encouraging systematic investigation and comparison of novel material sets and device

configurations that couple electronic, ionic and photonic modes of charge transport to comprehensively emulate complex neuronal characteristics.

First, the intimate ionic-electronic (ionotronic) coupling in halide perovskite semiconductors was utilized to create memristive synapses with analog-like conductance transitions. Co-existence of ion migration-relaxation kinetics and tunable injection barriers were observed to define the degree of weight plasticity, more profound in organic cation containing halide perovskites. This study reports the first comprehensive investigation of halide perovskites as artificial synapses with insights into novel ionotronic material design and neural network simulations demonstrating the computational capability of this material set.

Realizing the advantages of a FET configuration in achieving smooth conductance transitions with a gated control of plasticity, a dual-gated approach was next proposed, with one mode (ionotronic) capturing the effect of local activity correlations and the other (electronic) representing global neuromodulations, accounting for the immense interplay between local and global neuromodulations at a unitary level. High-mobility amorphous metal oxide semiconductors (IWO) were configured in a dual-gated architecture with a solid-state ionic dielectric [P(VDF-HFP)-[EMIM][TFSI]] and a bottom SiO₂ insulator for the same. This study reports the first demonstration of heterosynaptic or three-factor plasticity rules^[137,138] and coincidence detection in a single neural element, and also reports highly energy-efficient neuristors (among the lowest reported till date) operating in the sub-threshold regime.

Identifying the benefits of an optoelectronic computing platform that harnesses the advantages of both electron and photon-based computations, neuromorphic transistors programmable via multimodal electrical and optical pulses were finally designed based on 2D TMDCs like MoS₂ and ReS₂ with synergistic gating controls intimately modulating the carrier concentration. Such transistors were constructed to operate in multiple modes, namely- electronic, ionotronic and phototronic, exploiting the advantages of electrons, ions and photons for concurrent compute and store operations. The high degree of modulatable plasticity allowed the same device to be compatible with both SNN and DNN algorithms via an interplay between Hebbian metaplasticity, homeostasis and association, alleviating complex circuit design requirements (seminal

report). Drawing inspiration from optogenetics, these neuristors were finally integrated with soft dielectric elastomeric actuators to create an artificial eye with learning and memory behaviours that resemble a human eye. Such a fusion of the concepts of optogenetics, neuromorphic electronic systems and soft robotics would pave way for behavioural robots with bioinspired cognition and learning abilities.

In summary, the investigations undertaken in this dissertation address many of the critical challenges in realizing bio-inspired in-memory computing elements with shrewd material selection and novel device configurations.

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Chapter 3

Experimental Methodology

This chapter briefs the rationale behind the selection of materials and device configurations adopted for this study and also details the fabrication and characterization techniques employed to investigate the physical, optical and electrical properties of these materials and devices.

3.1 Rationale for selection of materials and device configurations

In contrast to the conventional memory technology, neuromorphic applications set unique requirements on the hardware switching devices. Emulation of synapses necessitates adaptive non-volatile analog-like switching transitions and continuously distributed conductance states, while artificial neurons require an accumulative behaviour with volatility. Furthermore, while STDP-based SNNs demand bidirectional temporal plasticity of weights/conductances, DNNs emphasize more on conductance linearity and symmetric weight updates for machine learning algorithms and vector matrix multiplications^[1]. Very recently, second-order drift memristors^[2,3], electrochemical metallization cells^[4] and diffusive memristors^[5] have been engineered to approximate the biological Ca^{2+} dynamics based on metal atom diffusion, thermal dissipation^[2], mobility decay^[6] and spontaneous nanoparticle formation. A common feature in all these systems is the insertion/extraction of mobile ions, directly or indirectly altering the electronic conductivity. Hence, a hybrid ionic-electronic conduction mechanism could be considered vital to approximate the biological neural dynamics.

An ionic semiconductor which intimately combines rapid electronic transitions with slow drift-diffusive ionic kinetics would enable dynamic tuning of memristive conductance-states, allowing efficient emulation of synaptic characteristics and catering for novel low-power architectures that exploit electronic properties of the semiconductor. Halide perovskites are facilely processable ionic semiconductors that have lately revolutionized the field of optoelectronics with their superior electronic properties, such as low defect-densities and long carrier-diffusion lengths^[7]. Ionic motion in halide perovskites induce hysteresis, slow photocurrent decays and above bandgap photovoltages^[8] without compromising on their excellent optoelectronic properties such as low carrier effective mass and high photoluminescence quantum yields, allowing construction of high-performance solar cells and light-emitting diodes (LEDs)^[9]. Hysteresis observed in the I-V curves are considered deleterious by the photovoltaic community, often disparaging the hybrid ionic-electronic/ ionotronic conduction in these materials. However, this mixed ionic-electronic conduction could be harnessed to approximate the biological neural dynamics. Hence, the ionic-electronic (ionotronic) coupling in halide perovskite semiconductors were investigated to create memristive synapses with smooth conductance transitions.

In contrast to the abrupt switching transitions in a two-terminal memristor configuration, a three-terminal FET configuration exhibiting time-dependent hysteresis would result in much smoother conductance transitions. Moreover, the gated control of hysteresis and threshold voltage shift could be utilized to modulate the degree of plasticity even further. For example, the transistors could be programmed to operate in the sub-threshold region, resulting in larger weight changes at ultralow power due to the larger sub-threshold swing. The polarity on the gates could be used to control the level of potentiation / depression and even switch between short and long-term plasticity for SNNs. With regards to DNNs, the transistors could be biased to operate in its triode regime to achieve linear weight changes. All these characteristics would enable more complex features like heterosynaptic plasticity, homeostatic regulation and associative learning to be emulated in a single element, previously impossible with standard two-terminal memristors, thus making the FET configuration a superior alternative.

Ionic dielectrics with extremely large electrical double layer (EDL) capacitance have been extensively utilized for ultra-low voltage operation of both organic and inorganic transistors. Apart from ultra-low voltage operation, most of these ionic dielectrics also depict a gate controllable hysteresis, but have been underutilized till date. A combination of this together with high-mobility semiconductors would yield prototypical platforms for ultra-low power neuromorphic electronics with highly smooth conductance transitions. Since the gate control elevates the degree of achievable plasticity, encompassing multiple gates to synergistically control the channel conductance seems logical. Realizing the advantages of a multi-gated FET configuration, the next study utilized high-mobility amorphous metal oxide semiconductors (IWO) in a dual-gated configuration with a solid-state ionic dielectric [P(VDF-HFP)-[EMI][TFSI]] and a bottom SiO₂ insulator.

Information transmission via light-pulses as opposed to voltage-packets could unlock exceptionally fast transmission speeds with less cross-talk, high parallelism, low noise and nearly unlimited bandwidth. Neuromorphic transistors programmable via multimodal electrical and optical pulses would pave way for novel synergistic architectures encompassing advantages of both electron and photon-based computing platforms. Such artificial synapses with augmented plasticity would enable the design

of robust neuromorphic circuitry with drastically lesser neural elements, overcoming the stringent circuit density requirements and fabrication challenges necessary to match the computational capability of the human brain. Utilizing photons as global virtual interconnects would help overcome electrical interconnect limitations, mitigate thermal loss and decrease the footprint and circuit density requirements at the system level. This entails the need of atomically-thin semiconducting channels with opto-electronically modulatable carrier concentration, and synergistic optoelectronic gating strategies to address the memconductance states in these semiconducting channels.

With ultrafast charge carrier dynamics^[10,11], optoelectronically tunable carrier concentration^[12,13] and atomic scalability^[14], 2D transition metal di-chalcogenides (TMDCs) like MoS₂ and ReS₂ present an enviable platform that could take advantages of both photon and electron-based computing. Encompassing synergistic gating controls, namely- electronic, ionotronic and phototronic, these semiconducting platforms enable optoelectronic neuromorphic elements with an unmatched degree of plasticity and hence, justifies systematic investigations. While the effects of synergistic controls on the achievable plasticity were intensively investigated in the MoS₂ system, ReS₂ transistors were deployed as optogenetic actuators together with soft dielectric elastomeric actuators to create a dummy optogenetic toolkit for behavioural robotics.

3.2 Device Fabrication

3.2.1 Ionic-Electronic Drift-Diffusive Halide Perovskite Memristive Synapses^[15]

Indium tin oxide (ITO) coated glass substrates ($7 \Omega \cdot \text{cm}^{-2}$) were cleaned in soap, deionised water, and ethanol solution. Substrates were then subjected to oxygen plasma treatment for 15 minutes, followed by deposition of PEDOT: PSS (the hole transporting layer (HTL)) (Clevios P VP Al 4083) via spin coating (4000 rpm for 60 s). Samples were annealed at 140 °C for 10 minutes in air, after which the perovskite films were spin coated (5000 rpm for 30 s) from equimolar precursor solutions and annealed at 100 °C for 15 minutes under nitrogen environment to remove the solvent residue. Three types of precursor solutions were used, i.e. 1 M CH₃NH₃Br – PbBr₂, 1 M CH(NH₂)₂Br – PbBr₂ in Dimethylformamide (DMF)-Dimethyl sulfoxide (DMSO) mixture solvent (25 % DMSO), and 0.5 M CsBr – PbBr₂ in DMSO solvent. Due to the low solubility of CsBr in the solvent, 0.5 M CsBr and 0.5 M PbBr₂ in DMSO solvent was used to deposit the CsPbBr₃ film instead. In case of methylammonium and formamidinium

systems, toluene was dripped for 25 seconds during spin coating to facilitate formation of compact films. 45 nm of bathophenanthroline (Bphen) was then thermally evaporated, followed by evaporation of 7 nm calcium and 100 nm aluminium. All evaporation processes were carried out at a base pressure of 4×10^{-6} Torr with the active device area defined by shadow masks during calcium and aluminium evaporation. Devices were finally encapsulated using ultraviolet (UV)-curable epoxy and glass cover (Figure 3.1). These devices had an active area of 12 mm².

Figure 3.1^[15] **Device architecture.** Architecture of an artificial synapse with halide perovskites as the active switching materials. © “From R. A. John, N. Yantara, Y. F. Ng, G. Narasimman, E. Mosconi, D. Meggiolaro, M. R. Kulkarni, P. K. Gopalakrishnan, C. A. Nguyen, F. De Angelis, S. G. Mhaisalkar, A. Basu, N. Mathews, *Adv. Mater.* **2018**, 1805454. Reprinted with permission from John Wiley and Sons.”

3.2.2 Dual Gated Ionic-Electronic Synaptic Transistors^[16]

Solid-state ionic dielectric preparation and characterization: The ionic liquid [EMIM][TFSI] was initially dried in vacuum for 24 hours at a temperature of 70 °C. Next, P(VDF-HFP) and [EMIM][TFSI] were co-dissolved in acetone with a weight ratio of 1:4:7. The ion gels (10 μm) were further dried in vacuum at 70 °C for 24 hours to remove the residual solvent, after which it was cut with a razor blade, and then laminated onto the substrate of choice.

Neuristor fabrication and characterization: IWO thin films (thickness ~7 nm) were deposited on SiO₂(300 nm)/Si wafers at room temperature using a radio frequency (RF) magnetron sputtering technique with a In₂O₃:WO₃ (a-IWO) (98 : 2 wt %) target at a gas mixing ratio of Ar : O₂ (20 : 1), total chamber pressure of 5 mtorr and RF power of 50W. ITO source and drain contacts (thickness ~100 nm) were then sputter deposited

through a shadow mask using a In_2O_3 : SnO_2 (90 : 10 wt%) target. The devices were then annealed at 200°C for 30 minutes in ambient environment for optimized transistor performance. Ion gels were laminated on to these to create dual-gated neuristors (Figure 3.2).

Figure 3.2^[16] **Device architecture.** Chemical structures of the [EMIM][TFSI] ionic liquid (top) and the P(VDF-HFP) copolymer (bottom) which are cured to obtain free-standing ion gels (*left*). The proposed dual-gated architecture of oxide neuristors (*right*). "Reprinted with permission from R. A. John, N. Tiwari, C. Yaoyi, * Ankit, N. Tiwari, M. Kulkarni, A. Nirmal, A. C. Nguyen, A. Basu, N. Mathews, *ACS Nano* **2018**. © [2018] American Chemical Society."

3.2.3 Synergistic Gating of Electro-Iono-Photoactive 2D Chalcogenide Neuristors^[17]

A scotch-tape method was used to exfoliate MoS_2 flakes from bulk crystal and was transferred onto a degenerately doped Si substrate with 285 nm SiO_2 . The electrodes were patterned via photolithography, followed by thermal evaporation of Cr/Au (5/50 nm) and subsequent lift-off process (Figure 3.3). The ionic liquid [N, N-diethyl-N-(2-methoxyethyl)-N-methylammoniumbis-(trifluoromethylsulfonyl)-imide (DEMETFSI)] was dropped on to the channel area and contacted with a probe tip. This served as the top gate dielectric while SiO_2 served as the bottom insulator.

Figure 3.3^[17] Device architecture. The proposed multi-gated architecture of MoS₂ neuristors. © “From R. A. John, F. Liu, N. A. Chien, M. R. Kulkarni, C. Zhu, Q. Fu, A. Basu, Z. Liu, N. Mathews, *Adv. Mater.* **2018**, 1800220. Reprinted with permission from John Wiley and Sons.”

3.2.4 A Dummy Optogenetic Toolkit with Photosensitive Neuristors and Soft Robots

ReS₂ neuristor fabrication: A scotch-tape method was used to exfoliate ReS₂ flakes from bulk crystal and was transferred onto a degenerately doped Si substrate with 285 nm SiO₂. The electrodes were patterned via photolithography, followed by thermal evaporation of Cr/Au (5/50 nm) and subsequent lift-off process (Figure 3.4).

Figure 3.4 Device architecture. The proposed architecture of ReS₂ neuristors.

Actuator fabrication and performance: The dielectric elastomer actuator (DEA) was made of an elastomeric layer subsequently coated with compliant electrodes on opposite sides. Commercially available 3M acrylic tape (VHB 4910) was chosen as the elastomeric layer and carbon-based electrodes (Carbon powder (Sigma Aldrich) &

Carbon conductive grease (MG Chemicals)) were preferred as the compliant electrodes of the actuator. The elastomeric film was pre-stretched biaxially to 300 % of its original dimension using an universal stretching machine (CTC Ironworks) (Figure 3.5). Pre-stretching led to reduction of film thickness, contributed to suppression of the failure mode known as the pull-in stability and improved the dielectric breakdown strength of the elastomer, enhancing the performance. The pre-stretched film was first taken out on a big rigid frame (steel) and finally placed on smaller device frames (acrylic, outer diameter – 10 cm, inner diameter – 8 cm). Circular masks of 3 cm diameter were cut from wax paper (parafilm) and placed at the centre of the film on both sides. Carbon powder, followed by carbon conductive grease was brushed on both sides to form compliant electrodes. Carbon and copper tapes were used for making electrical connections.

Figure 3.5 DEA Fabrication. The figure depicts various stages of the actuator fabrication.

Demo Setup: The electrical setup includes a microcontroller (Arduino UNO MCU), a relay switch, a high voltage transformer (EMCO, CB101) and a DC Power supply (Aim TTi). The Arduino microcontroller acted as an ohmmeter and monitored the channel resistance of ReS₂ neuristors; and based on a pre-determined resistance threshold activated the relay. The relay switch served as an additional control for controlling the electrical input to the high voltage transformer from DC power supply. The relay switch also served as a protection for the Arduino UNO MCU against voltage surges. Using the Arduino UNO MCU, the relay switch was programmed to turn on the circuit at a pre-determined resistance threshold (1 M Ω). This completed the circuit between the DC power supply and the high voltage transformer, providing high voltage needed for

the DEA actuation. The schematic for the complete demo setup is shown in Chapter 7 Figure 7.12.

3.3 Characterizations and Simulations

3.3.1 Electrical Characterization

All electrical measurements in this dissertation were carried out in a Desert Cryogenics (Lakeshore) probe station using Keithley 4200-SCS semiconductor characterization system via custom defined pulsing programs with a coupled light source (Thorlabs Solis-445C, 525C, 623C) and a DC2200 driver in an external transistor–transistor logic (TTL) modulation configuration. Capacitance measurements were carried out using an Alpha A Analyzer, Novocontrol analyser over a frequency range of 1 Hz to 10 kHz.

Paired Pulse Facilitation (PPF) and temporal filter characterization: To characterize PPF, two voltage pulses of a specific amplitude and pulse width (device-dependent parameters) were applied to the device under test (DUT) and the current responses (EPSCs) were recorded simultaneously using the source measurement units (SMUs) of the 4200 SCS. A voltage list sweep program was used for these measurements and the pulse interval was varied to derive the exponentially-decaying behaviour of EPSCs.

Long-term plasticity characterization: For long-term weight analysis the following approach was used.

1. The device conductance was read using a small reading voltage (Eg: $V_{ds} = 0.1$ V was used to read the channel memconductance of IWO transistors-Chapter 5)
2. Necessary voltage waveforms were applied to the pre- and post-synaptic terminals of the device to induce non-volatile weight changes in conductance.
3. The conductance of the device was read simultaneously using the SMU.
4. The retention of the states were analysed by monitoring the conductance of the device after application of the ‘write’ pulses and the average retention time of the states were decided based on the behaviour of the device in the initial experiments. A small reading voltage was used to read the conductance states. For weight analysis, the retention curves were plotted and a specific time was chosen (Example: conductance of the oxide channels were monitored for 30 minutes after application of the waveforms). This value was compared to the initial conductance state to calculate weight change %.

5. For STDP analysis, specific sawtooth voltage waveforms (device-dependent) were applied at the pre- and post-synaptic terminals and the change in channel conductance was read and monitored as explained in steps 3 and 4.
6. For measurements that coupled the light source, one SMU was reserved for the light source. The controller was connected to the 4200 SMU via a TTL terminal provided with the DC2200 driver.

3.3.2 Field emission scanning electron microscopy (FESEM)

FESEM (JEOL JSM-7600F) was employed to characterize the topographical and cross-sectional images of the halide perovskite films. Please refer to Chapter 4 Figure 4.2 for the results.

Working Principle^[18]: Electron microscopes utilize short wavelength electrons instead of photons to image extremely small features (up to a few nm). Primary electrons generated from a field emission source are accelerated and focussed under a high electrical field in vacuum to produce a rastering beam that bombards the sample of interest. Secondary electrons released from the K-shell of the sample near the surface are detected by a detector, imparting information about the topography. Backscattered electrons, reflected upon interaction of the incident electrons with the atomic nuclei determines the image contrast as a function of the atomic number, revealing further information about the composition of the sample.

3.3.3 X-ray diffraction (XRD)

(XRD)-Bruker D8 Advance was used to probe the crystal structure of the halide perovskite films. Please refer to Chapter 4 Figure 4.2 for the results.

Working Principle^[19]: XRD is a rapid analytical technique primarily used for phase identification of a crystalline material. The analysis is based on constructive interference of monochromatic X-rays and a crystalline sample when conditions satisfy Bragg's Law ($n\lambda = 2d \sin \theta$). The lattice parameters is calculated based on the relation between the wavelength (λ) of electromagnetic radiation and the angle of diffraction (θ). When scanned over a range of θ , a characteristic x-ray diffraction pattern is generated, providing a unique “fingerprint” of the crystallinity of the sample.

3.3.4 Computational Details

To account for the differences in synaptic signatures observed in the three perovskite films and as a first judgement of the kinetics of migrating species, first principles calculations on MAPbBr₃, FAPbBr₃ and CsPbBr₃ were performed on their room-temperature stable phases (pseudo-cubic and orthorhombic, respectively). Density functional theory (DFT) calculations were carried out, within a plane wave/pseudopotential approach, as implemented in the PWSCF program of the Quantum Espresso software package.^[20] To accommodate the different point defects studied and their migration along the perovskite crystal, a rather large tetragonal unit cell containing 384 atoms (32 PbI₃ units) was built up. The PBE^[21] exchange-correlation functional was used along with ultra-soft, scalar relativistic pseudopotentials for all atoms. Plane wave cut-offs of 25 and 200 Ry were adopted for expansion of the wave function and density respectively, sampling the first Brillouin zone at the Γ point only. Electron-ion interactions were described by ultra-soft pseudopotentials with electrons from N, C 2s2p, H 1s, Pb 6s6p5d, Br 4s4p and Cs 5s5p6s electrons explicitly included in the calculations. Structural optimizations were performed with cell parameters fixed to the experimental values reported by Poglitsch and Weber.^[22] The scalar relativistic approach (SR) for structural optimizations was adopted, since spin-orbit coupling is known to play a minor role on the structure. Linear transit calculations were performed to calculate the energy profile along the migration paths of the defects, identify the saddle point, and estimate the energy barriers. Please refer to Chapter 4 Figure 4.10, Tables 4.5-6 for the results.

3.3.5 Fourier transform infrared (FTIR) spectroscopy

To determine the nature of interaction between the ionic liquid and polymer matrix (Chapter 5), Fourier transform infrared (FTIR) spectroscopy was performed using FTIR spectrum GX, PerkinElmer. Please refer to Chapter 5 Figure 5.2 for the results.

Working Principle^[23]: FTIR analysis relies on the vibration of molecular bonds at frequencies specific to the type of elements and bonds present in the sample. Most molecules absorb light in the infrared (IR) region of the electromagnetic spectrum, typically measured as wave numbers over the range $\sim 4000\text{ cm}^{-1}$ to $\sim 200\text{ cm}^{-1}$. A comparison of the emission spectrum of the IR source recorded with a sample in place against a background spectrum, provides a resultant absorption spectrum characteristic

to the chemical bonds and functional groups present in the sample. This technique is particularly useful for the identification of organic molecular groups and compounds due to the presence of a large variety of functional groups and side chains, all of which depict characteristic vibrational frequencies in the infrared range.

3.3.6 Differential scanning calorimetry (DSC)

The plasticizing effect of the ion gel (Chapter 5) was investigated using differential scanning calorimetry (DSC TA Instruments 2010) at a ramping rate of 10 °C /min. The samples were tightly sealed in aluminium pans, and the measurements were carried out while heating up the sample to 200 °C, followed by cooling down to –80 °C, at a heating and cooling rate of 10 °C min⁻¹. Please refer to Chapter 5 Figure 5.2 for the results.

Working Principle^[24]: Differential Scanning Calorimetry is a technique in which the difference in the amount of heat required to increase the temperature of a sample and reference are monitored with reference to temperature. Temperature of the sample holder is generally increased linearly with temperature and both the sample and reference are maintained at nearly the same temperature. Physical transformations like phase transitions in the sample alter the heat flow required to maintain the same temperature, depending on whether the process is exothermic or endothermic. For example, endothermic processes like melting increases the heat flow requirement, whereas exothermic phase transitions like crystallization reduces the heat flow requirement. The differences in heat flux correspond to the amount of heat absorbed or released or enthalpies during such transitions, enabling facile but precise investigation of all phase transitions that involve energy or heat capacity changes.

3.3.7 Thermogravimetric analysis (TGA)

The degradation (working) temperature of the ion gel (Chapter 5) was measured by thermogravimetric analysis (TGA-Q500). Please refer to Chapter 5 Figure 5.2 for the results.

Working Principle^[24]: Thermogravimetric Analysis is a technique in which the mass of a substance is monitored as a function of temperature / time under a controlled atmosphere and with a controlled heating rate. The equipment consists of a sample pan supported by a precision balance, residing in a furnace. The sample is heated or cooled during the experiment and the mass is monitored continuously. A purge gas controls the environment. Mass changes produces steps in the TGA curve or peaks in the

differential thermogravimetric (DTG) curve. Some of the effects usually studied include evaporation of volatile constituents like water, solvents, plasticizers and fillers; oxidative and thermal decomposition of organic substances, decarboxylation and condensation reactions.

3.3.8 Raman Spectroscopy

The thin flakes of MoS₂ (Chapter 6) and ReS₂ (Chapter 7) were identified by optical contrast conducted with Olympus BX51 microscope. Raman characterizations were performed to confirm the purity of the sample using Witec confocal Raman system under 532 nm laser excitation. Please refer to Chapters 6, 7 Figures 6.1 and 7.1 for the results.

Working Principle of Raman spectroscopy^[25]: Based on the inelastic scattering of monochromatic light, Raman spectroscopy is a versatile method for forensic analysis of samples. The incident laser beam induces periodical molecular deformations or vibrations upon interaction with the sample. Frequency of the scattered radiations enable qualitative analysis while the intensity accounts for quantitative analysis. During this process energy is exchanged between the photon and the molecule such that the scattered photon differs from the incident photon in the presence of a Raman-active mode. The difference in energy is accounted by a change in the rotational and vibrational energy of the molecule and gives information on its energy levels. However, spontaneous Raman scattering is very weak since ~ 99.999 % of all incident photons undergo elastic Rayleigh scattering with no change in the emitted frequency in the absence of a Raman-active mode. In the presence of a Raman-active mode, a reduction in frequency called the Stokes frequency indicates a basic vibrational state and an increase (Anti-Stokes) represents an excited vibrational state at the time of interaction.

3.3.9 Photoluminescence (PL) spectroscopy

The thin MoS₂ flakes (Chapter 6) were subjected to photoluminescence measurements to identify nature of the band-gap. Please refer to Chapter 6 Figure 6.1 for the results.

Working Principle of Photoluminescence spectroscopy^[26]: Photoluminescence spectroscopy is a contactless, versatile and non-destructive optical tool for probing the electronic structure of materials. Photon absorption excites electrons from their electronic ground state to higher electronic excited states, where vibrational relaxation triggers the excited electron quickly to the lowest vibrational level. Subsequent

relaxation to ground state occurs via radiative and non-radiative transitions due to internal conversions/quenching resulting in fluorescence/phosphorescence. The physical principle of photoluminescence spectroscopy is depicted by the Jablonski diagram. For semiconductor materials, the emitted photon during radiative recombination usually has an energy equal to the band gap, thereby providing a direct measurement of the bandgap energy and decay lifetimes, in turn shining light on the presence of impurities, dopant concentrations, structural defects and electron–hole recombination mechanisms.

3.3.10 Atomic Force Microscopy (AFM)

The sample thickness and morphology of the MoS₂ (Chapter 6) and ReS₂ flakes (Chapter 7) were investigated by atomic force microscopy (AFM; Asylum Research TS-150). Please refer to Chapter 6 Figure 6.1 and Chapter 7 Figure 7.1 for the results. *Working Principle of Atomic Force Microscopy (AFM)*^[27]: AFM is a kind of scanning probe microscopy in which a topographical image of the surface is generated based on the interactions between a cantilever tip and the sample surface. Scanning across a surface causes deflections of the cantilever away from the surface, which is picked up by a position-sensitive photo diode (PSPD) in response to the changes in direction of a reflected beam, bounced off the flat top of the cantilever by a laser. By using a feedback loop to control the height of the tip above the surface—thus maintaining a constant laser position—the AFM can generate an accurate topographic map of the surface features with resolution of the order of fractions of a nanometer.

