Surface potential shift in MoS₂ due to adsorption of H₂O

Ganatra, Rudren

2014

Ganatra, R. (2014). Surface potential shift in MoS₂ due to adsorption of H₂O. Master's thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/62212>

<https://doi.org/10.32657/10356/62212>

**NANYANG
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**Surface Potential Shift in MoS₂ Due to
Adsorption of H₂O**

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2014

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A thesis submitted to the Nanyang Technological University
in partial fulfillment of the requirement for the degree of
Master of Engineering

2014

Acknowledgements

I would like to express my gratitude and appreciation to the people without whom this work and my study at Nanyang Technological University would not have been possible.

First of all I would like to thank the University for supporting me academically, financially and in providing the research facilities which enabled me to grow both in knowledge and experience.

I am deeply grateful to my supervisor Prof. Zhang Qing for his strong support, patient guidance and calm understanding. He has always driven my motivation, given me the freedom and space to grow, and has always shown great faith in my abilities.

I would like to thank my colleagues for taking the time to help and understand various processes and equipment. I am especially thankful of Dr. Li Hong who taught me most of the skills I know.

I am also grateful to the laboratory staff, Muhd Fauzi Bin Abudullah and Hasman Bin Hassan for their kindly and dedicated efforts to help me set up the experimental equipment.

Last but not least, I would like to thank my family for their unconditional support no matter what the circumstances. Without them I would not be who I am today.

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Summary

In this thesis, the variation of work function or surface potential of MoS₂ due to adsorption of H₂O molecules under varying relative humidity conditions is studied in detail. MoS₂'s ultra-thin layered structure coupled with the presence of unsaturated d-orbitals from the transition metal molybdenum makes it an appealing candidate for designing gas sensors. In this work, the Kelvin probe force microscopy (KPFM) function of the atomic force microscope (AFM) was used to successfully map the surface potential of MoS₂ flakes of varying thicknesses as relative humidity levels are changed within a sealed AFM chamber. The effects of H₂O adsorption, desorption, doping and surface potential shift of MoS₂ have been studied in detail. After carrying out this study, a deeper understanding of the adsorption mechanism of H₂O and MoS₂'s surface potential response has been obtained.

The KPFM technique is used to obtain the surface work function or surface potential values of MoS₂ flakes with the variation of relative humidity levels to study charge-induced material doping due to H₂O adsorption on the surface of MoS₂. Through this technique, this study was able to quantitatively determine the surface potential response of MoS₂ to change in relative humidity levels between RH 10% and RH 70%. The shift in surface potential of was found to be very consistent across sample flakes with different thicknesses and surprisingly showed no noticeable hysteresis effect. Edges were found to possess a lower potential but also followed surface potential variation with humidity. The adsorption mechanism, lack of hysteresis and consistent material response are discussed.

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List of Abbreviations

MoS ₂	Molybdenum disulphide
AFM	Atomic force microscope
KPFM	Kelvin probe force microscopy
TMDC	Transition metal dichalcogenides
FWHM	Full with half maximum
PL	Photoluminescence
FET	Field effect transistor
SiO ₂	Silicon dioxide
IPA	Isopropyl alcohol
NMP	N-methyl pyrrolidone
DMF	Dimethylformamide
CVD	Chemical vapor deposition
LPCVD	Low pressure chemical vapor deposition
ITRS	International technology roadmap for semiconductors
DIBL	Drain induced barrier lowering
PMMA	Polymethyl methacrylate
STM	Scanning tunneling microscope
AM-AFM	Amplitude modulation atomic force microscope
FM-AFM	Frequency modulation atomic force microscope
EFM	Electrostatic force microscopy
MFM	Magnetic force microscopy
SKPM	Scanning Kelvin probe microscopy
CPD	Contact potential difference
RH	Relative humidity

Chapter 1 | Introduction

1.1 Motivation

Ever since the technique to obtain stable single-layer graphene^{1, 2} was reported, study of two-dimensional materials has gained a lot of interest and momentum. Modern advanced facilities have helped us to study atomically thick layered materials like graphene, transition metal dichalcogenides (TMDCs), topological insulators, etc. MoS₂ is one such two-dimensional material and belongs to the family of TMDCs. While MoS₂ has been under study for more than 5 decades in the fields of dry lubrication³⁻⁸, catalysis⁹⁻¹³, photovoltaics¹⁴⁻¹⁸ and batteries¹⁹⁻²⁵, it has only very recently attracted scientific attention as a semiconductor in nanoelectronics and optoelectronics. The presence of unsaturated d-orbitals of the transition metal molybdenum introduces many unique electronic properties. Its semiconducting properties allow MoS₂ to be incorporated not just in electronic devices but also optoelectronic devices. An in-depth and complete understanding of the electronic/optoelectronic properties of few-layer MoS₂ is thus strongly required.

1.2 Objectives

This work focuses on the work function change of few-layer MoS₂ with variation of relative humidity levels. This is the first attempted study of this kind. For this, we used atomic force microscopy (AFM) and Kelvin probe force microscopy (KPFM) methods to gain a clearer insight into Fermi level variations due to water adsorption on few-layer MoS₂ flakes. KPFM scans of few layer MoS₂ flakes under controlled variation of relative humidity were conducted to study the evolution of material work function and surface potential. Theoretical calculations on the interactions between few layer MoS₂ and adsorbed atoms or molecules have been conducted by others and few layer MoS₂ sensors have also been reported, but a clear understanding of how adsorbed molecular species affect the surface properties of the material is still lacking. This work shall endeavour to experimentally understand the interactions between few-layer MoS₂ and adsorbed H₂O molecules.