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Chapter 4^[1]

Ionic-Electronic Drift-Diffusive Halide Perovskite Memristive Synapses

An ionic semiconductor that couples slow drift-diffusive ionic kinetics with fast electronic transitions would enable dynamic energy-efficient analog-like switching of memconductance states. Here, the ionic-electronic (ionotronic) coupling in halide perovskite semiconductors is utilized to create memristive synapses with smooth conductance transitions. Co-existence of carrier injection barriers and ion migration enables comprehensive emulation of synaptic signatures like short and long-term plasticity, more noticeable for the larger organic cation (methylammonium and formamidinium) containing halide perovskites than their inorganic cesium counterpart. Configured as a memory storage array, these devices demonstrate learning, forgetting and fault tolerance, analogous to the human brain. Neural network level simulations of unsupervised learning validates the utility of these memristive synapses, paving way for novel ionotronic computing architectures utilizing halide perovskites as the active material.

^[1]This chapter is published substantially as John, Rohit Abraham, et al. "Ionotronic Halide Perovskite Drift-Diffusive Synapses for Low-Power Neuromorphic Computation." *Advanced Materials* (2018): 1805454.

4.1 Introduction

Comprehensive emulation of neural signatures demands adaptive memory elements with smooth analog-like transition of conductance states, good non-volatility and a large dynamic range^[2]. Despite remarkable progress, current solutions lag in these aspects, entailing systematic investigation of novel materials and device configurations for brain-inspired electronics. Harnessing diffusive ion mechanics, ionically-gated transistors offer a potential solution to this issue, but require coupling of two disparate ionically- and electronically-active material sets^[3,4]. Very recently, diffusive memristors^[5], second-order drift memristors^[6,7] and electrochemical metallization cells^[8] have been proposed as promising alternatives for abruptly-switching drift-memristors. These devices rely on field-driven metal atom diffusion^[5], thermal dissipation^[6], mobility decay^[9] and interfacial energy-driven relaxation^[5] to approximate the neural dynamics. However, they often require additional non-volatile elements in series for long-term storage of synaptic weights.

An ionic semiconductor that intimately combines slow drift-diffusive ionic kinetics with rapid electronic transitions would enable dynamic modulation and addressing of memconductance states. Halide perovskites are facilely processable ionic semiconductors that have lately revolutionized the field of optoelectronics with their superior electronic properties^[10]. Ionic motion within these materials have been accounted to induce hysteresis, slow photocurrent decays and above bandgap photovoltages^[11] in these devices. This hysteresis in the I-V curves is considered deleterious by the photovoltaic community, often disparaging the hybrid ionic-electronic/ ionotronic conduction in these materials. However, this mixed ionic-electronic conduction could be harnessed to approximate the biological neural dynamics.

Herein, the intimate electronic-ionic coupling in halide perovskites (namely methylammonium lead bromide ($\text{CH}_3\text{NH}_3\text{PbBr}_3/\text{MAPbBr}_3$), formamidinium lead bromide ($\text{CH}(\text{NH}_2)_2\text{PbBr}_3/\text{FAPbBr}_3$) and cesium lead bromide (CsPbBr_3)) are harnessed to build artificial memristive synapses with comprehensive emulation of both short- and long-term plasticity rules (Figure 4.1). Ionic effects modulate the electronic conductance state, mimicking intracellular Ca^{2+} - Na^+ - K^+ flux altering the resting-potential, while charge transport pathways mimic the synaptic cleft, and the device

conductance defines the synaptic weight. Co-existence of ion migration-relaxation kinetics and tunable injection barriers defines the degree of weight plasticity, cardinal for memory and learning. With higher activation energies for ion migration, weight changes are observed to be more profound in the organic cation (methylammonium and formamidinium) containing halide perovskites. These devices are next demonstrated as a reconfigurable and trainable memory array with good retention properties utilizing long-term non-volatile weight changes. Neural network level simulations of unsupervised learning based on experimentally-measured device properties, illustrate the computational efficiency of these drift-diffusive memristors, paving way for novel ionotronic neuromorphic architectures.

Figure 4.1 Biological and Artificial Synapses. (A) Schematic of the biological synaptic transmission. Arrival of an action-potential causes selective endocytosis and exocytosis of Na^+ , K^+ and Ca^{2+} deciding the extent of membrane polarization. (B) Architecture of an artificial synapse with halide perovskites as the active switching materials. Three different materials namely MAPbBr_3 , FAPbBr_3 and CsPbBr_3 are investigated as switching matrices. The memristive/hysteretic electrical effects in halide perovskites are utilized to create and modulate plasticity in these devices. © “From R. A. John, N. Yantara, Y. F. Ng, G. Narasimman, E. Mosconi, D. Meggiolaro, M. R. Kulkarni, P. K. Gopalakrishnan, C. A. Nguyen, F. De Angelis, S. G. Mhaisalkar, A. Basu, N. Mathews, *Adv. Mater.* **2018**, 1805454. Reprinted with permission from John Wiley and Sons.”

4.2 Results

Physical Characterization. X-ray diffraction (XRD) spectra of the deposited perovskite films are reported in Figure 4.2-A. MAPbBr_3 and FAPbBr_3 films depicted a cubic crystal structure (Pm-3m), while the CsPbBr_3 film revealed an orthorhombic crystal structure (Pnma). No additional phase or impurities were observed from XRD spectra of all films. Both MAPbBr_3 and FAPbBr_3 film were preferentially oriented towards (100) direction. Figure 4.2-B depicts the cross-sectional scanning electron

microscope (SEM) images of the halide perovskite films deposited on ITO-PEDOT: PSS. The artificial synapses were built by sandwiching the halide perovskite active layer with hole (HTL) and electron transporting layers (ETL). PEDOT: PSS was utilized as the HTL while Bphen served as the ETL. ITO electrode was used for hole injection while a stack of calcium-aluminium was employed to inject electrons into the device. The energy band diagram of the corresponding device architecture is shown in Figure 4.2-C. Device fabrication and physical characterizations are described in detail in the experimental section (Refer to Chapter 3 Sections 3.2.1 and 3.3).

Figure 4.2 Physical Characterization of halide perovskites and their DC I-V memristive characteristics. (A) XRD spectra of MAPbBr₃, FAPbBr₃, and CsPbBr₃ films respectively, (B) Cross-sectional SEM images of the halide perovskite films deposited on ITO-PEDOT: PSS. (C) Energy band diagram of the device architecture used. (D-F) Standard memristor characteristics for MAPbBr₃, FAPbBr₃ and CsPbBr₃-based thin film devices [Device structure: Au/perovskite/ITO]. © “From R. A. John, N. Yantara, Y. F. Ng, G. Narasimman, E. Mosconi, D. Meggiolaro, M. R. Kulkarni, P. K. Gopalakrishnan, C. A. Nguyen, F. De Angelis, S. G. Mhaisalkar, A. Basu, N. Mathews, *Adv. Mater.* **2018**, 1805454. Reprinted with permission from John Wiley and Sons.”

DC I-V Memristor Characteristics. Figures 4.2-D-F shows the DC I-V memristor

curves of the active halide perovskite layers [Device structure: Au/perovskite/ITO]. All the three active layers demonstrated switching capabilities with a butterfly-like memristor characteristics. Recently, several reports have investigated switching abilities of halide perovskites and have attributed the switching mechanism to vacancy-mediated migration of both halide and A-site cations^[12,13]. The switching characteristics of halide perovskites have been reported to heavily depend on the selection of top active electrode, the device area, use of protective oxide/organic layer, etc.^[14–17] In this study, the memristive/hysteretic property of halide perovskites is utilized as a proxy for developing synapses with modulatable plasticity and hence, investigations on factors like top active electrode, the device area, use of protective oxide/organic layer, etc. remain currently out of scope. The cyclability and retention characteristics are shown in the Appendix. Please refer to Figure A.1.

Figure 4.3 Short-term plasticity in halide perovskite memristors. (A) PPF index comparison between MAPbBr₃, FAPbBr₃ and CsPbBr₃. PPF index is defined as the amplitude ratio between the second (A2) and the first (A1) postsynaptic current [$PPF = \left(\frac{A_2}{A_1}\right) * 100\%$]^[18]. (B) PPF index variation with increasing pulse interval: comparison of MAPbBr₃, FAPbBr₃ and CsPbBr₃. An exponential decay fit is applied to obtain two characteristic timescales as shown in Table 4.1. All the devices under test depicted diode characteristics with the threshold (V_{th}) for sharp current increase varying from 2 to 2.5 V. Hence for a fair comparison between the three systems and not compromising on the energy consumption per spike, pre-conditioning pulses of + 3 V ($> V_{th}$) were chosen to simulate short-term plasticity. (C) Temporal high-pass filters enabled by frequency-dependent short-term plasticity of halide perovskite memristors. EPSCs in response to presynaptic stimuli trains of different frequencies (2-95 Hz) for MA-based memristors. The stimulus train at each frequency consisted of 10 stimulus spikes of amplitude + 3 V. (D) Filter gain (B_{10}/B_1) plotted as a function of pre-synaptic spike frequency. Note: B_{10} and B_1 are amplitudes of the 1st and 10th EPSC for each frequency

as shown in (C). © “From R. A. John, N. Yantara, Y. F. Ng, G. Narasimman, E. Mosconi, D. Meggiolaro, M. R. Kulkarni, P. K. Gopalakrishnan, C. A. Nguyen, F. De Angelis, S. G. Mhaisalkar, A. Basu, N. Mathews, *Adv. Mater.* **2018**, 1805454. Reprinted with permission from John Wiley and Sons.”

Classified based on the timescales of operation, short and long-term plasticity rules were investigated in these devices by recording excitatory post synaptic currents (EPSCs) in response to pre- and post-synaptic training sequences.

Short-term plasticity. An indication of low initial probability of neurotransmitter release, **paired pulse facilitation (PPF)** refers to a short-term form of homosynaptic facilitation in which the second of a pair of action potentials produces a larger EPSC as compared to the first. PPF indices of all the three devices yielded an exponentially-decaying temporal response analogous to chemical synapses^[19]. Short pulse intervals < ~ 50 ms, resulted in high PPF indices, indicating strong ionic retention and facilitation at such timescales, akin to the residual Ca^{2+} hypothesis. On a general note, the organic cation containing (MA and FA-based) systems depicted a higher retention and much slower decay when compared to inorganic Cs-based system. For example, MA-systems exhibited the highest PPF index ~ 192 %, when compared to 145 % for FA and 104 % for Cs-devices, for a pulse interval of 5.3 ms (Figure 4.3-A). This ratio decreased inversely with pulse interval, reaching ~ 100 % for the largest pulse interval of 2000 ms (Figure 4.3-B). In resemblance to the coupling of biological neurons, this curve fit well with an exponential decay equation.^[18,19]

$$y = B_1 * \exp\left(-\frac{x}{t_1}\right) + B_2 * \exp\left(-\frac{x}{t_2}\right) + y_0$$

where x is pulse interval time, y_0 is resting facilitation magnitude, B_1 & B_2 are facilitation constants, and t_1 and t_2 are characteristic time constants of the rapid and slow phases respectively (Table 4.1). The extracted rapid (t_1) and slow (t_2) time constants were comparable with the time scales previously reported for both emulated^[20] (25 ms) and biological systems^[21] (40-300 ms). Extending this concept, a training sequence of 10 presynaptic action potentials (amplitude = + 3 V) induced dynamic high-pass temporal filtering^[22] of signals via volatile changes in conductance with a frequency-dependent gain (Figures 4.3-C-D). In congruence with the PPF behaviour, the MA and FA-based halide perovskites depicted superior facilitation and larger filter gains ($\text{MAPbBr}_3 = 2.92$, $\text{FAPbBr}_3 = 1.74$ at 95 Hz) when compared to the

inorganic Cs-based system ($\text{CsPbBr}_3 = 1.34$ at 95 Hz), indicating slower relaxation time-constants in such organic-cation containing perovskites.

EPSC [drain current response to input synaptic spikes] and PPF index modulation with pulse interval for increasing pulse widths of presynaptic spikes is depicted in Figures 4.4-A, B. While larger presynaptic pulse widths induced higher EPSCs (**Spike-duration-dependent plasticity** (SDDP)), the PPF index reduced inversely. Here, PPF index curves for MA-system is presented for comparison. A maximal PPF index of 192% was obtained for the combination of smallest pulse width and interval of 10.5 ms and 5.3 ms respectively. Although higher pulse width of the prior spike possibly activated a larger number of ions, the depleted ion source for the subsequent second spike could have resulted in the lower effective retention and PPF index. All these modulations of PSCs and short-term indices as a function of the amplitude, number, polarity and frequency of presynaptic spikes, could be utilized as design knobs for implementing bio-inspired temporally-coded algorithms, in congruence with the quantal and stochastic models.^[23,24]

Table 4.1 Best fit values of PPF decay as a function of pulse interval. © “From R. A. John, N. Yantara, Y. F. Ng, G. Narasimman, E. Mosconi, D. Meggiolaro, M. R. Kulkarni, P. K. Gopalakrishnan, C. A. Nguyen, F. De Angelis, S. G. Mhaisalkar, A. Basu, N. Mathews, *Adv. Mater.* **2018**, 1805454. Reprinted with permission from John Wiley and Sons.”

Parameter	MAPbBr ₃	FAPbBr ₃	CsPbBr ₃
y_0	103.728	102.22	100.57
B_1	1498.42	194.3	2.4E8
B_2	33.14	25.87	1.75
t_1	1.62	2.28	0.28
t_2	138.92	55.63	57.82
R-Square	0.992	0.993	0.875

Figure 4.4-C-F shows the variation in EPSCs and PPF indices of all the three investigated systems among 32 devices fabricated in a single batch. The variation in EPSCs was less than 15 nA for MA-based devices as shown in Figure 4.4-C. FA and Cs-based devices followed a similar trend with Cs showing the least variation among the 3 systems on a general note. Although the PPF indices varied by about 50 % across MA and FA devices (Figure 4.4-D-E), all the devices depicted an exponentially

decaying behaviour with pulse interval similar to Figure 4.3-B and also depicted other short and long-term plasticity features comparable to those demonstrated in this study. Although Cs-based devices depicted the least variability (Figure 4.4-F), it falls behind in terms of the achievable degree of plasticity. Figure A.2 in the appendix shows variation in the raw EPSC values across these devices.

Figure 4.4 Short-term plasticity-extended and variations. (A) Spike-duration-dependent plasticity (SDDP): Postsynaptic current in the artificial synapse as a function of presynaptic spike width. (B) PPF index variation with pulse interval of MA devices for increasing pulse widths of presynaptic spikes. Variation in (C) initial conductance of MAPbBr₃-based devices and PPF indices of (D) MAPbBr₃, (E) FAPbBr₃, (F) CsPbBr₃-based devices fabricated in a single batch consisting of 32 devices. © “From R. A. John, N. Yantara, Y. F. Ng, G. Narasimman, E. Mosconi, D. Meggiolaro, M. R. Kulkarni, P. K. Gopalakrishnan, C. A.

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Figure 4.5 Energy Consumption. (A) Comparison of the ON-state energy consumption per spike (E_{on}) of the halide perovskite synapses. (B) Energy scaling of halide perovskite synapses with device area. © “From R. A. John, N. Yantara, Y. F. Ng, G. Narasimman, E. Mosconi, D. Meggiolaro, M. R. Kulkarni, P. K. Gopalakrishnan, C. A. Nguyen, F. De Angelis, S. G. Mhaisalkar, A. Basu, N. Mathews, *Adv. Mater.* **2018**, 1805454. Reprinted with permission from John Wiley and Sons.”

Extreme **low power consumption** of the human brain (~ 10 fJ per synaptic event) remains unmatched by any artificial neural network till date. Hence, our devices were benchmarked on power consumption to investigate the feasibility of realizing ultra-low power neuromorphic circuits. The ON-state energy consumption per spike (E_{on}) was calculated from the equation^[25]

$$E_{on} = I_{peak,first} \times t \times V$$

where $I_{peak,first}$ is the maximum value of the 1st generated EPSC for a single spike event, t is the spike duration, and V is the applied voltage. The energy consumption was normalized for an active area of 1 mm² for direct comparison with other state-of-the-art reports. FA and MA-based synapses outperformed the Cs-counterparts with an ON-state energy consumption of 23 nJ/mm² and 34 nJ/mm² per event respectively, making them one of the most energy efficient artificial synapses reported till date (Figure 4.5-A, Table 4.2). All the three systems under investigation depicted energy scaling in a

near linear manner across two orders of dimensional magnitude (Figure 4.5-B). Hence, with a future scaled version of these devices ($1 \mu\text{m}^2$), the energy consumption per event could be as low as couple of 10s of fJ/event. Table 4.2 shows a detailed comparison of the energy consumption our artificial synapses, benchmarked against state-of-the-art reports in literature.

Table 4.2 Comparison of energy consumption of our devices with literature. © “From R. A. John, N. Yantara, Y. F. Ng, G. Narasimman, E. Mosconi, D. Meggiolaro, M. R. Kulkarni, P. K. Gopalakrishnan, C. A. Nguyen, F. De Angelis, S. G. Mhaisalkar, A. Basu, N. Mathews, *Adv. Mater.* **2018**, 1805454. Reprinted with permission from John Wiley and Sons.”

Reference	^[15] Xiao et al. <i>Advanced Electronic Materials</i> 2.7 (2016): 1600100.	^[26] Wang, Yan, et al. <i>Advanced Materials</i> (2018): 1802883.	^[27] Tian, He, et al. <i>ACS Nano</i> 11.12 (2017): 12247-12256.	^[28] Shen, Jian-Xin, et al. <i>Advanced Materials</i> 30.12 (2018): 1706717.	^[29] Sun, Linfeng, et al. <i>Nano Letters</i> 18.5 (2018): 3229-3234.	This work
Device	MAPbI ₃ memristor	CsPbBr ₃ QD Flash Memory	(PEA) ₂ PbBr ₄ memristor	PMN-PT multiferroic heterostructures	MoS ₂ device with metal-insulator transition	Halide Perovskite Memristor
Energy Consumption per spike per unit area (nJ/mm ²)	5500	28	400	220	7200	MAPbBr ₃ : 34.5 FAPbBr ₃ : 23 CsPbBr ₃ : 153

Long-term Plasticity. An activity-dependent plasticity which results in a persistent enhancement/weakening of synaptic transmission, **long-term potentiation (LTP)** and **depression (LTD)** satisfies Hebbian criteria as a synaptic memory mechanism. In accordance with the Atkinson-Shiffrin multistore model, repeated presynaptic stimulations stabilized/consolidated the metastable volatile conductance-states to achieve LTP and LTD (Figure 4.6-A)^[30]. The degree of weight plasticity could be tuned by the number and amplitude of the training sequences (Figure 4.6, Table 4.3), resulting in controlled facilitation/depression in accordance with the quantal and probabilistic neurotransmitter release model^[31]. Upon training with 40 pulses of amplitude + 3 V, width 500 ms and interval 5 ms, MA-synapses depicted LTP with a net weight change of 24.32 %, followed by FA and Cs with 18.61 % and 5.54 % respectively. Slower relaxation of the organic cations once again accounted for the larger weight changes and higher retention of the memory states as depicted by the **Ebbinghaus forgetting curves**. Spaced repetition resulted in softening of the forgetting process, enhancing memory and learning. On increasing the amplitude of the training pulses from + 3 V to

+ 5 V, the degree of LTP in MA-synapses increased to 54.19 % from 24.32 %. FA- and Cs-based synapses followed a similar trend.

Figure 4.6 Long-term plasticity in halide perovskite synapses. (A) Classification of human memory based on the time scale of retention. The metastable conductance-states consolidated

to a permanent state on application of > 10 training pulses of width 500 ms and amplitude + 3 V. (*Left side*) Depicts short-term memory (STM) on application of 2 pulses of amplitude + 3 V, pulse width = 10.5 ms and interval = 5 ms. The current returns back to the original state on removal of the pulse, i.e. volatile change. (*Right side*) Depicts long-term memory (LTM) on application of 40 pulses of amplitude + 3 V, pulse width = 500 ms and interval = 5 ms. The current does not return back to the original state on removal of the pulse, i.e. non-volatile change. This depicts the STM-LTM transition in our devices. Training **(B)** MAPbBr₃, **(C)** FAPbBr₃ and **(D)** CsPbBr₃ synapses with large number of rehearsals resulted in higher weight changes, higher retention and slower decay of memory. Increasing presynaptic pulse amplitudes also resulted in higher weight changes, higher retention and slower decay of memory as indicated by **(E-G)**. © “From R. A. John, N. Yantara, Y. F. Ng, G. Narasimman, E. Mosconi, D. Meggiolaro, M. R. Kulkarni, P. K. Gopalakrishnan, C. A. Nguyen, F. De Angelis, S. G. Mhaisalkar, A. Basu, N. Mathews, *Adv. Mater.* **2018**, 1805454. Reprinted with permission from John Wiley and Sons.”

Table 4.3 Average values of the current states used for long-term plasticity analysis. © “From R. A. John, N. Yantara, Y. F. Ng, G. Narasimman, E. Mosconi, D. Meggiolaro, M. R. Kulkarni, P. K. Gopalakrishnan, C. A. Nguyen, F. De Angelis, S. G. Mhaisalkar, A. Basu, N. Mathews, *Adv. Mater.* **2018**, 1805454. Reprinted with permission from John Wiley and Sons.”

Material System	MAPbBr ₃	FAPbBr ₃	CsPbBr ₃
Initial current state (nA)	~ 1	~ 1	~ 1
Final current state (nA) after 10 pulses + 3 V	1.0606	1.0506	1.01248
Weight change % after 10 pulses + 3 V	6	5	1
Final current state (nA) after 20 pulses + 3 V	1.115	1.09223	1.02635
Weight change % after 20 pulses + 3 V	11.5	9	2.6
Final current state (nA) after 30 pulses + 3 V	1.1759	1.13847	1.04022
Weight change % after 30 pulses + 3 V	17.6	13.8	4
Final current state (nA) after 40 pulses + 3 V	1.24223	1.18747	1.05409
Weight change % after 40 pulses + 3 V	24	18.7	5.4
Final current state (nA) after 40 pulses + 4 V	1.37769	1.2624	1.08876
Weight change % after 40 pulses + 4 V	37.7	26	9
Final current state (nA) after 40 pulses + 5 V	1.54198	1.33446	1.13037
Weight change % after 40 pulses + 5 V	54	33	13

For long-term weight change analysis the following approach has been used in the chapter throughout:

1. Read the device conductance with $V = 0.5$ V.
2. Apply necessary voltage waveforms to induce non-volatile weight change/ long-term plasticity. In this chapter, the voltage amplitudes, number and pulse durations have been varied to modulate the LTP-LTD behaviour. For Figures 4.6 B-D, presynaptic pulses of amplitude + 3 V, width = 500 ms and pulse-interval = 5.3 ms were applied. The

number of training pulses were varied to obtain the graphs. For Figures 4.6 E-G, 40 pulses of width = 500 ms and pulse-interval = 5.3 ms were applied but with varying amplitudes of + 3-5 V.

3. Monitor the channel conductance 15 minutes after application of the waveforms to account for the non-volatile change in conductance and compare it to the initial conductance state to calculate weight %. These stable states observed 15 minutes after application of voltage pulses are the ones taken for analysis of linear weight changes. Table 4.3 provides a list of the raw initial and final current values used for our analysis. Observation of depression or decrease in conductance was best observed immediately after potentiation measurements and could be induced by applying reverse potential across the device. The degree of potentiation and depression was directly proportional to the total duration and amplitude of pulsing/biasing. Moreover, the rate of such weight changes was dependent on the active material composition as indicated in Figure 4.7.

Figure 4.7 Long-term plasticity-continued. For weight analysis, the conductance state was allowed to reach a stable steady state and the final conductance state was read by a reading pulse of + 0.5 V. Comparison of the long-term potentiation achieved in (A) MAPbBr₃, FAPbBr₃ and CsPbBr₃-based synapses trained with 40 pulses of amplitude + 3 V, width 500 ms and interval 5 ms. The graph depicts the decay of current 5 seconds after the application of these pulses. (B) The Ebbinghaus forgetting curve depicts the decline of memory retention with time. Highest numerical value of the long-term weight changes were normalized to compare the retention characteristics. Repetitive learning softened the forgetting behaviour. (C) Controlled LTP and LTD were achieved in our devices by applying a series of potentiating and depressing presynaptic spikes. Potentiating spikes were of amplitude + 3 V, while depressing pulses were – 3 V. The degree (slope) of potentiation and depression was dependent on the active material composition and could be further modulated with the amplitude and number of training pulses. Note: Samples with similar initial conductance states were taken for fair analysis. © “From R.

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Temporal correlations between the pre- and postsynaptic spikes created voltage-dependent changes in conductance/weight, establishing four forms of **spike-timing-dependent plasticity (STDP)** rules. A form of Hebbian learning, STDP is considered to be the first law of synaptic plasticity^[32] and forms the basis of associative learning^[33] and synfire chain stabilization^[34]. In pristine excitatory connections, precedence of presynaptic action potentials results in LTP whereas presynaptic activity following postsynaptic spikes causes LTD [Antisymmetric Hebbian]. For excitatory to inhibitory connections, LTP and LTD can be induced in the opposite manner [Antisymmetric anti-Hebbian], while in neocortex and neuromuscular junctions, the order does not play a role^[32] [Symmetric anti-Hebbian and Hebbian]. The precise relative timing of pre- and postsynaptic spikes significantly affects the sign and magnitude of weight changes. Portraying a variety of functional consequences in neural information processing, these different STDP forms reflect the complexity of the underlying cellular mechanisms. Here, four different forms of STDP were realized by modifying the shape of the pre-synaptic and post-synaptic spikes, effectively translating timing differences into voltage amplitude differences. The change in conductance (weight) was recorded as a function of the pulse interval between pre- and postsynaptic spikes as shown in Figure 4.8. Repeated arrival of pre-post or post-pre spike pairs led to resistance changes above the writing threshold in proportion to the voltage and time-integrated device conductance function ($f(V_{pre}-V_{post}), t$), where the net voltage on the device at each instant of time (t) is defined by the voltage difference between the pre- and post-spike ($V_{pre}-V_{post}$)^[4]. Changes in conductance were compared to the initial conductance value to convert the data to percentage weight changes (reading pulses of 0.5 V was utilized for this measurement). The device was then allowed to relax back or erased to the initial conductance state before the next measurement to avoid dependence of previous history. For example, when spike pairs corresponding to Figure 4.8-B (*left*) were applied at an interval ($t_{post-pre}$) of + 500 ms, the maximum net voltage developed across the device was $V_{pre}-V_{post} = (-1) - (+3) = -4$ V. This voltage difference was responsible for the non-volatile weight change and resulted in a decrease in conductance or LTD (*right*). On arrival of presynaptic pulses after postsynaptic pulses, i.e. $t_{post-pre}$ of - 500

ms, the maximum net voltage developed across the device was $V_{pre} - V_{post} = (+3) - (-1) = +4$ V and this resulted in an increase in conductance or LTP. Similarly, different voltage waveform shapes applied at the pre- and post-synaptic terminals resulted in four different forms of STDP. In general, the organic cation-containing systems depicted a higher modulatable STDP function with respect to their inorganic counterparts. Weight changes were predominant at small spike intervals and weakened with increasing intervals, indicating strong temporal correlations between the pre- and postsynaptic spikes. Flipping of the input waveforms caused switching from anti-Hebbian to Hebbian rules. The STDP time windows shown here in milli-seconds and weight changes are comparable to biological values^[35] and could be further tuned by modulating the width, number and shape of the input spikes Figure 4.8-C-E.

Figure 4.8. Hebbian spike-time-dependent plasticity (STDP) variants realized in halide perovskite synapses. (A) Difference in timing of the pre- and post-synaptic pulses (Δt) lead to potentiation (pre before post) or depression (post before pre). In circuit realizations, these differences in timing can be translated into voltage amplitude differences in various ways inducing weight changes (ΔW) in the system and hence, facilitating different types of STDP. The graph on the right side shows the commonly observed STDP curves in biology. Input waveforms (*left side*) applied at the pre and post-synaptic terminals to realize (B) antisymmetric anti-Hebbian, (C) antisymmetric Hebbian, (D) symmetric Hebbian, (E) symmetric anti-Hebbian learning rules (*right side*) in halide perovskite synapses. © “From R. A. John, N.

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Trainable Memory Array. These halide perovskite memristors were next experimentally configured as a 4x4 **reconfigurable and trainable memory array with fault tolerance** to further highlight the significance of our findings. (Figures 4.9-A-C). Fresh MA-based synapses were arranged in a pixelated array format with an initial low-conductance state (stage: i). The image of “N” was then programmed into the array using an external microcontroller that biased (5 V, 10 seconds) selected individual pixels on demand with others in floating-mode. The pixel resistances were then read (+ 0.5 V, 1 second) individually few minutes after the training process and the corresponding readout-conductance map reflected the image of “N”. With time, the conductance decreased analogous to forgetting in the human brain, but could be retrained with fewer training cycles as shown in stages: ii-iv, reflecting the learning ability of these synapses. After complete extinction of memory of “N” (described procedure in Figure 4.9-A), new patterns corresponding to “T” and “U” were programmed into the same array using facilitating (write) and depressing (erase) pulses as depicted in Figure 4.9-B. Fault tolerance and robustness against non-ideal input signals were tested by introducing spurious and random spikes (+ 1.5 V, 10 ms width) together with training pulses during the retraining process for the “N” pattern (Figure 4.9-C). The network remained highly sensitive to the training pulses (re-establishing of memory state) while insensitive to the spurious spikes (no permanent conductance change) at both active ([2,2], [4,1], [3,3]) and non-active ([1,2], [3,2], [4,3]) nodes. By varying the total writing-erasing time, it is possible to further fine-tune and exploit the wide range of conductance state and memory retention in these devices. In all these measurements, the memory state “0” was defined as conductance values < 250 nS and “1” as > 250 nS. The raw current values from the individual devices are shown in Figure A.4 in the appendix.

Based on the STDP behaviour of MAPbBr₃ synapses (Figure 4.8-C), a two-layer neural network was trained in a simulation to recognize handwritten digits selected from the Modified National Institute of Standards and Technology (MNIST) database^[36,37]. The input images were converted to spatio-temporal spike patterns by creating a Poisson spike train for each pixel with mean firing rate proportional to pixel intensity. Each

input was connected to a layer of 400 neurons through excitatory weights (initialized to random values) which were modified by STDP. A second layer of 400 inhibitory neurons induced competition in the network. Each inhibitory neuron was connected to a corresponding excitatory neuron and fired a spike whenever the excitatory neuron fired. Each inhibitory neuron inhibited all excitatory neurons making this a hard winner-take-all (WTA) circuit. Note that this was done for simplicity in simulations and WTA could be made with a smaller number of inhibitory neurons as well.

Figure 4.9 Neuromorphic halide perovskite memory array for pattern recognition. (A) A 4x4 array of halide perovskite synapses was implemented as a reconfigurable and trainable memory unit with fault tolerance. The image of “N” was programmed into the array using an external microcontroller biasing (5 V, 10 seconds) individual pixels on demand with others in a floating-mode. With time, these synapses exhibited extinction of memory analogous to forgetting but could be retrained faster to reach the same conductance levels. (B) After complete erasing of the image of “N”, “T” and “U” were also programmed and erased. (C) The memory array also exhibits good fault tolerance and robustness to spurious inputs. Spurious inputs of +

1.5 V, 10 ms did not affect the conductance state on a long time-scale and the pixels could be read successfully. **(D)** The proposed two-layer neural network that is trained in simulations to recognize handwritten digits selected from the MNIST database. All input pixels connect to each excitatory neuron in layer 1 through synapses equipped with STDP behavior. Each excitatory neuron connects to an inhibitory neuron in layer 2 through fixed weight excitatory synapses. Each inhibitory neuron connects to all layer 1 neurons using fixed weight inhibitory synapses inducing winner-take-all based competition among layer 1 neurons. The receptive fields of 100 neurons in the excitatory layer obtained after training on 6000 images are shown here. © “From R. A. John, N. Yantara, Y. F. Ng, G. Narasimman, E. Mosconi, D. Meggiolaro, M. R. Kulkarni, P. K. Gopalakrishnan, C. A. Nguyen, F. De Angelis, S. G. Mhaisalkar, A. Basu, N. Mathews, *Adv. Mater.* **2018**, 1805454. Reprinted with permission from John Wiley and Sons.”

The equations governing the network dynamics can be broadly divided into the neuronal update and weight update parts. The neuronal update equations governing the membrane potential $V(t)$ are:

$$\tau_{me} \frac{dV}{dt} = (V_{reset} - V) + RI_e$$

$$\text{If } V(t) > V_{th} + \theta, s(t) \begin{cases} s(t) \rightarrow 1, V(t) \rightarrow V_{reset} \\ s(t) \rightarrow 0 \end{cases}$$

where τ_{me} (membrane time constant) = 100 ms, threshold voltage (V_{th}) of the neuron = -52 mV, reset voltage (V_{reset}) = -65 mV, $s(t)$ is the spike output of the excitatory neuron, R (leak resistance of the neuron) = 10 M Ω and θ is a threshold adaptation parameter that is updated to keep excitation levels of the neurons after learning at a balanced state allowing other neurons to participate in the competition.

I_e denotes the total input current to the excitatory neuron. It can be further decomposed into an excitatory (I_{xe}) and inhibitory (I_{ie}) components as:

$$I_e = I_{xe} + I_{ie}$$

$$I_{xe} = g_{exe} W_{xe} X_{pre}, \text{ similarly } I_{ie} = -g_{ie} W_{ie} X_{post}$$

$$\tau_{X_{pre}} \frac{dX_{pre}}{dt} = -X_{pre} + (1 - X_{pre}) \sum_{t_i^s} \delta(t - t_i^s)$$

$$\tau_{X_{post}} \frac{dX_{post}}{dt} = -X_{post} + \sum_{t_i^s} \delta(t - t_i^{ex})$$

where X_{pre} is some variable mimicking temporal dynamics of the excitatory postsynaptic current (EPSC) created by excitatory synapses connecting input pixels to

layer 1 neurons, W_{xe} denotes corresponding plastic weights normalized to 1 and g_{exe} is a scaling constant. Similarly, X_{post} is the variable for temporal dynamics of the inhibitory PSC created by the synapses connecting layer 2 neurons with layer 1 neurons, W_{ie} denote corresponding fixed weights and g_{ie} is a scaling constant. Also $\tau_{X_{pre}} = 20 \text{ ms}$, $\tau_{X_{post}} = 80 \text{ ms}$, t_i^s and t_i^{ex} denote spike times of inputs and excitatory neurons respectively. Finally, the STDP learning equation is applied as follows:

$$\Delta W_{xe}(t_i^{ex}) = \eta(X_{pre}(t_i^{ex}) - X_{tar})(W_{max,xe} - W_{xe})^\mu$$

where $\mu = 0.2$, $X_{tar} = 0.4$, $\eta = 0.01$, $W_{max,xe} = 1$.

Here, μ defines the dependence of change in weight on current weight, X_{tar} is the target value of the presynaptic trace at the moment of a postsynaptic spike and η is the learning rate.

To mimic the hardware constraints of the halide perovskite memristor, the maximum weight was bound to $W_{max,xe}$ and the same voltage waveform X_{pre} was used as the memory trace to govern STDP as well as create the EPSC. Also, the measured STDP window for the halide perovskite synapses was around 2.5 sec; a time dilation factor was used to make the STDP window around 80 ms to speed up simulations. Since all waveforms were equally contracted by the same dilation factor, the dynamics were unchanged. With these settings, the network with 400 excitatory and 400 inhibitory neurons was simulated in MATLAB with 28x28 image inputs from the MNIST database of handwritten digits. The simulation procedure can be summarized as follows:

1. Spike inputs from the image are incident on layer 1 neurons. Each input pixel is connected to all layer 1 neurons.
2. By chance, one of these neurons, say the 20-th neuron in layer 1 (denoted by N_{20}^1), will be maximally excited since its random weights match best with the presented image. It will then fire a spike first. If no neuron fires a spike within the pattern duration, then the same input is again presented to the network but with all input firing rates increased by a constant factor.
3. Once a neuron in layer 1 fires, the corresponding neuron in layer 2 (for the example case above, it is N_{20}^2) will also fire due to high values of connecting weights. Note that each neuron in layer 1 only connects to the corresponding neuron in layer 2.
4. Inhibitory current is then applied to all neurons in layer 1 due to the inhibitory connections from a layer 2 neuron to all layer 1 neurons. This prevents other neurons

in layer 1 from firing. Hence, only weights connecting input to N^1_{20} gets modified by STDP. Weights corresponding to inputs with high firing rate get potentiated while others are depressed.

5. Move to next image and start from step 1.

When the network was presented with 6000 images in a random order and the simulation was run following the steps above, the receptive fields of the excitatory neurons in layer 1 started resembling the input digits through competitive learning as shown in Figure 4.9-D. Training the neural network using 6000 images resulted in an accuracy of 80.8 %. The major advantage of our proposed halide perovskite based STDP synapse is its low energy consumption during learning. Compared to other STDP implementations in CMOS^[38,39], this approach has the potential of $\sim 200X$ reduction in energy for learning. A future miniaturized memristor with an area of $1 \mu m^2$ will consume ~ 23 fJ/weight update (extrapolated from Figure 4.5-B). In comparison, memristor based synapses require ~ 30 pJ of write energy^[40] while CMOS solutions using floating gate synapses require about 4.5 pJ^[38,39]. Compared to other state-of-the-art halide perovskite memristor implementations (Table 4.2), FA-based memristors depict an 18 % reduction in write energy making them one of the most energy efficient artificial synapses reported till date.

However, their scalability, CMOS compatibility and stability in ambient still remain significant hurdles in realizing a large-scale neural network. Their chemical sensitivity makes them incompatible with optical lithography and other microfabrication processes. However, recent studies have demonstrated integration of halide perovskites as pixelated photon sensitive layers of CMOS image sensors^[41] and silicon nitride photonic integrated circuits by top-down processes^[42], opening up new possibilities of hybrid halide perovskite-CMOS neuromorphic architectures with perovskites serving as synapses and CMOS circuitry as neurons.

4.3 Discussion

Ion migration and charge-trapping effects have been suggested as possible mechanisms for the origin of hysteresis in halide perovskites, leading to slow photocurrent decay, above bandgap photo-voltages and switchable photovoltaic effects^[11,43,44]. Dependent

on the local defect structure, energy profile, scanning rate and grain boundaries, these deleterious effects of localized ion redistribution have been studied in detail by various spectroscopic and microscopic investigations^[44,45]. The wide variety of synaptic phenomena noted in our devices also support a mechanism of vacancy-mediated ion drift-diffusion, pointing to the mixed ionic–electronic conduction in these hybrid perovskites.

Galvanostatic measurements revealed similar electronic and ionic conductivities for all the three halide perovskite films, reiterating the hybrid electronic-ionic conduction in these systems (Figures 4.10-A-C, Table 4.4). Galvanostatic measurements were done on an Au/Al₂O₃/Perovskite/Al₂O₃/Au device configuration to evaluate ion-migration within the perovskite active layer alone. For galvanostatic measurements, the symmetric configuration allows electrons, holes, and ions to move freely from one electrode to the other (2 directions / linear current-voltage behavior). This is a widely accepted method to prove the existence of ionic migration in perovskites.^[44,46] Au strips were thermally evaporated using shadow masks and 2 nm of Al₂O₃ was deposited on top through atomic layer deposition (ALD). Perovskite layers were then spun coated on top of the sample with a procedure identical to the memristor fabrication to minimize possible differences between the active perovskite layers in both configurations. Upon bias application, positively charged A-cations and negatively charged bromide vacancies drift and accumulate near the negative and positive bias terminals respectively. The trend in ionic conductivities between MAPbBr₃, FAPbBr₃, and CsPbBr₃ remained consistent with previous observations in the memristor stack, reiterating ion migration in halide perovskites as the plausible explanation for the observed synaptic behavior in our synapses.

Figure 4.10 Proposed ionic and electronic conduction in halide perovskites. (A) Galvanostatic measurement setup for ion migration kinetics. Electronic resistance of the films extracted from (B) was used to decouple ionic resistance from the total resistance (ionic- blue region and electronic- yellow region) (C) for a constant current level. Al_2O_3 (2 nm) was used as an ion blocking layer for this measurement. (D) Vacancy-mediated migration-pathways for A-site cations and bromide anions with the calculated activation energies obtained from density functional theory (DFT) calculations. (E) Schematic of ion migration in halide perovskite synapses. Pulse induced ion redistribution in halide perovskites causes self p- and n-doping and defect passivation, resulting in better carrier injection into the devices. Removal of the bias causes the ions to relax back. This ion migration-relaxation (drift-diffusion) kinetics is modulated by the pre- and post-synaptic training pulse characteristics like amplitude and frequency, to create short and long-term plasticity. © “From R. A. John, N. Yantara, Y. F. Ng, G. Narasimman, E. Mosconi, D. Meggiolaro, M. R. Kulkarni, P. K. Gopalakrishnan, C. A. Nguyen, F. De Angelis, S. G. Mhaisalkar, A. Basu, N. Mathews, *Adv. Mater.* **2018**, 1805454. Reprinted with permission from John Wiley and Sons.”

In these measurements, voltage and subsequently resistance of device was measured at constant current for a specific period. The total conductivities (σ_{total}) were extracted from the slope (dominated by both electronic (σ_e) and ionic (σ_{ion} , $\sigma_{\text{total}} = \sigma_{\text{ion}} + \sigma_e$) components) of normal I-V measurements with a scan rate of 4 V/s. In galvanostatic

measurements, the measured resistance increased initially and finally saturated with time upon current extraction. At initial stages, resistance was dominated by both electronic and ionic components. The ionic response decreased with time as the ions gradually depleted and accumulated at both electrodes. Finally, the resistance saturated with all the mobile ions blocked at the electrodes, leaving the entire contribution from the electronic component. The electronic component was thus extracted from the resistance at saturation and the ionic counterpart was derived from the difference between total and electronic parts as tabulated in Table 4.4. The measured conductivities, of the order of 10^{-5} Sm^{-1} , are fully consistent with previous reports on related lead-halide perovskites^[47].

Table 4.4 The calculated ionic, electronic, and total conductivities of halide perovskite thin films with different cations. © “From R. A. John, N. Yantara, Y. F. Ng, G. Narasimman, E. Mosconi, D. Meggiolaro, M. R. Kulkarni, P. K. Gopalakrishnan, C. A. Nguyen, F. De Angelis, S. G. Mhaisalkar, A. Basu, N. Mathews, *Adv. Mater.* **2018**, 1805454. Reprinted with permission from John Wiley and Sons.”

	$\sigma_{\text{ion}} \text{ (S/m)}$	$\sigma_{\text{e}} \text{ (S/m)}$	$\sigma_{\text{total}} \text{ (S/m)}$
MAPbBr ₃	8.8×10^{-6}	6.4×10^{-5}	7.2×10^{-5}
FAPbBr ₃	8.3×10^{-6}	6.3×10^{-5}	7.1×10^{-5}
CsPbBr ₃	6.1×10^{-6}	1.1×10^{-5}	1.7×10^{-5}

Table 4.5 Calculated vacancy migration energy barriers (eV) for MAPbBr₃, FAPbBr₃ and CsPbBr₃ using the experimental cell parameters. © “From R. A. John, N. Yantara, Y. F. Ng, G. Narasimman, E. Mosconi, D. Meggiolaro, M. R. Kulkarni, P. K. Gopalakrishnan, C. A. Nguyen, F. De Angelis, S. G. Mhaisalkar, A. Basu, N. Mathews, *Adv. Mater.* **2018**, 1805454. Reprinted with permission from John Wiley and Sons.”

E_a	MAPbBr ₃	FAPbBr ₃	CsPbBr ₃
V_{Br^+}	0.09	0.12	0.13
$V_{\text{MA}^+/\text{FA}^+/\text{Cs}^+}$	0.56	0.61	0.32
$V_{\text{Pb}^{2+}}$	1.51		

Model and first-principles calculations. To account for the differences in synaptic signatures observed in the three films and as a first judgement of the kinetics of

migrating species, first principles calculations on MAPbBr₃, FAPbBr₃ and CsPbBr₃ were performed on their room-temperature stable phases (pseudo-cubic and orthorhombic, respectively) (Figure 4.10-D, Tables 4.5-6). The reported geometries are those of the transition states along each pathway. The yellow circles represent the initial and final ionic positions, with blue arrows indicating the migration pathway. (Atomic color codes: Purple: Cs; Red: Br; Light blue: Pb; Green: C; Blue: N; White: H.) (Figure 4.10-D). These calculations indicated that vacancy-mediated migration activation energies of both halide and A-site cations (i.e. MA, FA and Cs) were considerably lower than those for Pb²⁺ migration. Halide motion is predicted to be observable on a very short timescale (< 1 μs) due to its small migration activation energy (~ 0.1 eV for the three compounds). These timescales and comparable activation energies do not match the experimental phenomena presented here. On the other hand, significant differences in activation energy for A-site cation migration through the corresponding vacancies (V_{MA^-} : 0.56 eV, V_{FA^-} : 0.61 eV, and V_{Cs^-} : 0.32 eV) which can take place on a time scale of ~ ms to minutes, could be the origin of the transient responses noted here.^[48] Hence, this is hypothesized to be the primary contributing factor of the transient responses noted here since halide motion/relaxation with much lower activation energies are expected to play a role at much faster timescales (< 1 μs)^[48]. This is consistent with the degree of short and long-term synaptic plasticity observed in our devices, which followed the same trend as the vacancy-mediated migration activation energies for the A-site cations.

Table 4.6 Calculated defect formation energies (DFE) for A-cation vacancies. © “From R. A. John, N. Yantara, Y. F. Ng, G. Narasimman, E. Mosconi, D. Meggiolaro, M. R. Kulkarni, P. K. Gopalakrishnan, C. A. Nguyen, F. De Angelis, S. G. Mhaisalkar, A. Basu, N. Mathews, *Adv. Mater.* **2018**, 1805454. Reprinted with permission from John Wiley and Sons.”

no vdW	DFE ($E_f=0$, eV)
V_{MA^-}	-0.25
V_{Cs^-}	-0.27
Br-rich	
vdW	DFE ($E_f=0$, eV)
	eq_PbBr₂
V_{MA^-}	0.1
V_{Cs^-}	0.06

Our calculations on lead-bromide perovskites are consistent with results for lead-iodide compounds showing similar activation energies for MA and FA vacancy migration.^[49] The strong differences between organic (FA $\approx$ MA) and inorganic (Cs) vacancy-mediated migration activation energy is consistent with the cation size order (FA>MA >> Cs). Although both halide and cations are easy to diffuse, the synaptic behaviour in our study is heavily influenced by the cation movement due to the long pulse widths ($\sim$ ms) employed here.

The migration energy barriers remained similar when simultaneously optimizing the atomic coordinates and cell parameters. For V_{MA} (V_{FA}), the migration energy barriers of 0.56 (0.61 eV) at fixed cell parameters became 0.46 (0.61 eV) when allowing the cell parameters to optimize. Unfortunately, Cs-based systems did not converge on a reasonable thermally-stable structure when allowing cell relaxation. The formation of A-cation vacancies on the representative $CsPbBr_3$ and $MAPbBr_3$ compounds was further investigated. Several different levels of theory was checked and different corrections were applied to the charged species, but in any case, the results always showed comparable (i.e. within less than 0.1 eV see Table 4.6) defect formation energy (DFE) for V_{MA} and V_{Cs} . Thus, the leading factor in determining the different behaviour of the various A-cations was attributed to their migration energy barrier, with the possibly different DFE representing a fine-tuning contribution.

Therefore, it is hypothesized that upon pre-synaptic spike application, negatively charged bromide anions and A-cation vacancies **drift** and accumulate near the hole transporting material interface (self p-doping), while positively charged A-cations and bromide vacancies n-dope the electron transporting material interface (Figure 4.10-E); culminating in better carrier injection^[50]. The built-in electric field due to the band alignment between halide perovskites and transport layers and ion concentration gradient result in ion back-**diffusion**/relaxation on bias removal, as also noted in perovskite solar cells.^[51] Thus, the carrier injection barrier could be temporarily or persistently regulated, resulting in modulation of device conductance/synaptic weight. In the case of PPF, when the pulse interval was short, ions activated by the first spike do not relax back before application of the second spike. This results in more ions being

accumulated near the interfaces, which subsequently reduces the carrier injection barrier, hence increasing the PPF index. Higher PPF indices indicate slower net ion back-diffusion kinetics which could be attributed to slower cation migration, lower availability of mobile ions, smaller mobile ion formation energy or lower net built-in voltage (V_{bi}) in the organic-cation based systems. Similar film thicknesses, defect formation energies (DFE) (Table 4.6) and ionic conductivities (Table 4.4) indicated that a smaller mobile ion formation energy or lower V_{bi} across the organic cation-based system could be responsible for the stronger synaptic response. In addition to perovskite self-doping, ion accumulation at the injection layer interfaces could also modulate the conductivities of the injection layer itself (i.e. both PEDOT: PSS and Bphen)^[52]. Long-term plasticity (LTP and LTD) could also occur due to permanent pinning of ions at the PEDOT: PSS/perovskite and Bphen/perovskite interfaces at sufficiently large spike widths and numbers.

4.4 Conclusion

The often-overlooked but unique ionotronic conduction in halide perovskites was employed for the demonstration of the comprehensive synaptic signatures that closely emulate biological signal processing. The memristive behaviour was attributed to the co-existence of ion migration and carrier injection barrier in the system, which resulted in self-doping or passivation at the interfaces, and ion relaxation due to the built-in potential in these devices. Presynaptic stimuli first activated short-term plasticity in our artificial synapses and persistent stimuli consolidated the conductance states to achieve long-term plasticity. Delay between the presynaptic and postsynaptic action potentials created temporal correlations in weight changes, resulting in emulation of four forms of spike-timing dependent plasticity rules. Trained as a memory array, these devices depicted reconfigurability and fault tolerance to spurious and random inputs. Network-level simulations of unsupervised learning of handwritten digit images based upon experimentally measured device properties illustrated the power of these memristors for bio-inspired pattern recognition and image classification algorithms.

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Chapter 5^[1]

Dual Gated Ionic-Electronic Synaptic Transistors

Artificial neuromorphic circuitry often overlooks the immense interplay between local activities and global neuromodulations observed in biological neural networks, and hence fails to mimic complex biologically plausible adaptive functions like heterosynaptic plasticity and homeostasis. Here, comprehensive emulation of biorealistic neuronal behaviours like heterosynaptic plasticity, homeostasis, association, correlation and coincidence are demonstrated via a novel dual-gated architecture. Synergistic operation facilitates the effect of local activity correlations to be captured by one gate, while global neuromodulations are represented by the second gate, enabling higher order temporal correlations at the unitary level. The dual-gate operation also extends the dynamic range of conductance linearity for blind weight-update schemes, expanding the number of accessible memory states. Finally, operating neuristors in the sub-threshold regime enables weight plasticity with high gain, while maintaining ultralow power consumption of the order of femto-Joules.

^[1]This chapter is published substantially as John, Rohit Abraham, et al. "Ultralow Power Dual Gated Sub-Threshold Oxide Neuristors: An Enabler For Higher Order Neuronal Temporal Correlations." *ACS Nano* (2018).

5.1 Introduction

With massive parallelism, fault tolerance, self-learning and ultra-low power consumption, neural computing transcends serial processing in traditional von Neumann architectures^[2,3]. Learning in the human brain occurs via strengthening and weakening of synaptic connections, interconnecting each neuron to up to 10^4 other neurons^[4]. These modifications of synaptic connections- referred to as functional weight plasticity is classified into short and long-term plasticity based on their time scales of operation. Acting on a timescale of tens of milliseconds to a few minutes, short-term plasticity contributes towards the working memory and removes auto-correlations. On the other hand, long-term plasticity exists from minutes to hours, contributing majorly towards spatial memory storage^[5]. Emulation of this weight plasticity demands analog-like switching transitions and conductance linearity from the memory elements and hence, most studies focus on these aspects of synaptic behaviour. The massively parallel architecture of the human brain, i.e. the interconnectedness between neurons which forms the crux of information processing, is often overlooked, limiting the plasticity of artificial neural networks. This calls for the need of novel device configurations that can not only emulate fundamental local synaptic features, but which also incorporates response to global neuromodulations at an elemental level.

While traditional CMOS-based implementations require additional clock cycles and peripheral circuitry for weight-updates and synchronisation^[6], abrupt conductance transitions in drift-memristors^[7,8] limit their plasticity. Studies on electrolyte-gated transistors and ion-diffusive memristors focus only on emulation of basic short and long-term plasticity rules, and fail to emulate complex neuronal behaviours like heterosynaptic plasticity and homeostasis, dependent on interplay between local activities and global neuromodulations. With a gated control of channel conductance exploiting time-dependent hysteresis, the thin-film transistor (TFT) configuration offers a potential solution to this issue by employing synergistic multiple gates that can induce temporally distinct modulations on the carrier concentration.

Herein, artificial synapses with intimate electronic-ionic coupling are realized in an electric-double-layer (EDL) neuristor configuration with semiconducting indium-tungsten oxide (IWO) channels and solid-state ionic dielectrics based on poly

(vinylidene fluoride- co -hexafluoropropylene), P(VDF-HFP), and the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide, [EMIM][TFSI]. A dual-gated approach is proposed, where one mode (ionotronic- top ionic dielectric gated) captures the effect of local activity correlations while the other (electronic- back SiO₂ gated) represents global neuromodulations, accounting for the immense interplay between local and global neuromodulations at a unitary level. While high intrinsic carrier mobility and an established process flow justifies the selection of IWO^[9,10], maximizing and controlling the degree of such gating rationalizes the use of ionic gate dielectrics with large EDL capacitive coupling, intimately modulating the carrier concentration at the semiconductor-dielectric interface and satisfying the quest for ultralow power operation. High tensile strength of the structuring polymer allows convenient fabrication and lamination of free-standing solid-state ionic dielectrics on to the desired substrate via the ‘cut and stick’ processing strategy^[11]. This helps overcome the chemically volatile nature of liquid electrolytes, previously employed for such purposes^[12,13].

The dual-gated architecture permits independent operations in a pristine ionotronic mode-capturing the effect of local activity correlations or electronic mode-capturing global neuromodulations. Most importantly, it facilitates synergistic operation in a dual-gated additive/subtractive mode addressing the immense interplay between local and global neuromodulations, catering for metaplasticity and homeostasis. Temporal cross-correlations between the two gates induce heterosynaptic or three-factor plasticity rules^[14,15] that emulate the effects of neuromodulators like dopamine or noradrenaline. Persistent classical conditioning spurs associative learning between the gating modes with extinction/forgetting and recovery features. Finally, sub-threshold operation of these neuristors result in conductance/weight changes with maximum gain at ultra-low power and is utilized to create highly sensitive coincidence detectors imitating audio signal processors.

5.2 Results

Learning and memory in the human brain happens through activity-dependent modification (strengthening/weakening) of synaptic connections, referred to as **synaptic plasticity**^[4]. Similar activity triggered at 10⁴ such neuronal junctions/synapses forms the basis of parallel computing and distributed memory in the

human brain. Comprehensive emulation of these neuronal dynamics demands effective modulation of the local postsynaptic strength in response to local presynaptic action-potentials. In addition to this, since large groups of neurons receive common modulatory inputs in the form of neuromodulators such as dopamine, noradrenaline or acetylcholine signalling reward or surprise signals in biological networks^[16], modulation of learning rules by such global factors need to be accounted for as well. However, most studies focus only on the emulation of plasticity due to local temporal correlations. Global neuromodulations are often overlooked in artificial neural networks, diluting the attainable plasticity. Here, a dual-gated neuristor configuration is proposed with an ionotronic gate representing local presynaptic potentials and an electronic gate representing global modulations, modulating the post-synaptic channel conductance, read via the drain terminal (Figure 5.1-A). Device fabrication and physical characterizations are described in detail in the experimental section (Refer to Chapter 3 Sections 3.2.2 and 3.3).

In terms of transistor performance, the ionotronic-mode outperformed the electronic-mode in terms of the linear field-effect mobility ($\sim 79 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ to $9 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) and ultra-low voltage operation ($V_{\text{gs}} = 1.5 \text{ V}$ to 20 V) owing to the large EDL capacitance of the ion gels. (Figure 5.1-B-E). The linear field-effect mobilities were extracted from the transfer characteristics using the equation , where L is the channel length ($300 \text{ }\mu\text{m}$), W is the channel width ($1000 \text{ }\mu\text{m}$) and C_i is the gate dielectric capacitance. Devices in the global-gated (electronic) mode depicted a negligible clockwise hysteresis, while local-gated (ionotronic) mode clearly exhibited a larger anticlockwise hysteresis window of 1 V . Ultrafast interfacial trapping and detrapping of electrons in the forward and reverse voltage scans, due to surface adsorbates or presence of defects at the semiconductor-dielectric interface explained for the small clockwise hysteresis in the global-gated mode^[17]. Studies investigating the origin of traps in amorphous oxide semiconductors often attribute the hysteresis and V_{th} instabilities to charge trapping at the semiconductor-dielectric interface. Low-temperature I-V and capacitance measurements along with positive and negative bias stability tests have associated this to the presence of oxygen defects^[18] in the oxide semiconductors, which could work as both an electron trap as well as a shallow donor depending on its local structure. The presence of hole traps in the gate insulators during the fabrication process^[19] and the hydrogen content in gate dielectrics^[20] have also been found to be primary causes

contributing to this hysteresis. Detailed low-temperature optoelectronic measurements and impedance analyses need to be further conducted to reveal further information on the mechanism of trapping.

Figure 5.1 (A) Synaptic transmission steps (left) and the proposed multi-gated architecture of analog artificial oxide neuristors (right). Transfer and Output characteristics of IWO TFTs in the (B-C) electronic global-gated mode (D-E) ionotronic local-gated mode. While SiO_2

serves as the back-gate dielectric in the global-gated mode, ion gel serves as the top-gate dielectric in the local-gated mode. "Reprinted with permission from R. A. John, N. Tiwari, C. Yaoyi, * Ankit, N. Tiwari, M. Kulkarni, A. Nirmal, A. C. Nguyen, A. Basu, N. Mathews, *ACS Nano* **2018**. © [2018] American Chemical Society."

On the other hand, the migration-relaxation kinetics of mobile ions in the dielectric accounted for the anticlockwise hysteresis in the local-gated mode^[21]. Forward scan caused migration of cations towards the ion-gel – semiconductor interface, accumulating electrons in the IWO layer to form a conductive channel. This resulted in lower voltage requirements for the subsequent channel formation in the reverse scan, accounting for the anticlockwise hysteresis.

Prior to synaptic plasticity measurements, nature of the ion gels were investigated with a combination of Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Figure 5.2-A shows the specific capacitances of a 10 μm thick P(VDF-HFP) ion gel (measured by a scanning electron microscope (SEM) cross-sectional image - inset) sandwiched between two gold electrodes as a function of frequency ($C = -1/2\pi fZ''$, where Z'' is the imaginary impedance and f is frequency) using a dielectric spectrometer. The measured capacitances depicted a decreasing trend with frequency with the highest values of $\sim 7.5 \mu\text{F cm}^{-2}$ reported at low frequency (1 Hz). These large values result from the formation of electrical double layers at the electrode/ion gel interfaces. For transistor mobility calculations, specific capacitance value of $7.5 \mu\text{F cm}^{-2}$ was used as per literature^[11]. Fourier transformed infrared (FTIR) spectroscopy was used to investigate interactions between the polymer and ionic liquid in the ion gel by monitoring vibrational energies of the chemical bonds. Addition of EMIMTFSI into the polymer matrix resulted in the appearance of new peaks, namely: in-plane C-H bending peak of imidazolium ring at 846 cm^{-1} , C-S and S-N stretching peak at 788 cm^{-1} , S-N-S asymmetric stretching peak at 1054 cm^{-1} , N-H stretching peak at 1226 cm^{-1} and SO_2 asymmetric stretching peak of the counter anion TFSI at 1349 cm^{-1} . These together with the shifting of bands located at 1396 cm^{-1} (CH_2 wagging) and 1178 cm^{-1} (antisymmetric stretching of CF_2) clearly indicated strong ion–dipole interactions between the polymer and the imidazolium-based ionic liquid (Figure 5.2-B). Differential scanning calorimetry (DSC) results provided more direct evidence on the

plasticizing effect. As shown in Figure 5.2-C, the glass transition temperature of the material was lowered from -14.5 to -45.5 °C upon the addition of 33 wt% EMIMTFSI. Thermogravimetric analysis (TGA) revealed thermal stability of the ion gel above 350 °C (Figure 5.2-D).

Figure 5.2 Physical Characterization of the solid-state ionic dielectric. (A) Frequency dependence of specific capacitance for the free-standing ion gel dielectric. Inset shows scanning electron microscopy image of the ion gel. (B) FTIR, (C) DSC and (D) TGA spectra of the (PVDF-HFP) polymer, Ionic liquid (EMITFSI) and ((PVDF-HFP) +EMITFSI) ion gel.

Classified based on the timescales of operation, short and long-term plasticity rules^[8,22] were investigated in these devices by recording excitatory/inhibitory post synaptic currents (E/IPSCs)^[23] in response to pre- and post-synaptic training sequences. Temporally correlated activity initially created short-term volatile changes in channel

conductance, which upon persistent rehearsals consolidated into non-volatile long-term changes. These standard plasticity rules were first implemented independently in both global and local-gated modes of operation to benchmark the nature of plasticity achieved.

Short-term Plasticity. An indication of low initial probability of neurotransmitter release, **paired pulse facilitation (PPF)** refers to a short-term form of homosynaptic facilitation in which the second of a pair of action potentials produces a larger EPSC as compared to the first. The degree of facilitation in biological synapses is greatest when the Ca^{2+} ions are not allowed to return to the baseline concentration prior to the second stimulus, that is, when the pulse interval is kept shortest^[24]. Analogously, action potentials separated by small pulse intervals (< 50 ms), triggered higher EPSCs in the second presynaptic spike, resulting in high PPF indices, much larger than 100 %. The local-gated mode depicted much higher indices of ~ 181% when compared to ~ 138% of the global-gated mode for a pulse interval of 10 ms. Slower ion relaxation mechanism in the local-gated mode^[21] as supposed to ultrafast trapping mechanisms depleting the channel in the global-gated mode explained for this observation^[17,25]. Short intervals did not allow sufficient time for driving this process to completion and hence, the 1st EPSC was not allowed to return back to its original state. When the 2nd voltage spike was applied before complete relaxation of the 1st EPSC, the subsequent migration/detrapping process added on to the residual carriers, resulting in a higher 2nd EPSC and PPF. Increasing the intervals allowed sufficient time for ion relaxation/carrier trapping, resulting in an exponential reduction of the facilitation indices in accordance with the Ca^{2+} residual hypothesis by Katz and Miledi (Figures 5.3-A-C). The data fit well with an exponential decay function as shown below.

$$y = B_1 * \exp\left(-\frac{x}{t_1}\right) + y_0$$

where x is pulse interval time, y_0 is resting facilitation magnitude, B_1 is facilitation constants, and t_1 is characteristic time constants (Refer to Table 5.1 below). Presynaptic pulses of opposite polarity induced a decrease in short-term conductance or **synaptic depression**^[26] (Figures 5.3-D-F), resembling inactivation of voltage-gated Ca^{2+} channels or decreased pool of releasable synaptic vesicles^[27]. The local-gated mode depicted higher depression (reflected by lower values of depression indices ~ 55 %)

when compared to the global-gated mode ($\sim 70\%$), again indicating the slower relaxation of ions in this mode.

Table 5.1 Best fit values of PPF decay as a function of pulse interval. "Reprinted with permission from R. A. John, N. Tiwari, C. Yaoyi, * Ankit, N. Tiwari, M. Kulkarni, A. Nirmal, A. C. Nguyen, A. Basu, N. Mathews, *ACS Nano* **2018**. © [2018] American Chemical Society."

Configuration	y_0 (facilitation/depression)	B_1 (facilitation/depression)	t_1 (facilitation/depression)	R-Square (facilitation/depression)
Electronic	103.15/98.06	84.22/-109.32	11.27/-7.41	99.11/98.49
Ionotronic	113.1/97.49	147.87/-89.59	14.66/-13.67	94.98/98.98

As an extension to this concept, a training sequence consisting of 10 presynaptic action potentials of pulse width 20 ms (presynaptic amplitude = + 20 V (global-gated mode) and + 1.5 V (local-gated mode), drain bias = + 1 V (global-gated mode) and + 0.1 V (local-gated mode)) induced dynamic high-pass temporal filtering^[28] of signals via volatile changes in channel-conductance with a frequency-dependent gain as shown in Figures 5.3-G-I. Slow nature of ion migration-relaxation dynamics of the ionotronic-mode resulted in larger filter gains (209 at 33 Hz) when compared to the electronic-mode (18 at 33 Hz)^[29,30]. Removal of the pulses resulted in the decay of post-synaptic currents (PSCs) back to the initial state due to carrier trapping (global-gated) and ion relaxation (local-gated) mechanisms, analogous to **short-term plasticity**^[31].

Energy Consumption. With neuristors operating at 1 mV (V_{ds}), the local-gated operation boosted this high-gain behaviour with an ultralow power consumption ~ 9.3 fJ per synaptic event, comparable to biological synapses (~ 10 fJ per event)^[30] and one of the lowest reported till date (Figure 5.4-A, Table 5.2). The energy consumption per spike (E_{on}) was calculated from the equation^[32] $E_{on} = I_{peak,first} \times t \times V_{ds}$; where I_{peak} is the peak value of the 1st generated EPSC for a single spike event, t is the spike duration, and V_{ds} is the applied drain voltage. The energy consumption values also depicted directly proportional scaling with device dimensions as shown in Figure 5.4-B. The high electron mobility of IWO enables unprecedented transistor miniaturization and circuit thinning. This could be utilized as a strategy in future to decrease the energy consumption even further. These amorphous metal oxides are compatible with the CMOS technology and have been commercialized for the TFT LCD technology^[33,34]

utilizing its high OFF-resistance and low-noise profiles, opening up new avenues for large-scale implementation.

Figure 5.3 A pair of presynaptic action potentials (pulse width = 20 ms, interval = 10 ms, input waveforms are shown as inset) triggered a pair of excitatory postsynaptic currents (EPSCs) with increasing amplitude due to hysteresis. This phenomenon known as paired pulse facilitation (PPF) reflects the number of residual carriers during trapping-detraping mechanisms in the global-gated mode (A) and ion migration relaxation kinetics in the local-gated mode (B). (C) PPF index, defined as $[PPF = \left(\frac{A_2}{A_1}\right) * 100\%]$ is plotted as a function of inter-spike interval to demonstrate the decay process. It quantifies the degree of facilitation and indicates the vesicular release probability, in agreement with the residual Ca^{2+} hypothesis by Katz and Miledi.^[24] (D-F) Reversal of polarity of presynaptic action potentials result in short-term depression or paired pulse depression, with the indices dependent on pulse width and interval of the presynaptic action potentials, similar to facilitation. Frequency dependent volatile changes in conductivity/weights create high-pass filtering of signals in the (G) global-

gated and (H) local-gated modes of operation. (I) Frequency of presynaptic action potentials determine the gain of temporal filters. "Reprinted with permission from R. A. John, N. Tiwari, C. Yaoyi, * Ankit, N. Tiwari, M. Kulkarni, A. Nirmal, A. C. Nguyen, A. Basu, N. Mathews, *ACS Nano* **2018**. © [2018] American Chemical Society."

Figure 5.4 Energy Consumption. (A) Comparison of the ON-state energy consumption per spike (E_{on}) of oxide neuristors in the global and local-gated modes of operation. E_{on} was calculated from the equation $E_{on} = I_{peak,first} \times t \times V_{ds}$; where I_{peak} is the peak value of 1st generated EPSC, t is the spike duration, and V_{ds} is the applied drain voltage.^[32] Scaling down of device dimensions and reducing spike durations to sub-millisecond levels could be also utilized as strategies to decrease the energy consumption per event even further. The values reported are for the best performing devices. (B) Variation of energy consumption with device scaling. "Reprinted with permission from R. A. John, N. Tiwari, C. Yaoyi, * Ankit, N. Tiwari, M. Kulkarni, A. Nirmal, A. C. Nguyen, A. Basu, N. Mathews, *ACS Nano* **2018**. © [2018] American Chemical Society."

Table 5.2 Comparison of Energy Consumption with state of the art. "Reprinted with permission from R. A. John, N. Tiwari, C. Yaoyi, * Ankit, N. Tiwari, M. Kulkarni, A. Nirmal, A. C. Nguyen, A. Basu, N. Mathews, *ACS Nano* **2018**. © [2018] American Chemical Society."

Reference	^[35] Yang, Chuan Sen, et al. <i>Advanced Materials</i> 29.27 (2017): 1700906.	^[13] Yang, Jing-Ting et al, <i>Advanced Materials</i> (2018): 1801548.	^[36] Xu, Wentao, et al. <i>Nano Energy</i> 48 (2018): 575-581.	^[37] Zhu, Jiadi, et al. <i>Advanced Materials</i> 30.21 (2018): 1800195.	^[38] Sun, Linfeng, et al. <i>Nano letters</i> 18.5 (2018): 3229-3234.	This work
Device	MoO ₃ transistor	WO ₃ transistor	Conjugated polyelectrolyte based memristor	WSe ₂ transistor	MoS ₂ device with metal-insulator transition	IWO transistor
Energy Consumption per spike (fJ)	9600	36000	10	30	72	9.3

Long-term plasticity. Persistent rehearsals with longer pulse widths consolidated the weight changes, leading to permanent non-volatile changes in channel conductance - **long-term plasticity**^[8,39]. Widely considered a primary mechanism for learning and memory, long-term plasticity can bi-directionally modify synaptic strength—either potentiation or depression^[40]. Figure 5.5 depicts the long-term weight changes associated with the two independent modes of operation under different polarities of training. While persistent pulsing at -20 V activated long-term potentiation in the global-gated mode, $+1.5$ V activated long-term potentiation in the local-gated mode. Application of 10 facilitating pulses of pulse width 500 ms resulted in a larger weight change of 57 % for the local-gated mode when compared to 18 % in the global-gated mode. Slow relaxation nature of the ions in the local-gated mode again accounted for this behaviour as also depicted by the **Ebbinghaus forgetting curves** (Figure 5.6-A). Spaced repetition (modulation with increased number of training sequences) resulted in softening of the downward slope of the forgetting curve, indicating increase in the strength of memory with repetitive learning. Opposite polarity of presynaptic activation induced depression (reduction of conduction) as expected, with the local-gated mode depicting larger weight changes when compared to the global-gated mode (Figure 5.5). For long-term weight analysis the following approach was used.

1. Read the channel conductance with $V_{ds} = 0.1$ V.
2. Apply necessary voltage waveforms to induce non-volatile weight change/ long-term plasticity.
3. Monitor the channel conductance 30 minutes after application of the waveforms and compare it to the initial conductance state to calculate weight %.

In the global-gated mode of operation, non-volatile changes in conductance indicated permanently stored charges at the semiconductor-dielectric interface due to carrier trapping dynamics. On the other hand, permanent pinning of ions in the ion gel or creation of additional oxygen vacancies in the underlying amorphous oxide semiconductor accounted for the larger non-volatile changes in channel conductance and hence higher weight changes in the local-gated mode. Such time-dependent channel hysteretic behaviour due to charge-trapping dynamics has been previously observed in transistors via current transient measurements^[17,41].

A refinement of Hebb's theory, **Spike-timing-dependent plasticity (STDP)** is considered to be the first law of synaptic plasticity^[42] and forms the basis of associative

learning^[43]. In pristine excitatory connections, precedence of presynaptic action potentials result in long-term potentiation (LTP) whereas presynaptic activity following postsynaptic spikes causes long-term depression (LTD) [Antisymmetric Hebbian]. For excitatory to inhibitory connections, LTP and LTD is induced in the opposite manner [Antisymmetric anti-Hebbian], while in neocortex and neuromuscular junctions, the order does not play a role^[42] [Symmetric anti-Hebbian and Hebbian]. The precise relative timing of pre- and postsynaptic spikes significantly affects the sign and magnitude of long-term synaptic modification. Portraying a variety of functional consequences in neural information processing, these different STDP forms reflect the complexity of the underlying cellular mechanisms.

Figure 5.5 Long-term Plasticity. Representative Long-term potentiation (LTP) (A) and depression (LTD) (B) in global-gated mode. LTP (C) and LTD (D) in the local-gated mode. The devices were pre-programmed to a common initial conductance state prior to these measurements for a fair analysis. "Reprinted with permission from R. A. John, N. Tiwari, C. Yaoyi, * Ankit, N. Tiwari, M. Kulkarni, A. Nirmal, A. C. Nguyen, A. Basu, N. Mathews, *ACS Nano* **2018**. © [2018] American Chemical Society."

Figure 5.6 Long-term Plasticity-continued. (A) The forgetting curve depicts the decline of memory retention with time. Highest numerical value of the long-term weight changes in the two operational modes were normalized to compare the retention characteristics. Repetitive learning softened the forgetting behaviour in both modes as shown. Input waveforms used for STDP measurements in the (B) global-gated and (C) local-gated modes respectively. A read pulse of + 0.1 V is applied at the drain terminal to read the memconductance states before and after the STDP write operations. (D) Relative timing between pre- and postsynaptic spikes created voltage differences across the neuristors, permanently strengthening and weakening the synaptic connections, also called Spike-timing-dependent plasticity (STDP). While the weight change pattern in the global-gated mode followed a STDP rule, a “reverse” STDP (rSTDP) rule was exhibited in the local-gated mode. "Reprinted with permission from R. A. John, N. Tiwari, C. Yaoyi, * Ankit, N. Tiwari, M. Kulkarni, A. Nirmal, A. C. Nguyen, A. Basu, N. Mathews, *ACS Nano* **2018**. © [2018] American Chemical Society."

To emulate STDP, the initial channel conductance was read by a reading spike ($V_{read} = +0.1$ V, 10 ms). Writing spike patterns (V_{write}) (Figure 5.6-B-C) were then applied and the change in conductance/weight was recorded as a function of the pulse interval between pre- and postsynaptic spikes. The timing difference created effect writing voltages ($f(V_{pre}-V_{post}), t$) across the device, which when crossed the threshold voltage, created long-term facilitation/depression in global/local-gated synapses on the repeated arrival of presynaptic spikes a few hundred milliseconds before the postsynaptic action potentials. The resultant conductance change was finally read again with the V_{read} pulse. Weight changes were predominant at small pulse intervals, and weakened with increase in the interval, reflecting strong temporal correlations between the pre- and postsynaptic spikes. Positive effective writing voltages above the threshold resulted in a permanent increase in conductance in the local-gated mode, due to permanent pinning of the ions in the ion gel at the semiconductor-dielectric interface saturating the Helmholtz layer

or creation of additional oxygen vacancies in the underlying semiconducting oxide channel. In contrast to this, positive effective writing voltages resulted in depression in the global-gated mode indicating electron detrapping during the pulse application and subsequent slow trapping of carriers on removal of positive pulses/bias^[17,30]. Changes to the order of arrival reversed the polarity of effective writing voltages and direction of weight-change, following an asymmetric Hebbian rule in the global-gated mode and an asymmetric anti-Hebbian in the local-gated mode of operation (Figure 5.6-D)^[44]. While the exact roles and interplay between Hebbian and anti-Hebbian rules are still not clear, it is reassuring that our neuristors can be configured to display either rule providing the flexibility desirable in neuromorphic hardware without the need for additional circuits as would be needed in standard CMOS implementations. The STDP time windows shown here in milli-seconds and weight changes are comparable to biological values^[45] and could be further tuned by modulating the pulse width, number and shape of the input spikes.

Advantages of the proposed dual-gated configuration.

Multi-level Memory. Data centric applications like on-line machine learning continue to demand scaling of non-volatile memory elements for increased storage, but are always limited by stringent fabrication complexities. In this context, development of multilevel memories seem to be a more viable alternative^[46]. Creating such multilevel memories would require adaptive memory elements with a dynamic wide linear conductance range and distinguishable read-out states. Cognitive tasks like pattern recognition and classification also demand synaptic devices with excellent conductance linearity (CL) and multi-level cell (MLC) characteristics^[47]. With non-linear and asymmetric weight updates during potentiation and depression, most drift memristors depict restricted memory windows due to the differences in switching kinetics of filament formation and dissolution^[48].

Figure 5.7 Dual-gated configuration enables multi-level memory in neuristors. Linear variation of channel conductance with write operations featuring 8 (3-bit storage) distinct conductance levels for all 3 operational modes but spanning different conductance ranges. Symmetric presynaptic voltage write-pulses of constant magnitude + 1.5 V (local-gated), +20 V (global-gated) and number (10) were applied to generate the conductance linearity curve. The memconductance states were addressed using a drain bias of + 0.1 V. "Reprinted with permission from R. A. John, N. Tiwari, C. Yaoyi, * Ankit, N. Tiwari, M. Kulkarni, A. Nirmal, A. C. Nguyen, A. Basu, N. Mathews, *ACS Nano* **2018**. © [2018] American Chemical Society."

With a wide linear conductance range limited only by the triode region of operation, neuristors become superior substitutes for computationally intensive applications like dot product engines (DPEs), which require such ‘blind update’ schemes.^[49,50] As a proof of concept, linear symmetric postsynaptic conductance changes featuring 8 distinct levels (equivalent to 3-bit storage) were recorded for all three modes of operation- global, local and dual-gated, with symmetric presynaptic write-pulses of constant magnitude and width (Figure 5.7). The net capacitive coupling defined the linear incremental addressing of memory states and the conductance range. Large capacitive coupling across electrical-double-layers resulted in a wider linear conductance range for the local-gate mode with respect to the global-gated mode.

Configuring the neuristor in a dual-gated additive mode resulted in charge carrier accumulation due to a combination of both local and global modes, resulting in a larger memory window when compared to the independent operations. At the system level with provisions for pulsing either gate or both, this leads to an increase in number of conductance states with an increased storage capacity of ~ 4.5 bits/synapse from the original 3 bits. Thus, adopting such multi-gated architectures to create multi-level memories becomes a superior alternative for mapping continuous weights to discrete conductance levels, with the dynamic range constrained only by the triode region of neuristor operation.

Non-volatile conductance linearity. The symmetry of weight plasticity determines the efficiency of crossbar neuromorphic computational kernels like vector–matrix multiplication and parallel rank 1 weight updates, and significantly improves classification accuracy of backpropagation schemes^[49]. In contrast to structural transformations which decides the switching behaviour in PCMs and filamentary RRAMs, the gating mechanisms employed here create softer non-abrupt changes in channel conductance, resulting in better linearity. Optimized writing schemes resulted in near-linear symmetric weight changes with symmetry in both facilitation and depression, as depicted in Figure 5.8. In congruence with previous observations, the large EDL capacitances in the local-gated mode of operation resulted in ultralow switching voltages and a much larger memory window when compared to the global-gated mode. The dual-gated mode extended this window even further upon additive operation of the two gating modes (Figure 5.8-A). Similar to short-term homeostasis, subtractive operation of the second gate created a negative feedback to offset excessive excitation or inhibition in the other mode, resulting in long-term **homeostasis**^[51,52]. Thus, the rate of facilitation and depression could be fine-tuned with high precision by selectively activating individual gating modes (Figure 5.8-B-D).

Figure 5.8 Modulations of strength of LTP-LTD realized *via* multiple gating. (A) Controlled facilitation and depression were achieved in our devices by applying a series of potentiating and depressing presynaptic spikes. Potentiating spikes for the global-gated mode involved spikes of amplitude - 20 V and pulse width 500 ms, and + 1.5 V for the local-gated mode. The dual-gated mode allowed weight modulations with improved strength. For the dual-gated mode, both global and local presynaptic spikes were applied simultaneously. (B) Long-term potentiation achieved in the global-gated mode is regulated by depression in the global, local and dual-gated modes *via* selective gating. The slopes of depression depend on the operation mode activated to homeostatically stabilize the runaway synaptic potentiation. Long-term potentiation in the local (C) and dual-gated modes (D) are regulated by depression in the other modes. Potentiating spikes for the global-gated mode involved spikes of amplitude - 20 V and pulse width 500 ms, and + 1.5 V for the local-gated mode. For the dual-gated mode, both global and local presynaptic spikes were applied simultaneously. "Reprinted with permission from R. A. John, N. Tiwari, C. Yaoyi, * Ankit, N. Tiwari, M. Kulkarni, A. Nirmal, A. C. Nguyen, A. Basu, N. Mathews, *ACS Nano* **2018**. © [2018] American Chemical Society."

Figure 5.9 Dual-gated configuration enables higher order temporal correlations in neuristors. Modulation of temporal filter characteristics with additional gating. Level shifting was achieved with the second control gate and without any additional circuitry. "Reprinted with permission from R. A. John, N. Tiwari, C. Yaoyi, * Ankit, N. Tiwari, M. Kulkarni, A. Nirmal, A. C. Nguyen, A. Basu, N. Mathews, *ACS Nano* **2018**. © [2018] American Chemical Society."

Short-term homeostasis. Beyond these standard bio-inspired plasticity rules, the proposed dual-gated configuration enables higher order temporal correlations, association and homeostatic regulation at a single-device level, alleviating strict circuit density requirements needed to match the computational complexity of the human brain. Like all electronic hardware, unit-level fluctuations causes serious malfunctioning of neuromorphic circuitry. In Hopfield networks, this results in multiple solutions or localized minima states for each input due to the dynamic shift of threshold voltages of individual neurons^[53,54]. In competitive learning networks, high intrinsic firing rates of some neurons may prohibit learning abilities of other neurons. In biology, a regulatory mechanism called homeostasis stabilizes the neural network, but most circuitry fail to emulate this^[55]. Inclusion of homeostasis in silicon synapses require additional circuits increasing the power and footprint^[56]. However in the proposed dual-

gated configuration, the additional gate could be employed as homeostatic feedback inputs, applying correction currents to the input of neurons as shown in Figure 5.9; i.e., the two gates could be configured to act subtractive to each other, preventing synaptic runaway dynamics and establishing homeostasis. Carrier accumulation in the channel due to capacitive coupling of the local-gated mode could be modulated by appropriate biasing at the global gate and vice versa, level-shifting the temporal filter characteristics. For example, positive biasing at the global-gate shifted the temporal filter characteristics activated by the local-gate in the positive direction, whereas negative biasing resulted in a negative shift without affecting the frequency-gain characteristics. In contrast to the STDP-based homeostasis previously reported^[30], this implementation extends the homeostatic regulation to short-term plasticity rules, stabilizing the neural network at both short and long time scales of operation.

Heterosynaptic Plasticity. In addition to the additive and subtractive operation, synergistic capacitive coupling allows intimate interactions between the two gating modes. One of the gates could be employed as a switch controlled via presynaptic rate-coded schemes or neuromodulation schemes like dopaminergic, noradrenergic, muscarinic, and nicotinic receptors^[14,57] to dynamically regulate weight changes caused by the other gating control, resulting in a higher order of plasticity, also called **heterosynaptic plasticity or three-factor learning**^[58–62]. Compared to metaplastic memristive implementations based on activity priming^[63,64], this incarnation supports weight updates based on temporal correlation between three signals – local presynaptic activity, global neuromodulatory signals and postsynaptic activity, modulating the STDP windows on demand (Figure 5.10). Similar implementations with standard CMOS circuitry requires additional capacitors and peripherals for weight updates and access^[65,66]. However the proposed dual-gated configuration allows temporal modulations caused by the modulatory terminal to interact with the changes created by the first presynaptic gate and post-synaptic source terminal, resulting in multiple correlated terms and higher-order correlations without any additional peripheral circuitry.

For example, independent operation in the local-gated mode resulted in long-term depression on repeated arrival of the presynaptic spikes a few hundred milliseconds before the postsynaptic action potentials. In the dual-gated mode, this net long-term

depression was further modulated by temporal correlations of the additional global modulatory terminal, which augmented the depression if repeated arrival of the modulatory spikes occurred a few hundred milliseconds after the postsynaptic action potentials. Repeated arrival of the global modulatory input a few hundred milliseconds before the postsynaptic action potentials created counteracting facilitation effects, that negated the depression due to the first set of pre-post spikes. It should be noted that homeostasis can be obtained by connecting the pre-synaptic spikes to both the gates -- it is thus a subset of the range of possible dynamics achievable by this neuristor and is the first demonstration of heterosynaptic plasticity in a single device.

Figure 5.10 Heterosynaptic Plasticity. (A) depicts the input waveforms applied at the pre and post-synaptic terminals. Higher order temporal correlations were achieved *via* interaction between two different presynaptic action potentials and the postsynaptic action potential,

creating real-time modulations of the standard STDP behaviour. **(B)** The dual gating approach allowed the second gate terminal to modulate the weight changes caused by the first gate, augmenting the plasticity and enabling higher order temporal correlations. The nature and degree of the effective conductance/weight change depended on temporal correlations between the postsynaptic sequence and two different input sequences (pre-synaptic and modulatory), resulting in heterosynaptic plasticity. "Reprinted with permission from R. A. John, N. Tiwari, C. Yaoyi, * Ankit, N. Tiwari, M. Kulkarni, A. Nirmal, A. C. Nguyen, A. Basu, N. Mathews, *ACS Nano* **2018**. © [2018] American Chemical Society."

Classical conditioning experiments^[67,68] created **association** between the presynaptic inputs as shown in Figure 5.11. Initially, while the unconditioned ionically gated stimuli (equivalent to food) activated salivation / unconditioned post-synaptic response (PSC > 12 μ A), electronically gated voltage pulses / conditioned stimuli (equivalent to bell) failed to trigger salivary response (PSC < 12 μ A, stage: i) in the artificial Pavlov's dog. Persistent simultaneous training resulted in effective association between the two stimuli marked by post-synaptic responses higher than the salivation response threshold with large retention (stages: ii-iii). However, repeated training sequences with the unconditioned stimuli alone resulted in extinction of the association (stage: iv), akin to forgetting in the human brain. The association could be recovered back by retraining, analogous to the biological learning curve (stages: v-vi).

Figure 5.11 Schematic of the concept of Pavlov's dog experiment for associative memory.

Prior to conditioning, the Pavlov's dog salivated to unconditioned stimuli alone (stage: i). Here, 12 μA was set as the threshold for salivation. Persistent training with simultaneous application of unconditioned and conditioned stimuli created association between them, after which the Pavlov's dog salivated to independent application of conditioned stimuli (stages: ii-iii). The association was weakened and became extinct with time on training with conditioned stimuli alone (stage: iv). However, retraining helped recover this association within a shorter time scale (stage: v-vi). "Reprinted with permission from R. A. John, N. Tiwari, C. Yaoyi, * Ankit, N. Tiwari, M. Kulkarni, A. Nirmal, A. C. Nguyen, A. Basu, N. Mathews, *ACS Nano* **2018**. © [2018] American Chemical Society."

Sub-threshold operation of neuristors. Finally, insights into merits of operating neuristors in the sub-threshold region ($V_{\text{gs}} < V_{\text{th}}$ and I_{ds} changes exponentially with V_{gs}) are provided^[69]. **Coincidence detectors** emulating auditory brainstem neurons^[70,71] are demonstrated to portray the advantages of sub-threshold operation (Figure 5.12-A). Delayed spike trains representing tapped delay lines from each ear were applied at two

distinct in-plane gate terminals of the neuristor, to emulate spatial localization of a sound source based on interaural time differences (ITD) as proposed by Jeffress model.. This resulted in symmetric weight-changes as a function of the delay but irrespective of the order of arrival, analogous to interaural sound localization schemes. The weight changes when operating neuristors in the sub-threshold region, were observed to be far more profound (2 – 4 x) when compared to the above-threshold regime, indicating much higher spatiotemporal correlation sensitivities and wider memory windows in the sub-threshold regime(Figure 5.12-B-C).

Figure 5.12 Coincidence Detection. (A) Schematic of the neuronal basis underlying interaural time difference (ITD) based audio signal-processing, (B) Spikes applied at two physically separate local and global gates. The depicted waveforms represent an example of the above-threshold region of operation. (C) Input spikes applied with a delay at two physically separate gate terminals, akin to ITD as proposed by Jeffress model, created symmetric weight changes or coincidence. Coincidence detectors operating in the sub-threshold region depicted a wider weight change window, reflecting higher sensitivity. "Reprinted with permission from R. A. John, N. Tiwari, C. Yaoyi, * Ankit, N. Tiwari, M. Kulkarni, A. Nirmal, A. C. Nguyen, A. Basu, N. Mathews, *ACS Nano* **2018**. © [2018] American Chemical Society."

The same observation held true for long-term STDP-based weight change experiments. STDP measurements were performed at each step of gate voltage increment corresponding to the transfer characteristics of the synaptic transistor. Input waveforms were designed with the reading voltages equivalent to the gate voltage increments ($V_{\min} = V_{\text{gs}}$) and the effective writing voltages corresponding to the difference between the maximum and minimum voltage levels ($V_{\max} - V_{\min}$, where $V_{\min} = -V_{\max}$) as shown in Figures 5.13-A-C. These temporally correlated waveforms created effective voltage

amplitude differences across the channel, resulting in weight changes corresponding to $V_{\max} - V_{\min}$, while the order of arrival of pre and post-synaptic sequences decided their direction of weight change (facilitation/depression). These weight changes resulted in a threshold voltage shift of the neuristors and when normalized to the initial weights depicted a clear dependence on the operating region of the transistor as shown in Figure 5.13-D-E. The sub-threshold region of operation resulted in larger weight changes because of the minute initial weights read by small gate voltages. The magnitude of weight changes decreased as the neuristor shifted from sub to above-threshold region of operation, indicating decreased sensitivity to temporal correlations. Operation in the global-gated mode was chosen as the model here due to the hysteresis-free behaviour and hence ease of understanding; however, the conclusions are valid for the local-gated mode as well. The cross-over point of the weight-changes and absolute weights in the graph indicates the region at which the neuristor could be biased for a good trade-off between high-sensitivity in weight change as well as high value of absolute weights.

While thermal noise in sub-threshold FETs is generally higher than its above-threshold counterparts, the signal-to-noise ratio (SNR) can be improved by summing outputs of many synapses together and scales as square root of N where outputs of N synapses are summed. This is exactly the mode of operation in neural networks and hence sub-threshold operation is a good fit for such kinds of applications where the fundamental operation is a vector-vector multiply.^[72] The three terminal structure of this memristive device largely mitigates the second issue of capacitive crosstalk and hence, possible sneak paths can be cut-off effectively using floating gates^[73].

Figure 5.13 Sub-threshold operation of neuristors. Long-term weight changes and STDP learning rules programmed in the sub-threshold region yielded higher conductance changes when compared to above-threshold region. (A) depicts symmetric potentiation and depression weight changes achieved as a function of the gate voltage. Input waveforms corresponding to (B) was used for STDP measurements at each step of gate voltage corresponding to the transfer characteristics of the neuristor. Weight changes were defined by effective write voltages ($V_{write}=V_{max}-V_{min}$) and read voltages equivalent to V_{min} were used to read the memconductance states (C). (D-E) Programming of neuristors create long-term weight changes in channel conductance (weight), reflected as threshold voltage (V_{th}) shifts of neuristors as a function of the programming gate voltage. "Reprinted with permission from R. A. John, N. Tiwari, C. Yaoyi, * Ankit, N. Tiwari, M. Kulkarni, A. Nirmal, A. C. Nguyen, A. Basu, N. Mathews, *ACS Nano* **2018**. © [2018] American Chemical Society."

5.3 Conclusion

The dual-gated architecture enables emulation of complex neuronal behaviours like heterosynaptic plasticity, homeostasis, association, correlation and coincidence- all in a single neuristor. The ionotronic mode captures the effect of local activity correlations while the electronic mode represents global neuromodulations, allowing higher order temporal correlations at a unitary level. Synergistic operation of these gating modes allows homeostasis to be established at both short and long time scales of operation, regulating the neural network activity. Additive operation extends the dynamic linear range of synaptic conductance and helps realize multi-level memories, increasing the

data storage ability of these neuristors. Limited only by the triode region of operation, these neuristors exhibit symmetry in the weight-update operation, significant for cognitive tasks like pattern recognition, classification and online machine learning algorithms. The gating interaction also creates temporal cross-correlations between the charge coupling modes, resulting in higher order temporal relations beyond the standard doublet STDP rules- akin to heterosynaptic plasticity. Classical conditioning experiments creates associative learning between the gating modes with bio-realistic features like extinction and recovery. Sub-threshold operation of transistors aids high gain conductance/weight changes at ultra-low power. These comprehensive results portray the advantages of a dual-gated sub-threshold operation of oxide neuristors, paving the way for metaplastic architectures with biologically plausible adaptation mechanisms dependent on local activity and global neuromodulations.

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Chapter 6^[1]

Synergistic Gating of Electro-Iono-Photoactive 2D Chalcogenide Neuristors

Artificial synapses with augmented plasticity will enable the design of robust neuromorphic circuitry with drastically lesser neural elements, overcoming the stringent circuit density requirements and fabrication challenges necessary to match the computational capability of the human brain. Here, MoS₂ neuristors are configured to mimic short and long-term plasticity rules exploiting a novel multi-gated architecture incorporating electrical and optical biases. Weight plasticity is established via synergistic operation of three modes, namely- electronic, ionotronic and photoactive. While carrier trapping dynamics are perturbed in the electronic mode, ion migration-relaxation dynamics are utilized in the ionotronic mode and trap-assisted slow recombination of photocarriers are harnessed in the photoactive mode of operation. With synergistic gating controls, this incarnation not only addresses modulation of synaptic weights with high precision, but also amalgamates neuromodulation schemes to achieve “plasticity of plasticity-metaplasticity” via interplay of Hebbian spike-time dependent plasticity and homeostatic regulation. Co-existence of such multiple forms of synaptic plasticity increases the signal processing capacity of artificial neuristors, enabling design of novel computationally-efficient bio-inspired architectures.

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6.1 Introduction

With ~ 86 billion neurons in synaptic communication making 10 quadrillion calculations every second, the human brain sets an unrivalled benchmark for parallel computational capacity^[2]. Learning in the human brain happens through short and long-term modification of synaptic weights interconnecting each neuron to up to 10^4 other neurons^[3]. For optimal neuronal firing, the electrochemical signalling dynamics maintains a balanced excitatory status quo via an integration/summation process combined with a mechanism that triggers action potentials above a threshold voltage, as per the leaky Integrate-And-Fire Model^[4]. Emulation of these neuronal dynamics necessitates artificial synaptic circuits with continuously modulatable (plastic) non-volatile conductances/synaptic weights^[5]. Most memristive solutions fall behind in terms of the dynamic range, linearity and symmetry of conductance/weight changes, making the hardware implementation of artificial neural networks with comparable computational complexity and viable dissipation of power extremely challenging.

Traditional CMOS-based solutions relying on passive memory elements to store synaptic weights require additional clock cycles for update operations and hence, impose power and scalability issues^[6]. Memristors^[7,8] with programmable resistance levels lag behind due to their abrupt conductance transitions and excessive write-noise nonlinearities, limiting the number of addressable states. From a technological perspective, device integrity expectations and highly stringent process requirements further worsens the challenge of fabricating high-density circuitry necessary to match the computational capability of the human brain^[9–11]. Incorporating artificial synapses with augmented plasticity would enable the design of robust neuromorphic circuitry with drastically lesser neural elements without compromising on the high performance.

With a gated-control of channel conductance, the field-effect transistor (FET) configuration exploiting time-dependent hysteresis seems encouraging in this respect, as supposed to abrupt state transitions in a two-terminal memristor. Controlling the degree of such hysteresis necessitates intimate ionic-electronic capacitive coupling strategies at the semiconductor-dielectric interface. Furthermore, optical programming of synaptic weights would help unravel new plasticity features utilizing the high speed and infinite bandwidth associated with such photon-based computing. This entails the need of atomically-thin semiconducting channels with opto-electronically modulatable

carrier concentration, and synergistic gating strategies to address the memconductance states in these semiconducting channels.

With ultrafast charge carrier dynamics^[12,13], optoelectronically tunable carrier concentration^[14,15] and atomic scalability^[16], 2D transition metal di-chalcogenides (TMDCs) present an enviable platform that could overcome the limitations of previously investigated material classes. Here, artificial synapses with optoelectronic weight plasticity are realized in a three-terminal field-effect configuration with Molybdenum disulphide (MoS₂) semiconducting channels. Embodying synergistic electronic, ionotronic and photoactive gating combinations, this configuration addresses different charge trapping probabilities, tuning synaptic weights with bidirectional modulability, Hebbian metaplasticity and homeostatic stability. Pavlov's dog experiments spurs associative learning between the gating modes, demonstrating a basic form of classical conditioning in our systems. These comprehensive results portray the advantages of employing multiple synergistic gating controls, paving way for multi-gated neural architectures with 2D chalcogenides as a viable material platform.

6.2 Results

Figure 6.1 (A) Raman-spectra of multilayer MoS₂ flake depicting the in-plane E_{12g} mode and the out-of-plane A_{1g} mode. (B) PL spectra indicating transition from direct to indirect bandgap

with increasing number of MoS₂ layers. (C) AFM image at the MoS₂ flake edge. (D) Optical image of the MoS₂ flake. © “From R. A. John, F. Liu, N. A. Chien, M. R. Kulkarni, C. Zhu, Q. Fu, A. Basu, Z. Liu, N. Mathews, *Adv. Mater.* **2018**, 1800220. Reprinted with permission from John Wiley and Sons.”

Physical Characterization of MoS₂. Raman and Photoluminescence (PL) characterizations of MoS₂ were conducted on samples of different thickness. As shown in Figure 6.1-A-B, the Raman spectrum depicted two typical peaks around 386 cm⁻¹ (E_{12g}) and 405 (E_{1g}) cm⁻¹ peaks. A blue shift of A_{1g} and red shift of E_{12g} was observed with increasing number of MoS₂ layers. This opposite direction of the frequency shift was partly attributed to the Columbic interaction and possible stacking-induced change in intra-layer bonding.^[17] Due to the quantum confinement effect, the MoS₂ crystal showed a crossover from the indirect bandgap in bulk to direct in monolayer form.^[18] As shown in Figure 6.1-B, the PL intensity of monolayer MoS₂ was much stronger than that of the bi-layer and tri-layer samples, indicating the direct band gap nature of monolayer MoS₂. Figure 6.1C-D shows the Atomic Force Microscopy (AFM) and optical images of the MoS₂ devices.

Figure 6.2 Biological and Artificial Synapse. (A) Schematic of biological synaptic transmission. (B) The proposed multi-gated architecture of analogous artificial MoS₂ synapses. © “From R. A. John, F. Liu, N. A. Chien, M. R. Kulkarni, C. Zhu, Q. Fu, A. Basu, Z. Liu, N. Mathews, *Adv. Mater.* **2018**, 1800220. Reprinted with permission from John Wiley and Sons.”

MoS₂ Neuristor Configuration. Figure 6.2-A-B elucidates the steps involved in biological synaptic communication and the proposed multi-gated device configuration. Devices in the electronic-mode utilised a bottom-gate top-contact configuration with

SiO₂ as the dielectric, while the ionotronic-mode was enabled by an ionic liquid [N, N-diethyl-N-(2-methoxyethyl)-N-methyl ammonium bis (trifluoromethylsulfonyl) imide (DEMETFSI)] contact. Device fabrication and physical characterizations are described in detail in the experimental section (Refer to Chapter 3 Sections 3.2.3 and 3.3). Both configurations depicted typical n-type depletion-operation with a linear mobility of 28 cm²V⁻¹s⁻¹ and 14.6 cm²V⁻¹s⁻¹ for the electronic and ionotronic modes respectively (Figure 6.3-A-D). The field-effect mobility was estimated from the linear region in the

I_d - V_g curve (V_g from 10 V to 30 V) by using the equation $\mu = \frac{dI_d}{dV_g} \times \frac{L}{WC_iV_d}$, where L

is the channel length (mention exactly), W is the channel width and C_i is the capacitance between the channel and the back gate per unit area ($C_i = \epsilon_0 \epsilon_r / d$; ϵ_0 is the vacuum permittivity, ϵ_r is the relative permittivity, and d is the thickness of SiO₂ layer), respectively. The channel length and width of the device were ~ 9 μ m and ~ 20 μ m, respectively and thickness of the MoS₂ flake was 9 nm. For ionotronic-mode, the capacitance was taken as 1.55 μ F/cm² for DEMETFSI from a previous study^[19]. The small electrochemical window of the ionic liquid limited the operational voltage range to -2 V to +2 V, but the large electrical-double-layer (EDL) capacitance allowed reliable switching in the ionotronic-mode within the small operational voltage window.

The electronic-mode operation clearly exhibited a clockwise hysteresis window of 8 V, while the ionotronic-mode depicted an anticlockwise hysteresis window of 0.5 V (Figure 6.3-A-B). In the case of electronic-mode, earlier investigations have indicated three possible origins for the observed clockwise hysteresis. According to the first theory, surface adsorbed moisture and O₂ molecules trapped electrons at positive voltages, thereby depleting the MoS₂ channel and leading to a positive V_{th} shift, while electron detrapping at negative voltages weakened carrier depletion in the channel, leading to a negative shift of V_{th} ^[20]. The second theory banked on defects at the MoS₂ - SiO₂ interface^[21,22], while the third theory suggested surface-adsorbed defects on MoS₂ to be responsible for this trapping-detrapping mechanism^[23]. In this case, the first and third theory could be ruled out as all measurements were done in high vacuum (10^{-7} mbar), thereby minimizing the probability of surface defects/adsorbates. Hence, the hysteresis behaviour observed in the electronic-mode could be attributed to interfacial defects at the semiconductor-dielectric interface, trapping and detrapping electrons in

the forward and reverse voltage scans. In the case of devices in ionotronic-mode, the anticlockwise hysteresis was attributed to mobile cations in the dielectric and its slow relaxation kinetics, which in turn doped and de-doped the channel based on the direction of voltage scan. Forward scan resulted in migration of cations in the ionic liquid (IL)-polymer dielectric toward the dielectric – semiconductor (MoS_2) interface, in turn accumulating electrons in the MoS_2 layer to form a conductive channel. This in turn resulted in the requirement of a lower voltage for channel formation in the reverse scan, emanating in anticlockwise hysteresis (Figure 6.3-E).

Figure 6.3 Transistor Characteristics. Transfer characteristics of (A) Back-gated MoS_2 – SiO_2 architecture (electronic-mode) (B) Top gated MoS_2 – IL configuration (ionotronic-mode). Output characteristics of devices in (C) electronic-mode and (D) ionotronic-mode. (E) Working principle of ionotronic MoS_2 electric-double-layer (EDL) transistors. (i) initial state of the ions in the ionic liquid dielectric before voltage is applied. (ii) on application of positive gate voltage pulse, cations (DEME) in the ionic liquid-polymer dielectric migrate and accumulate at the

dielectric-semiconductor interface inducing a channel current in the MoS₂ semiconducting layer. (iii) on removal of gate voltage pulse, the DEME cations gradually relax back to their initial positions, reducing channel conductivity and the drain current gradually decreases back to the resting current. © “From R. A. John, F. Liu, N. A. Chien, M. R. Kulkarni, C. Zhu, Q. Fu, A. Basu, Z. Liu, N. Mathews, *Adv. Mater.* **2018**, 1800220. Reprinted with permission from John Wiley and Sons.”

For emulation of synaptic signatures, the gate terminals were employed as presynaptic inputs while source/drain electrodes served as post-synaptic output terminals. Interfacial traps (electronic-mode) / ions in the ionic liquid (ionotronic-mode) mimicked the role of neurotransmitters, while channel conductance represented the synaptic weight. Post-synaptic responses (I_{ds}) were recorded as a function of the width, interval, frequency and number of repetitions of pre and post-synaptic inputs (V_g and V_s respectively) to comprehensively emulate synaptic signatures in accordance with various models of neurotransmitter release, namely- excitatory or inhibitory^[24], quantal^[25] and probabilistic^[26].

Figure 6.4 Short-term Plasticity. A single presynaptic spike input induces an excitatory postsynaptic current (EPSC) response in (A) electronic-mode, (B) ionotronic-mode. The current abruptly increases on application of the voltage spike and decays back to the resting current on removal of the voltage spike. A pair of presynaptic spikes (pulse width = 22 ms, interval = 5.3 ms) triggered a pair of EPSCs, with amplitude of the 2nd (A2) higher than the 1st (A1). This indicated facilitation due to carrier trapping / ionic retention in (C) electronic-mode,

(D) ionotronic-mode respectively. (E) PPF index, defined as the ratio of A_2/A_1 , that is $[PPF = (\frac{A_2}{A_1}) * 100\%]$ is plotted as a function of inter-spike interval to demonstrate the facilitation decay. It quantifies the degree of facilitation and reflects the synaptic vesicular release probability. It also gives an indication of the amount of residual and active Ca^{2+} according to the residual Ca^{2+} hypothesis by Katz and Miledi.^[27] In neuroscience, PPF is responsible for cognitive abilities involving temporal processes and determines the degree of associative learning. (F) Short-term depression emulated in electronic-mode synapses. © “From R. A. John, F. Liu, N. A. Chien, M. R. Kulkarni, C. Zhu, Q. Fu, A. Basu, Z. Liu, N. Mathews, *Adv. Mater.* **2018**, 1800220. Reprinted with permission from John Wiley and Sons.”

Short-term Plasticity. Chemical synapses create bidirectional (facilitation/depression) changes to the synaptic weight, classified as short and long-term based on the time scales of operation, according to the dual-process theory of plasticity^[28]. Arrival of an action potential depolarizes the synaptic membrane, causing influx of Ca^{2+} into the presynaptic membrane. When activated immediately by a temporally correlated action potential, residual Ca^{2+} concentration from the first pulse augments the Ca^{2+} activated by the second pulse, increasing the vesicular release probability and resulting in facilitation. This phenomenon called **Neural Facilitation / Paired-pulse facilitation (PPF)**^[29] was emulated in these devices by inducing **excitatory post synaptic currents (EPSCs)**^[30] in response to paired presynaptic spikes as shown in Figure 6.4, Table 6.1. Small pulse intervals (< 30 ms) triggered EPSCs with higher strength when compared to the priori spike resulting in strong facilitation indices $\gg 100$ %. Slower ion relaxation kinetics resulted in higher facilitation indices (~ 206 %) for the ionotronic-mode when compared to the electronic-mode (165 %) when activated with the same presynaptic pulse width and interval of 22 ms and 5.3 ms respectively. Larger pulse intervals weakened this amplification with the PPF indices reaching ~ 100 % for pulse intervals of 500 ms. Such temporal enhancement of synaptic connections mimicked **short-term potentiation (STP)** in excitatory glutamatergic synapses^[24,31,32]. In resemblance to chemical synapses^[33], the PPF index variation with pulse interval fitted well with an exponential decay function as shown below.

$$y = B_1 * \exp\left(-\frac{x}{t_1}\right) + B_2 * \exp\left(-\frac{x}{t_2}\right) + y_0$$

where x is pulse interval time, y_0 is resting facilitation magnitude, B_1 & B_2 are facilitation constants, and t_1 and t_2 are characteristic time constants of the rapid and slow phases. Detailed comparison of the decay time constants is presented in Figure

6.4-E, Table 6.1 below. PPF indices in the electronic-mode drastically reduced from 165% to ~100% as the pulse interval increased from 5.3 ms to 10.7 ms respectively. On the other hand, PPF decay was much slower for ionotronic-mode with the PPF indices well above 100% for pulse intervals up to 100 ms, indicating a larger facilitation window for the same. Similar activation by inhibitory presynaptic spikes resulted in **short-term depression (STD)** (Figure 6.4-F).

Table 6.1 Best fit values of PPF decay as a function of pulse interval. © “From R. A. John, F. Liu, N. A. Chien, M. R. Kulkarni, C. Zhu, Q. Fu, A. Basu, Z. Liu, N. Mathews, *Adv. Mater.* **2018**, 1800220. Reprinted with permission from John Wiley and Sons.”

Configuration	y_0	A1	A2	t1	t2	R-Square
Type I	100.95	120.25	158.6	3.86	3.86	0.9212
Type II	102.91	6e ⁶	92.4	0.44	20.36	0.9972

While electron trapping-detrapping dynamics at the semiconductor-SiO₂ interface explained for this behaviour in the electronic-mode, ion migration-relaxation kinetics at the ionic liquid-semiconductor interface (Helmholtz double layer) accounted for the same in the ionotronic-mode. Pulse intervals shorter than the relaxation dynamics of the trapped electrons/mobile cations in the electronic/ionotronic-mode, resulted in accumulation of residual carriers in the channel, which augmented the 2nd EPSC response, culminating in higher PPF indices. Large pulse intervals allowed sufficient time for this relaxation dynamics to take full effect prior to the second spike application, leading to lower residual carriers and PPF indices^[34]. As an extension of this STP behaviour, **quantal release**^[25] model of neurotransmitters was represented as post-synaptic weight changes in response to frequency-modulated action potentials. **Dynamic frequency dependent filters**^[35] (Figure 6.5-A-C) were demonstrated in both electronic and ionotronic-modes, akin to synapses with low vesicular release probability. In accordance with the PPF behaviour, the ionotronic mode depicted much larger filter gains of 16.51 as supposed to 1.86 in the electronic mode for the same activation frequency (45 Hz).

Figure 6.5 Short-term Plasticity-continued. EPSCs in response to presynaptic trains of different frequencies. The stimulus train at each frequency consisted of 10 spikes (A) + 50 V (electronic-mode) / (B) + 2 V (ionotronic-mode). (C) Filter gain $= A_{10}/A_1$ plotted as a function of presynaptic spike frequency. (D) SDDP: EPSC modulation with presynaptic pulse width. (E) Comparison of the ON-state energy consumption per spike (E_{on}) of the MoS₂ synapses as a function of presynaptic pulse width in the electronic and ionotronic-modes. E_{on} was calculated from the equation^[36] $E_{on} = I_{peak} \times t \times V$; where I_{peak} is the maximum value of generated EPSC, t is the spike duration, and V is the applied drain voltage. Further scaling down of device dimensions and reducing spike durations to sub-millisecond levels could be utilized as strategies to bring down the energy consumption per event. © “From R. A. John, F. Liu, N. A. Chien, M. R. Kulkarni, C. Zhu, Q. Fu, A. Basu, Z. Liu, N. Mathews, *Adv. Mater.* **2018**, 1800220. Reprinted with permission from John Wiley and Sons.”

The temporal accumulation of carriers in the channel allowed emulation of additional plasticity schemes like **spike-duration dependent plasticity (SDDP)** as a function of increasing presynaptic pulse widths (Figure 6.5-D). EPSC amplitude increased from 642 nA to 3.4 μA (electronic-mode), 4.6 to 320 nA (ionotronic-mode), for spike durations ranging from 10 to 500 ms. While devices in electronic-mode saturated quickly within presynaptic pulse widths of 33 ms, ionotronic-mode operation depicted a linearly increasing trend in the measured range without signs of any saturation. The difference in time scales of saturation indicated differences in availability of mobile charges in the two systems under test. Understandably, trapping-detrapping of electrons

occurred at much shorter timescales when compared to the slow ion induced electronic changes. The non-saturating behaviour of ionotronic-mode operation also indicated a larger reservoir of ions and charge carriers in the system. These differences could in turn be utilized to implement rate coded algorithms with concurrent multiple bit storage and processing capabilities. From SDDP, the probabilistic / stochastic nature of neurotransmitter release could be modelled by the equation, (post-synaptic current) $PSC \propto p * f(nV_{ap})$, where the vesicular release probability “p” relied on the pulse width of the presynaptic spikes and “n” represents the number of neurotransmitters released per event of an action potential (V_{ap}).

Ultra-low Energy Consumption. Despite remarkable progress in the field of neuromorphic devices, current technologies still lag behind their biological counterparts in terms of energy consumption (~ 10 fJ per synaptic event^[37]). Reducing energy consumption is therefore a primary concern. The on-state energy consumption per spike (E_{on}) was calculated from the equation^[36] $E_{on} = I_{peak} \times t \times V$; where I_{peak} is the peak value of the 1st EPSC, t is the spike duration, and V is the applied drain voltage. The ionotronic-mode operated at significantly lower power (~ 4.8 pJ/event, due to its large EDL capacitance) with respect to the electronic-mode (~ 13 nJ/event), when triggered with the same presynaptic spike (pulse width = 10.5 ms) (Figure 6.5-E, Table 6.2). Although still considerably higher than their biological counterparts, ion-mediated gating/ ionotronic-mode seems more promising in this regard. Other recently developed configurations involving stacked hexagonal boron nitride (hBN) - molybdenum disulfide (MoS₂) could allow access to even lower power operation in future^[38]. Using a future scaled version of these MoS₂ neuristors (active area = $1 \mu m^2$), the energy consumption per write will account to only 26.67 fJ, better than state-of-the-art memristors^[39] and simulated spintronic domain-wall magnets for spiking neural networks^[40]. Intrinsic high electron mobility of these MoS₂ channels enable unprecedented transistor miniaturization capabilities. Very recently, batch fabrication of thousands of MoS₂ MOSFETs have been reported using low-temperature CVD and other fully CMOS-compatible etching, passivation and metallization processes^[41,42]. This paves way for new opportunities with hybrid Si/TMDCs for large-scale neural network implementations.

Table 6.2 Comparison with state of the art. © “From R. A. John, F. Liu, N. A. Chien, M. R. Kulkarni, C. Zhu, Q. Fu, A. Basu, Z. Liu, N. Mathews, *Adv. Mater.* **2018**, 1800220. Reprinted with permission from John Wiley and Sons.”

Material	IZO	PEDOT:PSS-PEI	MgO/HfO ₂ -Ag Nanocluster	PDPP3T	P3HT-PEO nanowire	MoS ₂ TFT	Multi-gated MoS ₂ neuristor
Reference	Zhu, L.Q. et al. Nat Comm. 5, (2014). ^[43]	Van de Burgt, Y. et al. Nat Mat. 16, (2017). ^[11]	Wang, Z., et al. Nat Mat. 16, (2017). ^[7]	Zang, Y., et al. Adv Mat. 29, (2017). ^[44]	Xu W. et al. Sci Adv. 2, (2016). ^[37]	Arnold A.J. et al. ACS Nano 11, (2017). ^[45]	This work
Configuration	FET	NVRC	Memristor	FET	FET	FET	FET
On-state energy consumption per spike per unit area (mm ²)	17.5 nJ	10 nJ	3 mJ	62 nJ	58.5 nJ	0.83 J	26.67 nJ

Long-term plasticity. Gating protocols were next designed to program the synaptic weights with non-volatility and long-term plasticity, essential for neuromorphic computing algorithms. In addition to the ionotronic and electronic modes; a novel optical gating approach (photoactive-mode) utilizing defect-assisted slow recombination mechanisms was also harnessed to create permanent changes in the synaptic weight. These approaches were then conclusively combined to tune the synaptic weights with higher modulability and homeostatic stability.

Electrical programming of synaptic weights: Persistent activity-dependent changes in synaptic transmission such as **long-term potentiation (LTP)** and **long-term depression (LTD)** are considered cardinal for learning and memory storage. In glutamatergic systems, LTP is caused by high frequency activation of Mg²⁺-sensitive N-methyl-D-aspartate (NMDA) receptors and phosphorylation of α -amino-3-hydroxy-5-methyl-4-isoxazolepropionic acid (AMPA) receptors, resulting in large ion influx (Na⁺, K⁺, and Ca²⁺) into the synaptic membranes, creating a larger post-synaptic dendritic spine with enhanced synaptic strength^[46]. Unlike potentiation, low frequency activation of phosphatases dephosphorylates AMPARs decreasing the efficacy of a synapse, causing LTD. Here, LTP and LTD were invoked via persistent seasoning with pre and post-synaptic pulse sequences. Long-term measurements were conducted on fresh samples to avoid effects of history affecting the experiment. While persistent pulsing

at - 50 V activated LTP in the electronic-mode, + 2 V activated LTP in the ionotronic-mode. Increased number of training pulses resulted in a linear increase in weights as shown in Figure 6.6.

Figure 6.6 Long-term Plasticity (LTP). Increment in LTP strength as a function of persistent training in (A) electronic-mode (magnified view), (B) ionotronic-mode. © “From R. A. John, F. Liu, N. A. Chien, M. R. Kulkarni, C. Zhu, Q. Fu, A. Basu, Z. Liu, N. Mathews, *Adv. Mater.* **2018**, 1800220. Reprinted with permission from John Wiley and Sons.”

At all instances, the ionotronic-mode depicted weight changes larger than the electronic-mode. For example, application of 100 potentiating pulses induced higher weight changes ~ 223 % in the ionotronic-mode as supposed to 117 % in the electronic-mode (Figure 6.6). Reversal of presynaptic polarity reversed the direction of weight change, resulting in depression or decrease in conductance, the degree of which again depended on the total duration and amplitude of the presynaptic training sequences. The electronic-mode depicted a depression of 69 % when compared to 54 % in the ionotronic-mode, again indicating larger fraction of residual carriers in the ionotronic-mode. Congruent with short-term plasticity rules, persistent voltage pulses trapped large number of charge carriers at the semiconductor-dielectric interface resulting in a positive (LTP)/negative (LTD) shift of channel conductance^[45,47,48], dependant on the polarity of presynaptic pulses. Scanning rates were kept constant in all these measurements to avoid interference of any scanning-rate dependent hysteresis. Such time-dependent hysteresis due to charge-trapping dynamics has been previously observed in 2D TMDC based FETs via current transient measurements^[48,49].

Normalizing to the number of training pulses, the ionotronic-mode depicted larger retention characteristics in comparison to the electronic-mode, again indicating slower carrier relaxation dynamics in this mode of operation.

Figure 6.7 Long-term Plasticity (LTP)-continued. Increment in LTP strength as a function of persistent training in (A) photoactive-mode (variation with increment in light intensity ($\lambda = 445$ nm, 5.25 mW/mm²)). (B) Magnified view of the transient post synaptic conductance change on optical illumination ($\lambda = 445$ nm, 5.25 mW/mm²). (C) Variation in decay / relaxation time as a function of the percentage of incident optical power. © “From R. A. John, F. Liu, N. A. Chien, M. R. Kulkarni, C. Zhu, Q. Fu, A. Basu, Z. Liu, N. Mathews, *Adv. Mater.* **2018**, 1800220. Reprinted with permission from John Wiley and Sons.”

Optical programming of synaptic weights: The highly modulatable optoelectronic carrier concentration in atomically-thin 2D chalcogenide channels^[50,51] (here MoS₂) unlocks the possibility of addressing synaptic weights with photon pulses, capitalising on high-bandwidth optical communication protocols. A very strong LTP was induced in these devices when programmed with light pulses ($\lambda = 445$ nm) in the photoactive-mode. Upon illumination, the conductance increased rapidly and then gradually reached ~ 1 order of magnitude above the dark current. On removal of the optical illumination, the conductance exhibited an initial rapid drop followed by a gradual decay as depicted in Figure 6.7, maintaining a high-conductance state. The rapid transitions were attributed to band-to-band transitions, while the long-lasting gradual conductance change called persistent photoconductivity (PPC)^[52] was attributed to defect or trap centred slow recombination in accordance with the random local potential fluctuation (RLPF) model^[53]. Increased photon dosage resulted in enhanced device conductance and depicted slower decay dynamics, indicating slower recombination with more carriers occupying the sites of local potential minima, in congruence with

the RLPF model. This persistence in photoconductivity was harnessed to create long-term changes in post-synaptic conductance as shown in Figure 6.7. For the highest photo-dose, the device remained in the high-conductance state ($\geq 2.7 \mu\text{A}$) for a period more than 2 hours, emulating time-dependent stabilization or "**consolidation**" from STP to LTP^[54], in congruence with Atkinson and Shiffrin's "multistore model" of human memory^[8]. Utilization of such photon pulses would help unlock novel neural network architectures with optoelectronically modulatable plasticity, incorporating advantages of both electron-based and photon-based computing schemes.

Figure 6.8 Ebbinghaus Forgetting Curve. The graph depicts the retention of memory states (for 100 training pulses) in each mode of activation, namely- electronic, ionotronic and phototronic. The maximum current levels are normalized for a fair comparison of the retention properties.

Ebbinghaus Learning Curve: Slow relaxation nature of the carriers in the photonic and ionotronic mode resulted in larger weight changes and higher retention of the memory states as depicted by the **Ebbinghaus forgetting curves** (Figure 6.8). Spaced repetition resulted in softening of the downward slope of the forgetting curve, indicating modulation of the strength of memory and process of forgetting that occurs with the passage of time. From the above graph, the total PSC could be seen in general as a function of the number of neurotransmitters (n) released per event of an action potential (V_{ap}) as per the quantal theory, i.e., $PSC \propto f(nV_{ap})$.

Figure 6.9 Interplay of Hebbian Metaplasticity and Homeostatic Regulation. (A) Input waveforms used to generate STDP data in the ionotronic and electronic-modes respectively. The pulse width used for this measurement = 500 ms. (B) Spike-timing-dependent plasticity (STDP) and “reverse” STDP (rSTDP) achieved with the electronic and ionotronic-modes respectively. Differences in trapping probabilities modulated the PSCs and relative timing between the output and input spikes modified the strength of synaptic weights through facilitation and depression. Reversal of pre- and post-synaptic terminals resulted in reversal of the STDP protocols, as indicated by the dotted lines. (C) Controlled facilitation and depression achieved in our devices with the multi-gated architecture. STDP modulation and homeostatic regulation in the (D) electronic (Asymmetric Hebbian) and (E) ionotronic-mode (Asymmetric anti-Hebbian) of operation. (F) Symmetric Hebbian STDP protocol observed in the photoactive-mode of operation. © “From R. A. John, F. Liu, N. A. Chien, M. R. Kulkarni, C. Zhu, Q. Fu, A. Basu, Z. Liu, N. Mathews, *Adv. Mater.* **2018**, 1800220. Reprinted with permission from John Wiley and Sons.”

Synergistic gating enables “plasticity of plasticity- Metaplasticity” via interplay between Hebbian plasticity and Homeostatic feedback regulation^[55]. Temporal correlations between the pre- and post-synaptic spikes created voltage and time dependent weight changes in conductivity, establishing various forms of spike-timing-dependent plasticity (STDP) rules in our systems. A refinement of Hebb’s theory, STDP is considered to be the first law of synaptic plasticity and is believed to underlie learning and memory by competitive strengthening and weakening of synapses in

neural networks^[56]. In glutamatergic connections, strengthening/LTP occurs if the presynaptic action potential precedes the post-synaptic firing ($t_{\text{post-pre}} > 0$, where δt is the relative time interval between the pre- and post-synaptic spikes), while presynaptic potentials following post-synaptic spikes ($t_{\text{post-pre}} < 0$) causes weakening/LTD. Operation in the electronic-mode resulted in an asymmetric Hebbian STDP protocol, while the ionotronic-mode operation depicted a “reverse” STDP (rSTDP)/asymmetric anti-Hebbian STDP protocol, reflecting co-existence of different coupling mechanisms within the same device (Figure 6.9-A-B)^[57]. Co-existence of such multiple forms of synaptic plasticity increases the efficacy of memory storage and processing capacity of artificial neuristors, enabling design of highly efficient novel neural architectures.

Moreover, the individual gating controls could be coupled to further fine-tune facilitative/depressive weight changes, emulating different molecular pathways and neuromodulators for induction and expression of STDP. This ‘plasticity of plasticity’ or ‘metaplasticity’ demonstrated here reflects a dynamic regulation of plasticity via an internal modulation mechanism maintaining the synaptic efficacy within a dynamic range^[55]. For example, additive operation of electronic and ionotronic-modes in a dual-gated configuration enhanced the degree of facilitation/depression as shown in Figure 6.9-C. The weight changes increased with a higher slope of 3.13 when compared to 1.24 and 1.88 for purely electronic and ionotronic-modes respectively. Subtractive mode of operation helped stabilize weight changes in the STDP protocols, analogous to homeostasis observed in biology^[58]. Recent findings have revealed the homeostatic mechanism to be an on-demand rapid tuning of synaptic strengths, in contrast to the popular view of a slow, global phenomenon.^[59] Analogous to this, subtractive operation created a negative feedback mechanism to offset excessive excitation or inhibition, i.e., facilitation in the electronic-mode could be counteracted by depression of the ionotronic-mode and vice-versa. Thus, based on the net coupling of carriers, corresponding weight changes could be programmed with fine precision (Figure 6.9-D,E). Similarly, operation in photoactive-mode depicted very strong facilitation signatures analogous to runaway dynamics^[60] of synaptic weights, but could be regulated by negating homeostatic regulatory electronic and ionotronic-modes of operation (Figure 6.9-C). Large facilitation in photoconductance ($> 800\%$) was regulated by 22% depression (per step) activated by combinatorial operation of electronic and ionotronic-modes within the timescale of 150 seconds. Staying within

this time frame, the corresponding STDP protocol exhibited a net facilitation independent of relative time interval between the pre- and post-synaptic voltage spikes, viz. an symmetric Hebbian STDP behaviour (Figure 6.9-F). Complete homeostatic compensation was possible at larger time scales (~ 900 seconds). Thus, the positive feedback process of Hebbian plasticity with associative weight changes could be regulated by a homeostatic negative feedback process, constraining activity levels and maintaining stability- all within a single neural element. With combination of a low intensity photo-dose and high counteracting electrical erasing voltages, it becomes possible to tune this behaviour even further. To the best of our knowledge, this is the first demonstration of interplay between Hebbian and Homeostatic plasticity in a single artificial neural element. Compared to previous reports on metaplastic memristors with pre-synaptic activity-based priming^[61,62], the gate terminals are furnished as rate controls, similar to dopaminergic, noradrenergic, muscarinic, and nicotinic neuromodulations^[63,64]. This control gate may also be utilized as a homeostatic regulatory control to stabilize the neural network operation^[65,66]. Hence, this multi-gated optoelectronic approach enables novel artificial neural architectures with multiple operational modes and theoretically infinite plasticity. However, it should be noted that in practical implementations of the multi-gated approach with metaplasticity, the synapse needs to be disconnected from the neuron on a post-synaptic spike, as is commonly done in other non-volatile memory (NVM) based synaptic plasticity^[5,57,67,68] to prevent large surges in EPSCs due to any individual gating inputs from affecting the network dynamics.

Associative Learning. Finally, the famous **classical conditioning Pavlov's dog experiments**^[69,70] (Figure 6.10) were conducted to emulate associative learning in the human brain. In comparison to Pavlovian memristors⁶⁹ with temporal dependence of activation signals, this study implements classical conditioning in a field-effect transistor configuration with intimate coupling between optical and electrical pulses, unlocking novel neural network architectures with light as a global gate. Here, light pulses emulated food / unconditioned stimulus (US) activating salivation / unconditioned response (UR) from the post-synaptic terminal, while voltage pulses applied at the back gate emulated bell / conditioned stimulus (CS) for the dog activating a conditioned response (CR). Salivation (unconditioned response) was induced upon noticing food (stage a, stimulus of 10 light pulses, $\lambda = 445$ nm), marked by a

corresponding high-level current output above 500 nA (salivation response threshold). However at the beginning, the bell ring (stimulus of 10 voltage pulses) alone did not lead to any salivation (current < 500 nA, data not shown).

Figure 6.10 Classical conditioning Pavlov's dog experiment. (A) Schematic representing outline of Pavlov's dog experiment. (B) Voltage pulses/ conditioned stimulus (CS), (C) Optical pulses/unconditioned stimulus (US) and their responses. (D) Classical conditioning demonstrated by Pavlov's dog experiment. Initially, light pulses (unconditioned stimulus) led to an efficient unconditioned response (salivation) (state a). However, voltage pulses to the back gate (conditioned stimulus) did not lead to an efficient conditioned response before training (current < 500 nA, no salivation). Initial training sequences with conditioned and unconditioned stimuli did not result in effective association as depicted by state b. Repeated training led to strong association, after which conditioned stimulus alone could trigger salivation (states c-f, current > 500 nA). However, the PSCs decreased below the salivation threshold when triggered by conditioned stimulus alone without accompanying unconditioned stimulus for ~ 2 hours, indicating extinction of associative memory (state g). Finally, the association was recovered back faster with simultaneous conditioned and unconditioned stimuli (state h). © "From R. A. John, F. Liu, N. A. Chien, M. R. Kulkarni, C. Zhu, Q. Fu, A. Basu, Z. Liu, N. Mathews, *Adv. Mater.* **2018**, 1800220. Reprinted with permission from John Wiley and

Sons.”

The initial training routines (10 cycles) with simultaneous feeding and ringing the bell resulted in salivation, but failed to produce an associative response in the dog (stage b). Persistent training with simultaneous feeding and ringing the bell (40 cycles) resulted in gradual association between the ring (conditioned stimulus) and food (unconditioned stimulus), marked by post-synaptic currents higher than the salivation response threshold (stage c, d). The subsequent conditioned stimuli (alone) produced currents higher than the salivation threshold for ~ 2 hours, indicating an efficient association (learning) between the food / unconditioned stimulus and the bell / conditioned stimulus (stage e, f). Important classical conditioning signatures of **extinction** and **recovery**^[71] were also realized in our system. A series of voltage pulses (conditioned stimuli) applied to the “well-trained” dog without accompanying unconditioned stimuli, resulted in decrease of PSC (mimicking depression) below the salivation threshold after ~ 2 hours. This extinction process (stage g) correlated with the elimination of old information in the human brain. This conditioned reflex was again rebuilt or recovered on additional “retraining” (stage h). It was observed that the number of retraining cycles (15) required to re-accomplish the same level of association was less than the initial number of training cycles (20), indicative of the memory.

6.3 Conclusion

In summary, comprehensive synaptic behaviours were demonstrated for the first time in 2D MoS₂ three-terminal devices with a synergistic multi-gated configuration operating in three modes, namely- electronic, ionotronic and photoactive. The memory behaviour was linked to the origin of hysteresis and was attributed to electron trapping-detrapping at the semiconducting channel, migration-relaxation of ions in the IL gate dielectric and slow trap assisted recombination depending on the gating configuration. Pre-synaptic voltage stimuli initially activated STP/STD and persistent training consolidated the channel conductance to achieve LTP/LTD. Synaptic plasticity was fine-tuned by temporal correlations between presynaptic and post-synaptic action potentials, and the three gating modes were combined to realize Hebbian STDP metaplasticity with homeostatic regulation. Finally, classical conditioning using simultaneous paired stimulation of unconditioned optical and conditioned voltage pulses resulted in associative learning with extinction and recovering abilities.

Compared to previously reported artificial electrical synapses, such optoelectronic synapses pave way for efficient metaplastic computing elements that alleviates the circuit density requirements needed to match computational complexity of the human brain. However, some of the challenges which have to be overcome for large-scale usage of this technology include development of reliable integration with underlying CMOS electronics, ionically gating large array of transistors and managing the differences in voltage amplitudes between the different modes of operation.

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Chapter 7

A Dummy Optogenetic Toolkit with Photosensitive Neuristors and Soft Robots*

Neuristors with gate-controllable hysteresis emulating synaptic signatures have recently received considerable attention for neural network implementations. Inspired by Optogenetics-the technology that utilizes light in a non-invasive manner to remotely control neuronal activity, ReS₂ neuristors are demonstrated here as optogenetic actuators modulating neural plasticity with optical stimuli. These devices are initially benchmarked on light-modulated plasticity features compatible with both spiking and deep neural network algorithms. Harnessing synergistic optical potentiation and electrical depression, an optoelectronic non-von Neumann abacus with multistate compute-and-store ability is demonstrated. Next, photons are utilized as global neuromodulatory signals specifically targeting light-sensitive elements in a neural network array, highlighting the spatiotemporal precision and specificity of this approach. Finally, these neuristors are integrated with soft dielectric elastomeric actuators to create an artificial eye with human eye-like learning behaviours. This framework provides the first steps towards creating an optogenetic toolkit for behavioural robotics.

*This chapter is currently being prepared as a manuscript.

7.1 Introduction

The recent outburst in processing and memory requirements to meet the growing demands of artificial intelligence (AI) and machine learning, has triggered tremendous interests towards brain-inspired non-von Neumann computing paradigms. While software-based mathematical algorithms to emulate the signal-processing of the human brain has received considerable attention, hardware implementation of artificial neural networks still remains highly challenging^[1]. In contrast to mass storage and conventional logic operations, neuromorphic applications set unique requirements on the hardware switching devices, namely- analog-like switching transitions and continuously distributed conductance states. Furthermore, different computational schemes demand distinct switching properties from devices. While spiking neural networks (SNNs) following a spike-timing dependent plasticity (STDP)-based learning rule require bidirectional plasticity of weights/conductances, deep neural networks (DNNs) emphasize more on wide dynamic conductance range and conductance linearity for machine learning algorithms and vector matrix multiplications^[2].

Most solutions based on traditional complementary metal oxide semiconductor (CMOS) devices^[3], lack inherent hardware learning abilities and rely on software programming^[4] to implement complex neural networking tasks, restricting their usage. Synaptic weights are typically stored in leaky, noisy, power and area-inefficient capacitors and conventional random access memories (RAMs)^[5], and often require additional digital-to-analog (DAC) converters, increasing their power and aerial footprint. Very recently, the internal state dynamics in second-order drift memristors^[6,7], electrochemical metallization cells^[8] and diffusive memristors^[9] have been engineered to overcome the traditional abrupt switching transitions observed in drift memristors.^[9] Based on metal atom diffusion, thermal dissipation^[6], mobility decay^[10] and spontaneous nanoparticle formation, these solutions are capable of natively approximating the biological Ca^{2+} dynamics, paving way for novel computing architectures.

Concurrently, the field of neuroscience has seen remarkable progress in monitoring and controlling the biological connectome (neural patterns) through a technique called optogenetics. Optogenetics is a photo-stimulated neuromodulation technique that combines concepts from optics, genetics, imaging and electrophysiology to monitor,

control and manipulate neuronal activities in living cells^[11,12]. With higher speed, spatiotemporal precision, specificity, and minimal tissue damage, optogenetics offer explicit advantages over its electrical, pharmaceutical and genetic counterparts for probing rapid-firing neuronal circuits^[13]. Very recently, optogenetic perturbation of intracellular Ca^{2+} expression in the olfactory sensory neurons and CA1 hippocampus was observed to alter the synaptic plasticity, contextual memory formation and escape response in mice^[14,15]. Similarly, escape responses in the form of muscle contractions, freezing behaviour, camouflage and other cellular signalling pathways have also been monitored and manipulated in a number of organisms ranging from nematodes to fruit flies to fishes to mammals^[16–20].

This strategy of utilizing light to tune the learning and memory behaviours can be similarly adopted to modify the weight plasticity in artificial neural circuitry, but remains unexplored till date. This would allow optical stimuli to be utilized as an *ex situ* behavioural manipulator for AI circuitry controlling the learning rates on demand, and could also open up possibilities as a non-contact debugging tool to diagnose and fix faulty electrical circuitry. This calls for the need of atomically-thin low band-gap semiconducting channels as active switching matrices, that would enable intimate optoelectronic control over the charge carrier concentration and conductance transitions. On integration with organism-like soft robots, this strategy could be utilized to create AI-powered behavioural robots that adapt and learn to changing environments and stimuli. This setup under ideal conditions could also act as an *in vitro* physical simulator of the cognitive behaviour of an organism, aiding *in silico* studies of opsins.

In this work, we propose to utilize photo-receptive neuristors and dielectric elastomeric actuators (DEAs) to emulate the entire optogenetic setup, or in other words create a dummy optogenetic toolkit. Such a fusion of the field of optogenetics, neuromorphic electronic systems and soft robotics would pave way for artificially intelligent robots with organism-like cognition and learning abilities. Creating a dummy optogenetic toolkit demands comprehensive emulation of each of the individual components—namely optogenetic actuators or opsins, optogenetic sensors and the cell or organism itself. While optogenetic actuators or opsins like channelrhodopsin and halorhodopsin temporally manipulates electrical and biochemical events via specific targeting mechanisms, optogenetic sensors like genetically encoded calcium indicators (GECIs)

facilitate monitoring and recording of neuronal activities^[21,22]. From the device perspective, this necessitates photo-programmable artificial memristive synapses capable of storing and modifying the synaptic weight plasticity information in response to optical stimuli, analogous to opsins. The device conductance or weights should also allow active monitoring of the modulated carrier concentration, akin to optogenetic sensors.

With a gated control of channel conductance exploiting time-dependent hysteresis, the field-effect transistor (FET) configuration is promising in this regard with concurrent synaptic weights storage and signal-processing capabilities^[23,24]. Employing photo-receptive low bandgap semiconductors would allow photo-modulations of the channel conductance via optical gating, in addition to the conventional electronic gating. 2D transition metal dichalcogenides (TMDCs) offer several attractive features in this regard with their atomic-level scalability, tunable bandgap and opto-electronically modulatable carrier concentrations^[25]. Very recently, synergistic electronic, ionic and photonic gating of 2D chalcogenide neuristors were demonstrated enabling emulation of metaplasticity, homeostasis and association- all in a single device^[26]. Drawing inspiration from this, a dummy optogenetic toolkit comprised of rhenium disulphide (ReS₂) photoactive neuristors and soft robotic actuators is proposed and realized. The neuristors implemented in a FET configuration with optoelectronically modulatable plasticity act as photoreceptive weight-storage banks, dawning the role of opsins and synapses. Carrier trapping-detrapping mechanisms at the ReS₂-SiO₂ interface, controlled synergistically via optical and electronic gates, mimic the intracellular Ca²⁺ flux modulating the channel-conductance or synaptic weight, akin to optogenetic sensors. Finally, the DEAs embody the living cell or organism under study, completing the optogenetic toolkit.

Memory traces of past experiences, electrically encoded as temporal correlations between pre- and post-synaptic neurons, were initially modulated as a function of the wavelength and intensity of photon pulses resulting in photo-modulated spike-timing dependent plasticity (pSTDP) learning rules. Next, multi-level memories with 1024 addressable levels (10-bit storage) were programmed with optical pulses demonstrating high conductance linearity, as demanded by on-line machine learning algorithms, qualifying these neuristors as effective artificial opsins compatible with both spiking

(SNN) and deep (DNN) neural network algorithms. While optical-gating programmed long-term potentiation (LTP) into the channel conductance, the electronic-gating erased the states analogous to long-term depression (LTD), resulting in a symmetric bidirectional control of the weight changes. The optoelectronically modulated carrier concentration allowed active monitoring of the synaptic weights during these characterizations, akin to optogenetic sensors. Precise control over the weight changes were utilized to implement basic arithmetic operations analogous to an abacus, highlighting the memcomputing capability of these devices. Next, photons were utilized as global neuromodulatory signals targeting light-sensitive elements in a neural network array with high spatiotemporal precision, highlighting the utility of this approach. Finally, these neuristors were integrated with soft dielectric elastomeric actuators to realize an artificial eye with learning and memory behaviours that resemble a human eye.

7.2 Results

Physical and TFT Characterization of ReS₂ devices.

Figure 7.1 A-C shows the atomic force microscopy (AFM) and optical images of a ReS₂ sample. Height profile of the sample along the red line indicated the sample thickness (~ 5 nm). Raman characterization was performed to confirm the purity of the sample as shown in Figure 7.1-D. Device fabrication and physical characterizations are described in detail in the experimental section (Refer to Chapter 3 Sections 3.2.4 and 3.3). The ReS₂ neuristor depicted a typical n-type depletion-operation with a linear mobility of $26 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ (Figure 7.1-E-F). The field-effect mobility was estimated from the linear

region in the I_d - V_g curve (V_g from 10 V to 40 V) using the equation
$$\mu = \frac{dI_d}{dV_g} \times \frac{L}{WC_iV_d},$$
 where L is the channel length, W is the channel width and C_i is the capacitance between the channel and the back gate per unit area ($C_i = \epsilon_0\epsilon_r/d$; ϵ_0 is the vacuum permittivity, ϵ_r is the relative permittivity, and d is the thickness of SiO₂ layer), respectively. The sub-threshold swing was estimated to be ~ 2.5 V/dec, while the on-off ratio was greater than 10^6 for a drain voltage (V_{ds}) of 0.1 V. The channel length and width of the device was $\sim 9 \text{ }\mu\text{m}$ and $\sim 20 \text{ }\mu\text{m}$ respectively, and thickness of the ReS₂ flake was ~ 5 nm.

Figure 7.1 Physical and TFT Characterization of ReS₂ devices. (A-C) AFM and optical images of a ReS₂ sample, respectively. (B) Height profile of ReS₂ flake along the red line in (A), depicting a thickness of ~ 5 nm. (D) Raman spectra of ReS₂. (E-F) Transfer and Output characteristics of ReS₂ neuristors. Inset shows the device architecture.

Compatibility with SNNs.

Learning in the brain occurs via strengthening and weakening of synaptic connections, interconnecting a myriad of neurons^[27]. This modification of synaptic strength, referred to as weight plasticity is classified as short and long-term based on their time scales of operation. Acting on a sub-second timescale, short-term plasticity predominantly serves as a working memory; while long-term plasticity lasting from minutes to hours is

responsible for spatial memory storage and forms the basis of learning mechanisms^[28]. Combination of LTP and LTD, when triggered by spike time correlations is referred to as spike time dependent plasticity (STDP)^[29], and underlies learning and information storage in the brain. To qualify as effective artificial opsins compatible with SNN algorithms, the neuristors were initially benchmarked on the degree of manipulation of STDP windows as a function of the optical stimuli.

Figure 7.2 Electrical asymmetric Hebbian STDP rules in ReS₂ neuristors. (A-B) Input waveforms used for STDP measurements. **(C-D)** Conductance variations corresponding to LTP and LTD without and with optical illumination. **(E)** STDP: Long-term weight changes as a function of the interval between pre- and post-synaptic spikes ($\text{Time}_{\text{post-pre}}$) (dark).

A spike-based formulation of Hebbian learning, STDP is considered to be the first law of synaptic plasticity and underlies the basis of associative learning across several species from locusts to fishes to rats to humans^[27,30,31]. Memory traces of past experiences were encoded as temporal correlations between electrical pre- and post-synaptic neurons, resulting in a temporally asymmetric form of Hebbian learning. Temporal correlations between pre- and postsynaptic spikes significantly defines the sign and magnitude of long-term synaptic modification, referred to as the STDP function or learning window, and varies tremendously across synapse types, dendritic compartments and brain regions^[30,32]. The ReS₂ neuristors investigated here, exhibited a standard asymmetric Hebbian STDP rule in response to the electrical pre- and post-synaptic stimuli as shown in Figure 7.2. Repeated arrival of pre-post or post-pre spike pairs translated into time-integrated voltage amplitude differences between the pre- and post-synaptic neurons ($V_{\text{pre}} - V_{\text{post}}$), which when crossed the threshold for non-volatile changes, induced LTP/LTD in the channel conductance^[26] (Figure 7.2-A-D). The conductance was monitored before, during and after application of the spike pairs, and

was recorded as a function of the pulse interval between pre- and postsynaptic spikes (Figure 7.2-E). The resultant weight changes depended on the net effective voltage developed across the device integrated over a time t . For example, when spike pairs corresponding to Figure 7.2-A was applied to the device at an interval ($t_{\text{post-pre}}$) of + 500 ms, the maximum net voltage developed across the device was $V_{\text{pre}} - V_{\text{post}} = (-30) - (+30) = -60$ V and this resulted in a permanent increase in the channel conductance or LTP (~ 79 %) as depicted by Figure 7.2-C. On arrival of presynaptic pulses after postsynaptic pulses, i.e. $t_{\text{post-pre}}$ of - 500 ms (Figure 7.2-B), the maximum net voltage developed across the device was $V_{\text{pre}} - V_{\text{post}} = (+30) - (-30) = +60$ V and this resulted in a decrease in conductance or LTD (~ 68 %), as shown in Figure 7.2-D. These measurements were repeated for several combinations of spike intervals and the weight changes were plotted as a function of $t_{\text{post-pre}}$ as shown in Figure 7.2-E. Weight changes were predominant at small pulse intervals, and weakened with increase in the interval, reflecting strong temporal correlations between the pre- and postsynaptic spikes.

Illumination with red light ($\lambda = 623$ nm) induced long-term potentiation at all intensities, resulting in a positive shift of the STDP functions (Figures 7.3-A). The shift depicted a direct relationship with the intensity of optical excitation. Increasing the intensity of optical stimuli from 65 to 230 mW/cm² resulted in an increased LTP from 83 to 117 % for $t_{\text{post-pre}} = +500$ ms, in comparison to 79 % for the pure electrical STDP. The shift also depicted a wavelength dependence as expected. Illumination with lower wavelengths (green, $\lambda = 525$ nm and blue, $\lambda = 445$ nm) induced higher degree of manipulations of the STDP function due to the higher energy of irradiation as shown in Figure 7.3-B-C. Figure 7.3-D compares this behaviour for all the three wavelengths used in this study. For the same intensity of illumination (65 mW/cm²), blue illumination caused a 94 % LTP, while green and red illuminations accounted for 90 % and 83 % respectively. With regards to the LTD window, all optical stimulations counteracted the electrical LTD effects as depicted in the figures. Such an interaction between the photo-generated carriers and electrically-induced recombination effects resulted in net conductance/weight changes as shown in the Figure 7.3. This becomes particularly evident for the cross-over regions (marked by the dashed circle in the figures) when illuminated with the highest dosage of optical stimuli. Upon illumination with red light (230 mW/cm²), the devices depicted LTD for $t_{\text{post-pre}}$ upto 2000 ms,

indicating dominance of the electrical LTD effects. For intervals beyond 2000 ms, the effects of electrical LTD weakened, resulting in a net LTP. For the highest photo-dose of green and blue light, the photo-LTP completely compensated the electrical-LTD at all spike intervals, resulting in potentiation irrespective of the temporal correlations between the electrical pre and post-synaptic spikes. Removal of the optical stimulation resulted in retrieval of the original STDP function as shown in Figure 7.4. This modulation of STDP windows with light or **photo-modulated spike-timing dependent plasticity (pSTDP)** resembles biological optogenetics measurements, qualifying these neuristors as effective optogenetic actuators or opsins compatible with SNN protocols.

Figure 7.3 photo-modulated Spike Timing Dependent Plasticity (pSTDP) learning rules in ReS₂ neuristors. The devices were subjected to optical stimulations during the STDP

measurements. This resulted in a modulation of the STDP window as a function of the wavelength and intensity of photo-dosage and exposure, akin to optogenetic measurements. The graphs (read row-wise) depict the modulations of STDP upon illumination with (A) red (623 nm), (B) green (525 nm) and (C) blue (445 nm) light, as a function of the intensity of photo-dosage. (D) compares the modulations as a function of the wavelength of illumination for intensities 65, 130, 200 and 230 mW/cm².

Figure 7.4 photo-modulated Spike Timing Dependent Plasticity (pSTDP) learning rule and recovery of the original STDP function. Removal of the optical stimulation resulted in retrieval of the original STDP function as shown above.

Compatibility with DNNs.

With unmatched prowess in solving complex mathematical problems, DNNs encompassing powerful backpropagation algorithms have revolutionized the field of machine learning for several tasks including pattern recognition and classification. For the training of DNNs, crossbar arrays of memristive elements implementing highly parallel multiply-accumulate operations at the data locations are predicted to save six orders of magnitude in both energy efficiency and speed, when compared to conventional von Neumann central processing units (CPUs)^[33]. To unlock this potential, requires analog weights to be encoded into the device conductances via blind update (write) and access (read) operations, accelerated in parallel via simple Kirchhoff's circuit laws^[34]. However, most memristive solutions lag behind in this aspect due to numerous device infidelities like write and read non-linearity, noise and device-to-device variation. Recently, write noise, conductance linearity (CL) and multi-level cell (MLC) characteristics have been identified as the major limiting factors to achieving high-accuracy in computationally intensive tasks like vector-matrix multiplication and parallel rank 1 weight updates- the backbone of numerous

backpropagation algorithms^[35,36]. Unfortunately, most memristive devices depict a thermal-feedback based structure-altering switching mechanism resulting in highly non-linear state changes, fundamentally limiting their feasibility with such algorithms^[34]. Recognizing that novel materials/devices with fundamentally different resistive switching mechanisms is required to improve device linearity and hence higher algorithm training accuracy, very recently non-volatile redox cells (NVRCs) based ion insertion/extraction with low switching energies and write noise, and excellent CL, non-volatility and MLC (200-500 states) were proposed as promising alternatives^[33,37]. Backpropagation simulations with near perfect accuracies, much higher than state-of-the-art phase change memories (PCMs) and filamentary RRAMs were demonstrated, reiterating the significance of CL, MLC and write noise requirements for such adaptive memory elements.

Harnessing defect or trap centred slow recombination of photo-generated carriers, a phenomenon known as persistent photoconductivity (PPC)^[38], memconductance states were optically programmed in these ReS₂ neuristors with near-ideal conductance linearity and a wide dynamic range. Compared to electrical writing, photo-programming offers an orthogonal alternative for accessing such multi-level memories^[39]. Upon illumination the conductance increased rapidly, and gradually dropped to states higher than the initial conductance states, exhibiting excellent non-volatility and retention characteristics. Increased photo-dosage resulted in a larger number of carriers occupying the sites of the local potential minima, leading to slower recombination, higher retention and a slower forgetting process, in accordance with the random local potential fluctuation (RLPF) model^[40]. To demonstrate the extremely high density of non-volatile states available for analog computation in these neuristors, the devices were exposed to an input optical pulse train of constant pulse width and interval (10 s, $\lambda = 623$ nm, 65 mW/cm² intensity). Real-time monitoring of the conductance changes revealed a precise stepped increase in conductance from 1 to 163 nS with a step size of ~ 0.15 nS, equivalent to 1024 distinct conductance states or 10-bit equivalent (Figure 7.5-A-B).

Figure 7.5 Optically addressable multi-level memory for DNNs. (A) An input optical pulse train of constant pulse width and interval (10 s, 65 mW/cm² intensity (inset) resulted in a precise stepped increase in conductance equivalent to 1024 distinct conductance states or 10-bit equivalent. (B–D) shows a magnified version of the conductance states (1–16) depicted in (A). During these measurements, the devices were electrically biased at a constant voltage of –40 V to ensure a low initial conductance state. The switching transitions depended solely on the accumulation and retention of photo-generated carriers. Inset in each graph shows the conductance states (1009–1024). As expected, increased photo-dosage increased the slope further extending the dynamic range, while maintaining linearity as shown in (E–G). The graphs depict states 1–16 as an example.

Shorter wavelengths demonstrated a higher slope, wider conductance range and higher retention characteristics, indicating faster learning rates and a higher signal-to-noise ratio (SNR). The conductance range spanned from 1 nS to 1.13 μS and 1.28 μS for the green and blue wavelength stimuli (65 mW/cm² intensity) respectively. While the green stimuli depicted a step size of ~1.1 nS, the blue stimuli resulted in a step size of ~1.25 nS for 65 mW/cm² intensity of irradiation (Figure 7.5-A,C-D). During each optical “write” operation, the increase in conductance corresponded to the photo-generation of carriers in the semiconducting channel, while during each “read” operation, the conductance state remained stable demonstrating excellent non-volatility and retention due to the PPC effect. The subsequent photo-generation added on to the carrier concentration resulting in a near-ideal conductance linearity. To maximize the dynamic range of linear response, the devices were electrically biased at a constant voltage of –40 V to ensure a low initial conductance state. The switching transitions depended

solely on the accumulation and retention of photo-generated carriers. As expected, increased photo-dosage increased the slope further extending the dynamic range, while maintaining linearity as shown in Figure 7.5-E-G. The number of distinct states were determined primarily by the programming pulse resolution and recombination kinetics of the photo-generated carriers, and hence, the programming pulses were optimized accordingly to achieve a near-perfect linearity. Hence, the number of states demonstrated in Figure 7.5 is by no means an upper limit for this device, but rather is a reflection of the measurement set-up. Such optical multilevel memories would suffice the high-density memory storage requirements for data centric applications like machine learning algorithms, utilizing the advantages of infinite bandwidth and high-speed of optical access protocols.

While optical gating enabled linear incremental non-volatile “write” steps, electronic gating facilitated the “erase” process via defect assisted trapping of the photo-generated carriers. Surface adsorbates and defects at the semiconductor-dielectric interface have been observed to act as carrier trapping and detrapping centres, causing hysteresis in current transient measurements^[26]. Here, the “erase” process modulated via the electronic gating created electron trapping centres, recombining and erasing the excess photo-generated charge carriers generated during the “write” process as shown in Figures 7.6-A-D. The “erase” pulses were optimized in both amplitude and pulse widths to achieve linear near-symmetric bi-directional weight changes- an important criteria determining the accuracy of backpropagation algorithms. Positive weight changes activated by 623 nm (red) optical stimuli were erased by electrical pulses of amplitude + 20 V. Higher erasing electrical voltages were applied at the back gate to counteract the higher degree of potentiation induced by shorter wavelength optical stimulation. For instance, positive weight changes of higher magnitude due to 525 / 445 nm optical activation were erased by electrical pulses of amplitude + 35 / 40 V respectively.

Stability of the individual states, retention and dynamic range becomes cardinal evaluation parameters in the case of such multilevel memories, since the on-off ratio between the continuously modulated conductance states lie close to each other^[39]. A higher dynamic range would ensure improved device reliability, increased number of distinctly addressable states would improve the memory storage capabilities, while excellent retention properties would ensure stable device operation^[33,41]. A test of write

endurance (1600 switching cycles – 800 “write” and 800 “erase” steps between the 1st 16 conductance states) revealed high endurance and low write noise in the investigated devices for all wavelengths of optical stimulation. Figures 7.6-E-G shows a magnified view of the conductance response during the first 128 voltage-controlled “write” and “erase” operations. The conductance changes exhibited predictable, saw-tooth-like conductance steps without any degradation in the overall channel conductance.

Figure 7.6 Analysis of endurance during “write”-“erase” operations. Application of synergistic optoelectronic pulses (A) result in precisely controlled near-symmetric bidirectional weight changes via optical potentiation and electrical depression as shown in (B-D). Higher erasing electrical voltages were applied at the back gate to counteract the higher degree of potentiation induced by shorter wavelength optical stimulation. (E-G) Magnified view of the

conductance response during the first 128 voltage-controlled cycling tests. (H-M) ΔG vs G plots – a measure of endurance and write noise during cycling tests. Plots (H, J, L) depict the variation in the changes in conductance during “write” operations, while (I, K, M) depict the variations during the “erase” operations for red, green and blue wavelengths of optical stimuli.

The results of the remaining cycles were condensed to conductance change (ΔG) vs absolute conductance (G) plots for both potentiation and depression as shown in Figures 7.6-H-M. These plots revealed the probability distribution about the average change in conductance (ΔG_{avg}). Each switching transition was repeated 50 times to obtain a reliable fit of parameters. An ideal memristive device should depict a narrow distribution centred about ΔG_{avg} over the entire range of G ^[8]. Probability distribution plots of the ReS₂ neuristors depicted exceptionally high write linearity with an average signal-to-noise ratio ($\Delta G_{avg}^2 / \sigma^2$; σ - standard deviation) of 33, 32 and 61 respectively (among the highest reported till date, second to only LISTA^[8]) for red, green and blue wavelength optical “write” and their corresponding electrical “erase” operations. In comparison, state-of-the-art filamentary RRAMs and PCMs showed orders of magnitude greater nonlinearity and lower signal-to-noise ratios (< 1)^[42]. In addition to excellent linearity in conductance transitions, the neuristors demonstrated excellent retention properties after “write” operations (Figure 7.7). The devices were switched between the 1st and 16th conductance state by appropriate optical “write” and electrical “erase” operations and the conductance states were read by a reading voltage of 0.1V. The neuristors depicted excellent retention characteristics (tested up 10⁴ seconds) for all the three wavelengths of optical stimulation.

Figure 7.7 Retention of the non-volatile states. The devices were switched between the 1st and 16th conductance state and the conductance states were read by a reading voltage of 0.1V. The neuristors depicted excellent retention characteristics (tested up 10⁴ seconds) for all the three wavelengths of optical stimulation, namely (A) red, (B) green and (C) blue.

Figure 7.8 Optical Abacus Operation. Precise optical potentiation and electrical depression enabled facile emulation of arithmetic operations, analogous to an abacus. Multiple neuristors were employed to represent the unit's (blue bead), ten's (red bead) and counter's (green bead) place and programming steps were designed as per the arithmetic operation under calculation. Optical stimulations resulting in potentiation represented rightward sliding of the beads, while electrical stimulations causing depression represented leftward sliding of the beads. The modulus operandi of the operations are indicated with necessary illustrations as insets.

Optoelectronic abacus operations.

Precise control of weight changes over both potentiation and depression cycles (as depicted in Figure 7.6) enabled facile emulation of basic arithmetic operations akin to an abacus. These simple memcomputing operations banked on the incremental accumulation and depletion of charge carriers in the semiconducting channel upon appropriate optical and electrical stimulation. Very recently, Feldmann et al.^[43] demonstrated an optical abacus that performed basic arithmetic operations of addition, subtraction, multiplication and division based on incremental crystallization of PCMs. While this all-optical configuration embodied the advantages of ultra-fast signalling and ultra-high bandwidth capabilities intrinsic to light, the system level design was highly complicated with the need for mode-locked lasers, on-chip waveguides, grating couplers, pump probes, pulse pickers and beam splitters. Moreover, this configuration was limited to only addition and multiplication operations directly, while subtraction and division were realized using the numbers complement approach. With precisely controlled optical potentiation and electrical depression steps realized via photon and electron pulses, the investigated ReS₂ neuristor configuration facilitated facile emulation of arithmetic operations akin to an abacus.

Here, two neuristors were used to represent the first (blue) and second (red) digits of the base-10 number system (Figure 7.8). Both devices were pre-programmed to a common low conductance state (1 nS, representing ‘0’) prior to any calculations. In abacus, this is represented by an extreme left shift of all the beads. For an addition operation of ‘27+14’ (Figure 7.8-A), the 1st neuristor was optically programmed with as many steps as the augend (‘7’ in this case) by appropriately designed optical pulses ($\lambda = 445$ nm, 65 mW/cm² intensity). In abacus, this is represented by right shift of an appropriate number of blue beads. This was followed by programming steps equivalent to the addend ‘4’. When the sum reached ‘10’, the unit’s place neuristor was “RESET” to the initial conductance state by an appropriately designed electrical pulse (extreme left shift of all the blue beads). Concurrently, the second neuristor representing the ten’s place was updated by a single optical programming pulse (carry over, $\lambda = 623$ nm, 65 mW/cm² intensity) to hold ‘1’ temporarily. In abacus, this carry over operation is represented by a right shift of a single red bead. Subsequently, programming steps equivalent to the remainder (‘1’) was carried out to get a final sum of ‘1’ in the unit’s

place. Similar operations were carried out on the second neuristor (currently holding '1' from the carry over) resulting in a final sum of '4' in the unit's place. The conductance states of both neuristors were read by a reading voltage of 0.1 V to get the result '41'. Multiplication of '7x3' was implemented as successive additions in a manner similar as explained above (Figure 7.8-B). Carry over operations included appropriate electrical 'RESET' operations at the neuristor representing the unit's place and concurrent optical update operations at the ten's place, resulting in a correct product '21'. For the subtraction operation of '27-14' (Figure 7.8-C), the neuristors were initially programmed to represent the minuend ('7'), before proceeding with appropriately designed electrical "erase" pulses corresponding to the subtrahend ('4'), to get the final result '3' in the unit's place. Similar operations at the ten's place yielded '1'. The conductance states were read by 0.1 V to get the final correct result '13'. For the division operation '15/5', a third neuristor was programmed (as a counter) with appropriate optical updates ($\lambda = 525 \text{ nm}$, 65 mW/cm^2 intensity) for each complete subtraction of the divisor '5' from the dividend '15', to get the final quotient of '3' as shown in Figure 7.8-D. The carryover, counter update operations and control of the light sources were carried out via an external microcontroller in the current testing setup. However, for real-life practical implementations, all these operations could be carried out via on-chip peripheral circuitry. Most importantly, all arithmetic calculations and data storage were carried out simultaneously in the three neuristors employed here, paving way for a non-von Neumann optoelectronic memcomputing architecture.

Utilizing photon pulses as a global but selective neuromodulatory scheme.

Brain functions emerge through coordinated neural circuit activity within and across multiple cerebral cortex regions. The key goal in neuroscience is to decipher how these circuits generate the computational patterns underlying learning and behaviour, and this requires perturbation of the activity of specific cell types or circuits in a temporally precise manner^[44]. With high spatial and temporal precision, optogenetics overcomes most pitfalls of traditional methods relying on electrical stimulations. Intensive research efforts in developing optogenetic actuators and sensors has increased the ability to manipulate and observe such neural activity. Global yet selective perturbation are key

factors in all such studies, and an artificial optogenetic actuator and sensor should suffice similar addressing requirements with high spatio-temporal precision.

Figure 7.9 Photon pulses as a global neuromodulatory scheme. (A) Input optical pulse and electrical bias applied on the neuristors. (B) Spatial conductance map of the devices in the initial state. Spatial conductance maps of the neuristors when subjected to (C) red ($\lambda = 623$ nm), (D) green ($\lambda = 525$ nm) and (E) blue ($\lambda = 445$ nm) optical stimuli for intensities varying from 65 to 230 mW/cm².

To demonstrate the global addressing capabilities of light, a 36-element ReS₂ array was assembled and was subjected to various wavelengths and intensities of optical stimuli as shown in Figures 7.9-A-E. The initial conductance of the devices varied from 1 to 10 nS and was not pre-programmed to a common conductance value on purpose (Figure 7.9-B). This was done to demonstrate an initial conductance-independent response to the optical stimulations. Upon illumination the conductance increased rapidly, and gradually dropped to states higher than the initial conductance states, exhibiting excellent non-volatility and retention characteristics due to the PPC effect, similar to Figure 7.5. On application of an input optical pulse train of constant pulse width and

interval (10 s, $\lambda = 623$ nm, 65 mW/cm^2 intensity), the conductance increased in a precise stepped manner with an average step size of ~ 0.15 nS (Figure 7.9-C). Higher intensities of 130, 200 and 230 mW/cm^2 resulted in average stepped increments of ~ 0.57 , 1 and 1.4 nS respectively. Shorter wavelengths demonstrated higher modulations as expected. While the green stimuli depicted stepped increments from ~ 1.1 to 9.5 nS, the blue stimuli resulted in increments from ~ 1.25 to 11 nS for intensities 65 and 230 mW/cm^2 of irradiation (Figure 7.9-D-E). During each optical “write” operation, the increase in conductance corresponded to the photo-generation of carriers in the semiconducting channel, while during each “read” operation ($V_{ds} \sim 0.1$ V), the conductance state remained stable demonstrating excellent non-volatility and retention due to the PPC effect. These spatial conductance maps demonstrate optical stimuli as a global neuromodulatory input, akin to optogenetic measurements. Such global neuromodulations could enable instantaneous activation of a large patch of neurons, enabling investigations into the neuronal behaviour within a larger homeostatic network-level setting.

Spatiotemporal precision and specificity are other key advantages that need to be mimicked to comprehensively emulate the optogenetic actuators and sensors. To address this, a 36-element array comprising of 16 light sensitive ReS_2 and 20 insensitive IWO neuristors was assembled as shown in Figure 7.10-A. All neuristors were initially programmed to a common low conductance state (5 nS). Upon illumination with red light (10 s, $\lambda = 623$ nm, 230 mW/cm^2 intensity), the channel conductance of the ReS_2 neuristors depicted a non-volatile increment (5 nS to 6.5 nS) due to the low bandgap (1.5 – 1.8 eV) and PPC effect, as explained previously. On the other hand, the channel conductance of IWO neuristors remained constant (5 nS) due to their large bandgap (3.6 eV) and nature of defects at the IWO- SiO_2 interface. A spatial conductance map readout of the array resembled the image of “N” with the light sensitive ReS_2 neuristors spatially arranged to resemble this alphabet as shown in Figure 7.10-B. Subsequent spatial rearrangement of the light sensitive ReS_2 neuristors to match images of “T” and “U”, resulted in similar conclusions with selective activation of only the light sensitive neuristors (Figure 7.10-C-D). Illumination with green light (10 s, $\lambda = 525$ nm, 230 mW/cm^2 intensity) resulted in an increase in conductance states from 5 nS to 14.5 nS, while blue light (10 s, $\lambda = 445$ nm, 230 mW/cm^2 intensity) resulted in an increase from

5 nS to 16 nS. These results demonstrate the specificity of a photon-based “write” operation, globally capable of addressing light-sensitive neural elements on demand with high specificity.

Figure 7.10 Specificity of the photon-based write pulses. (A) A 36-element array comprising of 16 light sensitive ReS₂ and 20 insensitive IWO neuristors were assembled and initially programmed to a common low conductance state (5 nS). Spatial conductance maps of the neuristors when subjected to (B) red ($\lambda = 623$ nm), (C) green ($\lambda = 525$ nm) and (D) blue ($\lambda = 445$ nm) optical stimuli (intensity = 65 mW/cm²). Illumination with optical stimuli selectively activated the light sensitive low band-gap ReS₂ neuristors without affecting the light insensitive high band-gap IWO neuristors. A spatial conductance map readout of the array resembled the images of “N”, “T” and “U”, with the light sensitive ReS₂ neuristors spatially arranged to resemble these alphabets. These results demonstrate the specificity of a photon-based “write” operation, globally capable of addressing light-sensitive neural elements on demand with high specificity.

Besides monitoring specific neural activity, optogenetics is also utilized as a neuromodulatory tool altering neural activity. Application of an optical sinusoidal

signal, analogous to a global clock resulted in a modification of the synaptic weights of the ReS₂ neuristors as depicted in Figure 7.11-A. Optical stimulation of 445 nm (blue) resulted in a stronger weight change when compared to 623 nm (red) as explained previously. The channel conductance increased to a final value of 102 nS for the blue wavelength stimulation as supposed to 13 nS for the red. This large contrast in weight change modulation was utilized in an array-level setting to selectively modulate the firing rate of corresponding neurons based on the final value of synaptic weights. A 6x6 array of ReS₂ neuristors were selectively subjected to sinusoidal global clocks of red and blue wavelengths. As observed previously, neuristors subjected to the blue wavelength of irradiation resulted in a larger modulation of the synaptic weights with the final spatial conductance map corresponding to ~ 102 nS, while the red-activated elements depicted a conductance ~ 13 nS. A neuronal firing threshold of 80 nS was pre-set in the array such that only synapses crossing this threshold caused neuronal firing. Hence, only neuristors activated by the blue wavelength triggered neuronal firing while the red-activated ones remained inactive (Figure 7.11-B).

Figure 7.11 Selective neuronal firing with optical stimuli. (A) Application of sinusoidal global optical clock signals to the ReS₂ neuristors resulted in a long-term weight modulation as depicted by the graph on the right. An electrical bias of - 40 V was applied during these measurements to enable a common low initial conductance state of ~ 5 nS. (B) A 36-element array comprising of 36 ReS₂ neuristors was assembled and initially programmed to a common low conductance state (5 nS). Selective illumination with optical sinusoidal optical clock stimuli (red and blue) activated the neuristors with each device depicting a non-volatile weight change corresponding to the wavelength. Some of the devices were manually blocked during this illumination experiment (as depicted by the black bars) to realize selectivity. The blue wavelength of irradiation triggered weight changes in the devices as expected, resulting in a

final spatial conductance map ~ 102 nS, crossing the pre-set firing threshold of 80 nS. On the other hand, the red wavelength stimulation triggered weight changes to a final value of ~ 13 nS, inactivating neuronal firing.

Figure 7.12 A comprehensive optogenetic toolkit. The photoreceptive neuristors were integrated with soft dielectric elastomeric actuators to comprehensively emulate the biological optogenetic toolkit. The photoreceptive neuristors mimicked the role of opsins and synapses, monitoring the channel conductance/ synaptic weight, akin to optogenetic sensors and the DEA embodied an artificial eye, completing the optogenetic toolkit. Figure shows the flowchart (**A**) and photograph (**B**) of the setup utilized for this experiment.

As a final demonstration, these neuristors were integrated with soft dielectric elastomeric actuators to comprehensively emulate the biological optogenetic toolkit. The neuristors with optoelectronically modulatable plasticity act as photoreceptive weight-storage banks, dawning the role of opsins and synapses. The slow

recombination of photo-generated carriers, controlled synergistically via optical and electronic gates mimic the intracellular Ca^{2+} flux, modulating the channel-conductance or synaptic weight, akin to optogenetic sensors. Finally, the DEAs embody the living tissue or organism under study, completing the optogenetic toolkit.

Figure 7.12 shows the flowchart and photograph of the setup utilized for this experiment. The elastomer fabrication is detailed in the experimental section (Refer to Chapter 3 Sections 3.2.4). In a typical human eye, the iris regulates the amount of light entering the eye. Circular muscle fibers of the iris contract upon bright light illumination, reducing the size of the pupil; while in dim light, these circular muscles relax and the radial muscles contract, dilating the pupil. In a similar manner, photo-modulations of the channel conductivity of the ReS_2 neuristor beyond a pre-set threshold triggered neuronal firing (represented here as an Arduino-controlled relay switch), causing contractile motion of circular muscles of the iris of the artificial eye (DEA) (Figure 7.13-A).

Figure 7.13 Artificial eye. (A) In a typical human eye, the iris regulates the amount of light entering the eye. In bright light, the iris's circular muscle fibers contract, reducing the size of the pupil; while in dim light, these circular muscles relax and the radial muscles contract, dilating the pupil. DEAs are configured here to constrict in a manner resembling the circular muscles. The lateral and areal strains or the amount of constriction can be tuned via the applied

voltage. **(B)** On integration with photo-receptive neuristors, the artificial eye demonstrates learning and adaptive memory behaviour analogous to the human eye. **(C)** On integration with standard photodiodes, the artificial eye does not demonstrate any learning behaviour.

Upon optical illumination with blue light ($\lambda = 445 \text{ nm}$, 65 mW/cm^2 , 40 seconds), channel resistance of the ReS₂ neuristors ('retina') decreased from $\sim 1.5 \text{ M}\Omega$ (high resistance state) to $\sim 0.25 \text{ M}\Omega$ (low resistance state). The channel resistance was monitored via an Arduino microcontroller configured as an ohmmeter, with a potential divider circuit comprising of an array of known resistors covering a wide resistance range. On crossing a pre-set threshold of $1 \text{ M}\Omega$, the Arduino triggered a relay switch, which in turn controlled a DC power supply and a transformer, providing 6 kV to actuate the actuator. The design of the actuator limited the strains to central non-active area. On application of voltage, the electrostatic stresses produced in the active region ('iris') caused a visual change (contraction) in the dimensions of the central non-active area ('pupil'), akin to pupilar constriction of the human eye (Figure 7.13-B). Lateral (measured along the diameter) and areal (change in area) strains analysed with Image J software (Fuji) yielded values of 20 % and 36 % respectively. The strain induced could be further tuned based on the voltage as depicted in the graph (right). Due to the PPC effect, the devices maintained its low resistance state and gradually recovered to the high resistance state as seen in the graph (right). This memory effect in turn manifested as a persistence of pupilar constriction (eye remains closed even after removal of optical stimuli) as can be seen from the photographs (Figure 7.13-B). This phenomenon resembles fear conditioning of the blink reflex or in general an escape response, observed in humans and many other organisms, reiterating the fact that this optogenetic toolkit could be utilized to create behavioural robots that learn and adapt to their stimuli^[45–47]. The memory response could be further tuned or conditioned with increased rehearsals as depicted in the graph (right). Repetition of optical stimuli increased the memory effect with devices maintaining the low resistance state for about 280, 800 and 2000 seconds for the 1st, 2nd and 3rd cycles of repetition, demonstrating a continuous learning process.

A control experiment was carried out with a standard light-dependent resistor (LDR) to compare the memory and learning behaviour of the ReS₂ neuristors (Figure 7.13-C). Upon optical illumination (same as before), the resistance dropped suddenly from $\sim$

62.5 k Ω to $\sim 200 \Omega$. The relay, now programmed to fire at 1 k Ω (new pre-set threshold as per the resistance of the LDR) actuated the artificial eye similar to the previous case. However, switching off the light resulted in a sudden increase back to the original high resistance state, due to the lack of memory, in turn relaxing and opening the artificial eye. Thus, although the standard photodiode resulted in a faster response and could be potentially trained like a blinking robot, the lack of memory curtails its applicability as a trainer circuitry compatible with AI algorithms.

7.3 Conclusion

In conclusion, photo-receptive ReS₂ neuristors with optoelectronically modulatable plasticity were integrated with soft robotic actuators (DEAs) to create a dummy optogenetic toolkit for behavioural robots. The neuristors mimicking optogenetic actuators were benchmarked to be compatible with both SNN and DNN algorithms via systematic investigations of photo-modulated STDP and linear blind-update learning rules. Precise control of weight changes over both potentiation and depression cycles enabled facile emulation of basic arithmetic operations akin to an abacus. The arithmetic calculations and data storage were carried out simultaneously in the three neuristors employed here, paving way for a non-von Neumann optoelectronic memcomputing architecture. Critical advantages of optogenetics, namely- global and selective modulation of neural activity were next implemented in an array comprising of light sensitive ReS₂ and insensitive IWO neuristors. Spatial conductance maps revealed the wavelength and intensity modulations possible with photon pulses and this contrast in response was utilized to activate firing of a specific patch of neurons. As a final demonstration, these neuristors were integrated with soft dielectric elastomeric actuators to create an artificial eye, with learning and memory behaviours that resemble a human eye. Such a fusion of the concepts of optogenetics, neuromorphic electronic systems and soft robotics would pave way for behavioural robots with bioinspired cognition and learning abilities.

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Chapter 8

Discussion and Future Work

This chapter draws together the threads of this dissertation. The extent to which the hypotheses were addressed is briefly discussed with a summary of the results. The drawbacks and implications are reflected and new opportunities and strategies for future work are identified.

8.1 Summary

Drawing inspiration from the recent promising design of mixed ionic-electronic conductors approximating the biological Ca^{2+} dynamics^[1–3], this dissertation tackles the hardware switching requirements for bio-inspired computations by adopting novel memristive device configurations encompassing ionically and optically-active semiconductors and dielectrics.

Ionic semiconductors in halide perovskites were initially investigated in a two-terminal memristive configuration^[4]. The mixed ionic-electronic conduction was harnessed to realize artificial synapses with programmable plasticity. Investigations were carried out on halide perovskites containing both organic and inorganic cations, namely $\text{CH}_3\text{NH}_3\text{PbBr}_3$ (MAPbBr_3), $\text{CH}(\text{NH}_2)_2\text{PbBr}_3$ (FAPbBr_3) and CsPbBr_3 . Vacancy-driven ion migration effects self-doped the active layer and modulated the electronic injection barriers at the electron and hole-transporting interfaces, demonstrating composition-dependent plasticity features. With higher activation energies for ion migration, the weight changes were observed to be more profound in organic cation (methylammonium and formamidinium) containing halide perovskites when compared to their inorganic cesium counterpart. Trained as a memory array, these devices depicted reconfigurability and fault tolerance to spurious and random inputs. Network-level simulations of unsupervised learning of handwritten digit images based upon experimentally-measured device properties illustrated the power of these memristors for bio-inspired pattern recognition and image classification algorithms.

Next, hysteretic transistors demonstrating smooth gate-controllable conductance transitions were investigated as artificial synapses. In this FET configuration, ion migration-relaxation dynamics and carrier trapping-detrapping effects at the semiconductor-dielectric interface modulated the channel conductance, resulting in gate-modulated plasticity features^[5]. High-mobility amorphous metal oxide semiconductors (IWO) were utilized in a dual-gated configuration with a top solid-state ionic dielectric $[\text{P}(\text{VDF-HFP})\text{-}[\text{EMI}][\text{TFSI}]]$ and a bottom SiO_2 insulator. The EDL-gated ionotronic mode demonstrated significant power and plasticity advantages over the electronic bottom-gated control, reiterating the advantages of a mixed ionic-electronic conductance modulation for analog-like switching transitions. The gate control elevated the degree of achievable plasticity and hence, both these gates were

synergistically combined to realize more complex neuronal characteristics like heterosynaptic plasticity, association and co-incidence detection.

To further incorporate additional modulations via optical inputs, low band-gap 2D transition metal dichalcogenides (TMDCs) like MoS_2 ^[6] and ReS_2 were next investigated as semiconducting channels for artificial synapses. Light was utilized as an additional gating control in these configurations. Such transistors were constructed to operate in multiple modes, namely- electronic, ionotronic and photoactive, exploiting the advantages of electrons, ions and photons for concurrent compute and store operations. Synergistic operation enabled emulation of complex neuronal signatures beyond the standard short- and long-term plasticity rules, increasing the computational efficiency of these devices. The highly plastic nature allowed the same device to be compatible with both SNN and DNN algorithms, enabling emulation of more complex neuronal behaviours like heterosynaptic plasticity, Hebbian metaplasticity, homeostasis and association- all with a single neural element, alleviating complex circuit design requirements.

8.2 Conclusions

- With regards to the degree of weight plasticity, the organic cation containing halide perovskites demonstrated higher PPF indices, temporal filter gains, LTP indices and longer memory retention, and also depicted lower energy consumption with respect to all-inorganic systems, encouraging a hybrid organic-inorganic material design of halide perovskite synapses. This motivates further investigations on this material set with ionic and electronic injection barriers tailored to enhance the plasticity.
- With the additional gate-control terminal modulating the hysteretic channel conductance, the three-terminal field-effect configuration promises higher plasticity when compared to the conventional two-terminal memristive configurations. Ionic gating of transistors has been demonstrated to operate at ultra-low power, entailing future works in this direction. Encompassing multiple gates to synergistically control the channel conductance seems promising and is discussed further in the section below.

- Incorporating the photo-active mode endows devices with an orthogonal complimentary programming scheme and enhances the achievable plasticity. Comparing the degree of plasticity in the electronic, ionotronic and photoactive modes of operation, it is concluded that while photoactive mode could only trigger LTP, the electronic and ionotronic modes could trigger both LTP and LTD. However, the LTP indices and memory retention were far stronger for the photoactive mode. Synergistic operation of all the three modes resulted in an optoelectronic computing platform that harnessed the advantages of both electron and photon-based operations. Such optoelectronic schemes pave way for highly plastic multi-gated computing architectures, discussed further in the section below.

8.3 Future Work

While key challenges with respect to analog-like switching transitions, dynamic conductance range and linearity were addressed to a considerably large extent with the various studies in this dissertation, these materials lag in terms of scalability, stability and uniformity relevant for real-life complex network-level computations. This dissertation addresses the challenges primarily from a fundamental material-design perspective with focus on emulation of synapses. This entails further systematic investigations on novel materials and architectural implementations, addressing the engineering challenges concurrently. Thus, the future work can be broadly classified into three sections- material, device and engineering challenges.

8.3.1 Avenues for further material exploration

- The possibility of exploring the perovskite family of ionic-electronic semiconductors for a novel application with an insight into the desired material characteristics and conduction mechanism, paves way for novel ionotronic neuromorphic architectures with halide perovskites as the active material. This motivates a further exploration of the compositional space of perovskites to study the correlation between the material properties and synaptic behaviour. Ruddlesden-Popper (2D) perovskites with bulkier organic ions, and incorporation of both 2D and 3D ions within the halide perovskite layer provides the possibility of more exquisite control^[7] (Figure 8.1).

- Since the interfaces play a significant role in defining the charge injection barriers, investigation of all-inorganic charge extraction layers and ion blockers would enable further insights into the ion migration mechanism under play. The local composition of the halide perovskite next to the interface could also be modified to ensure independent ionic/ electronic coupling at the interfaces with respect to the bulk^[8].
- Ion migration has been proved beyond doubt in halide perovskites, the degree of which depends on composition of cations and anions in the ABX_3 structure, morphology of thin-films, dimensionality, choice of hole and electron transport layers (TLs) – the interfaces, the applied electric fields and scanning rates^[9]. All these hysteretic phenomena could be inherently advantageous in creating memory elements with unique resistive switching properties and require further investigations.

Figure 8.1 depicts some examples of numerous halide perovskites that differ in their composition and dimensionality. The low-dimensionality perovskites possess highly localized electronic states with strong quantum confinement effects, which could unravel unique memristive switching properties.

- Temperature and moisture stability of these exotic materials is a big concern and needs to be addressed. Lead-free alternatives such as Bismuth, Antimony and Tin-based systems could be viable options, but requires systematic investigations. Demonstration over organic-inorganic hybrid and all-inorganic perovskites raise the appealing prospect that this material system could be further tailored for desirable

intimate ionic-electronic coupling that can deliver high-performance neuromorphic elements.

- The excellent photo-sensitive properties of halide perovskites were not harnessed for the memristive investigations in this dissertation. This opens up future opportunities where light could be utilized as an *ex situ* modulatory input to control the ionic migration with higher precision.
- Probing ion migration in halide perovskites require further systematic investigations. Very recently, techniques like piezoforce microscopy^[10] and voltage-assisted SEM-EDX^[11] have been utilized to study the migration of ions and defects in halide perovskites. Solid-state coulombic cells have also been configured with electrochemically contrasting interfaces to probe the nature of the conducting ion^[12]. This opens up new opportunities to combine synaptic characterizations with such probes to monitor the migration of defects across interfaces in real time. This would help to directly correlate the memristive/synaptic behaviour observed in halide perovskites to their vacancy-mediated migration effects.
- Likewise, the possibility of exploring the family of high-mobility amorphous metal oxide semiconductors and 2D transition metal di-chalcogenides (TMDCs) paves way for a series of novel demonstrations with these active materials. Low temperature metal-oxide fabrication processes like sputtering would enable realization of neuromorphic elements on flexible and implantable substrates, opening up new avenues in wearables^[13]. Combining with sensing elements, this would lead to new developments in event-based intelligent sensing platforms for Internet of Things (IoT)^[14] applications.
- All-2D TMDC-based FETs present unique device possibilities where crystalline, layered materials with atomically uniform thicknesses could be stacked on demand, without any lattice parameter constraints, leading to molecular-scale electronic devices^[15]. Other recently developed architectures involving stacked hexagonal boron nitride (hBN) - molybdenum disulfide (MoS₂) could allow access to even lower power operation in future^[16].

- While ionic dielectrics enable smoother conductance transitions via gate-controllable hysteresis and ensure ultra-low power operation, their stability against temperature and moisture are big concerns. While the adopted polymer-housing addresses this to some extent, it still remains a practical problem. Furthermore, ionic gating of an entire neural network comprising of billions of such transistors pose several processing and engineering challenges, apart from high leakage currents, sneak paths, stray capacitances, cross talk and write noise. Additional floating gates may be required to mitigate some of these effects like capacitive crosstalk and sneak paths, increasing the circuit complexity.
- Such polymer dielectrics encompassing ionically active electrolytes have been demonstrated to exhibit self-healing capabilities^[17]. Hence, the polymer chemistry in such dielectrics could be further tuned to induce self-healing properties^[18–20] in conjunction with the approximation of biological Ca^{2+} dynamics. This would set forth development of self-healable neuromorphic circuitry for e-skin applications^[21].

8.3.2 Opportunities with novel device configurations

- Multi-gated architectures that can induce temporally distinct modulations on the carrier concentration are demonstrated to increase the weight plasticity and memory storage capacity, enabling emulation of more complex neuronal behaviour like heterosynaptic plasticity, homeostasis and association- all in a single neuristor^[5,6]. However, some of the challenges which have to be overcome for large-scale usage of this technology include development of reliable integration with underlying CMOS electronics, ionically gating large array of transistors and managing the differences in voltage amplitudes between the different modes of operation.
- Recently, a dual ionic floating-gate architecture was proposed for amplified bio-detection^[22]. Adopting a similar architecture would not only solve the differences in gating voltage amplitudes, but would also open up possibilities of combining biosensing capabilities with AI, leading to intelligent bioelectronic devices.
- Optoelectronic computing devices utilizing photon pulses to write and address memory would help unlock novel neural network architectures where light could be

used as a global gate to selectively activate a patch of light sensitive neurons, interspersed between photo-insensitive neural elements. This design would also enable architectures with fewer number of interconnects, mitigating thermal loss and stray signals, hence improving the signal-to-noise ratio. However, eliminating light induced parasitic currents in hybrid-CMOS neural network architectures would remain challenging and would require additional reflective metal shielding structures to block the light from underlying silicon substrate.

- Preliminary simulations need to be performed while taking into account intrinsic limitations of such memristive devices. This would fuel large-scale network level implementations for robust data-centric applications such as natural language processing and real-time image recognition.
- Throughout this dissertation, various memristive implementations were harnessed to emulate biological synapses. Emulation of neurons still demands intensive research efforts. The switching mechanism and internal state variables of memristive devices could also be exploited to emulate neurons with high areal/power efficiency (Figure 8.2). As a synapse, NVMs are employed to achieve a continuum of conductance states; but as a neuron it requires to emulate an accumulative behaviour, ‘firing’ after crossing a pre-set threshold. Furthermore, volatility would facilitate leaky I&F dynamics, de-emphasizing the significance of non-volatility for such implementations. Seamless integration with dense synaptic arrays would result in a comprehensive implementation with concurrent signal-processing and memory storage capabilities.

Figure 8.2^[23] Circuit diagram of a biomimetic active memristor neuron and active memristor device characteristics. (A) Schematic structure of a biological neuron, showing that an action potential is fired near the axon hillock (under sufficient input stimulus) and propagates along the cell axon towards the output synapses. (B) Mechanism of voltage-gated Na^+ and K^+ ion flows across the cell membrane that accounts for the action potential generation and repetition across the nodes of Ranvier (myelin-sheath gaps). A similar mechanism exists in neurons that lack a myelin sheath. (C) Basic circuit topology of a two-channel active memristor neuron to emulate the neuronal dynamics in (B). A voltage-gated Na^+ (K^+) channel is emulated by a negatively (positively) d.c. biased active memristor device, which is closely coupled with a local membrane capacitor C_1 (C_2) and a series load resistor R_{L1} (R_{L2}). (D) Schematic structure and a scanning electron micrograph of a typical VO_2 active memristor nano-crossbar device (X_1 or X_2 in (C)). Scale bar: 100 nm. (E) Typical two-terminal quasi d.c. voltage-controlled (force V) and current-controlled (force I) I-V characteristics of a VO_2 active memristor device. A wide hysteresis loop exists in the voltage-controlled mode due to the Mott transitions (blue arrows). The same Mott transitions are manifested by an “S” shaped negative differential resistance (NDR) regime (highlighted by cyan color) with a much narrower hysteresis (red arrows) in the current-controlled mode. In its resting state, the resistor load line for memristor X_1 (or X_2) intersects with its I-V loci outside the NDR regime (green dotted line). An input current or voltage stimulus can shift the load line into the NDR regime (green dashed line) and elicit an action potential generation (spiking). © “From W. Yi, K. K. Tsang,

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8.3.3 Engineering Challenges

- In general, the temporal dynamics inherent in many of these memristive devices provide interesting neuromorphic functionality. However, the absence of a global learning architecture accompanying local STDP-based learning rules challenges the write operations per bit and energy estimations and remains an important limitation of SNN implementations^[24]. This entails significant research in array-level implementations of SNNs using memristive crossbars and development of algorithms tailored to the switching physics of devices involved.
- DNNs trained with supervised learning and error backpropagation have demonstrated success in handling real world computations such as image recognition and speech recognition. These algorithms employ large matrix and vector multiplications, conventionally parallelized on GPUs. While memristive devices have shown promise for such parallel compute and store operations in an analog fashion via simple Kirchhoff's law, scalability and classification accuracies matching GPU capabilities remains a significant research challenge due to device infidelities like write noise and non-linearity. This calls for the optimization of pulsing schemes tailored to meet the device physics requirements and systematic investigation of device infidelities like conductance non-linearity during the initial stages of materials selection and device development. Moreover, ultra-low power memristive solutions offering a significant speed-up or power advantage over existing solutions needs further investigations.
- The design of CMOS peripheral circuitry to effectively address these dense arrays of memristive elements with the high degree of connectivity that many network architectures demand is not addressed in this dissertation and requires careful attention.

Though many problems remain to be solved, memristive solutions continue to be potentially attractive for highly parallel, distributed, data-centric processing, entailing further intensive and extensive materials, algorithmic and hardware engineering investigations.

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APPENDIX

Figure A.1 Standard memristor characteristics for MAPbBr₃, FAPbBr₃ and CsPbBr₃- based thin film devices [Device structure: Au/perovskite/ITO]. All devices demonstrated cyclability ~ 100 cycles on an average (top). The graphs at the bottom shows retention of the high (HRS) and low (LRS) resistance states measure over 1 hour after the initial testing cycle.

Figure A.2 Variation in the EPSCs of MAPbBr₃, FAPbBr₃ and CsPbBr₃-based devices fabricated in a single batch consisting of 32 devices.

Figure A.3 Photograph of the experimental setup showing the 4x4 array of halide perovskite synapses implemented as a reconfigurable and trainable memory, addressed via an Arduino controller. The digital and analog pins of the arduino microcontroller were directly connected to the terminals of the device and pulsed “write” and “read” schemes accessed the individual memory elements on demand.

Figure A.4 A 4x4 array of halide perovskite synapses was implemented as a reconfigurable and trainable memory unit with fault tolerance. The image of “N” was programmed into the array using an external microcontroller biasing (5 V, 10 seconds) individual pixels on demand with others in a floating-mode. With time, these synapses exhibited extinction of memory analogous to forgetting but could be retrained faster to reach the same conductance levels. This figure denotes the raw current values recorded from the individual devices represented in Figure 4.9A. The memory states “0” and “1” were defined based on a threshold of 250 nS or a current of 25 nA.

Figure A.5 Training of the neural network. Representative weight visualizations for different stages of training of one epoch with N training samples with N varying from 100 to 10000. The accuracy corresponding to the figures are also denoted. The testing was done on the same 1000 samples.