1.3 Major Contribution of the Thesis

The major contribution of this thesis derives from the successful demonstration of strong and consistent changes in the surface work function of few-layer MoS₂ with variation in relative humidity levels. Substantial lowering of the surface potential of few layer MoS₂ flakes with increasing relative humidity suggests p-type doping caused by adsorbed H₂O species. Adsorption mechanisms are discussed and the significance of edge sites is also highlighted.

1.4 Organization of the Thesis

This work begins with a comprehensive literature review, excerpted from a review paper written by myself titled “Few Layer MoS₂ – A Promising Layered Semiconductor” that has just been accepted to be published in ACS Nano. The review spans chapters 2 to 4. Chapter 2 covers the material’s crystal structure, band structure and carrier physics. Chapter 3 continues with methods to obtain MoS₂ samples in terms of exfoliation as well as growth techniques. Chapter 4 expounds on MoS₂-based electronic devices ending in the current work on MoS₂ sensors. Chapter 5 provides an overview of atomic force microscopy (AFM) and followed by the principles of Kelvin probe force microscopy (KPFM) which is used throughout the experimental work conducted. Chapter 6 covers the experimental setup, methodology and discussions on the surface potential shift under variation of humidity conditions, followed by conclusions in Chapter 7.

Chapter 2 | Material Structure and Physics

2.1 Crystal Structure

The crystal structure of Molybdenum Disulphide has been under study for about 50 years^{2, 26-43} it has only recently gained attention for electronic and optoelectronic devices.⁴³ MoS₂ has a layered structure similar to graphene, with the individual two-dimensional layers stacked upon each other to form the bulk crystal (see Fig 1). Each crystal layer is about 0.65nm thick and is coupled to neighbouring layers by weak van der Waals forces. Single- to few- layer crystal flakes can thus be obtained using the mechanical exfoliation method, which shall be addressed later on.^{2, 26, 27, 31, 38, 39, 43-45}

Each two-dimensional MoS₂ crystal layer consists of two planes of hexagonally-arranged sulphur atoms with a plane of hexagonally-arranged molybdenum atoms in between. The S-Mo-S atoms are covalently bonded in a trigonal-prismatic formation resulting in hexagonal honeycomb-like crystal structure. The hexagonal and octahedral crystal structures are the most commonly found crystal symmetry configurations for MoS₂. The former is semiconducting and the latter is metallic. The former was discovered much earlier than the latter.⁴⁴ In theory, the hexagonal structure is more stable than the octagonal structure.⁴⁶ The Mo-S bond length is around 2.4Å, the crystal lattice constant is around 3.1Å and the space between two adjacent layers is approximately 3.1Å.⁴⁵⁻⁵⁰

Figure 2.1 Crystal Structure of MoS₂ (a), Top view of monolayer hexagonal crystal structure of MoS₂. (b), Trigonal prismatic (2H) and octahedral (1T) unit cell structures. Reproduced with permission from (a) Macmillan Publishers Ltd: [Nature Nanotechnology](#), ref. 51, copyright © 2012 (b) ref. 52, copyright © 2011 American Chemical Society.

MoS₂ has been shown to possess very high mechanical strength and possesses a Young's modulus greater than that of steel.⁵³⁻⁵⁶ Monolayer of MoS₂ has marginally greater strength than the bulk crystal.⁵⁶ MoS₂ crystal layers can be deformed by up to 11% without fracture.^{53, 56} They can also be bent to a curvature of the radius of 0.75mm without losing their electronic properties⁵⁷. These properties make MoS₂ a promising material for flexible electronics. MoS₂ has piezoelectric properties and it can be utilized for sensitive mechanical transducers.⁵⁸ MoS₂ based nanomechanical

resonators can function in the HF and VHF bands and show a very high figure of merit of about 2×10^{10} Hz at room temperature.⁵⁹

Figure 2.2 The Raman and IR Active Phonons (a), Illustrations of the four Raman active phonon modes (E_{1g} , E_{2g}^1 , A_{1g} and E_{2g}^2) and one IR active phonon mode (E_{1u}) and their interlayer interactions. (b), Illustrations of the interlayer breathing and shear modes. (c), E_{2g}^1 and A_{1g} Raman peaks in few-layer flakes. (d, e), Evolution of low frequency spectra with increasing layer number of the interlayer breathing (B1 and B2) and shear (S1 and S2) modes using (d) the $\bar{z}(xx)z$ polarization configuration and (e) the $\bar{z}(xy)z$ polarization configuration. Reprinted with permission from (a, c) ref. 42, copyright © 2010 American Chemical Society (b, d, e) ref. 60, copyright © American Chemical Society 2013.

Bulk MoS₂ belongs to the D_{6h} crystal structure space group while monolayer MoS₂ belongs to the D_{3h} space group.^{46, 48, 60-62} D_{6h} possesses inversion symmetry, while D_{3h} lacks inversion symmetry. Optical second harmonic microscopy is a very useful tool in characterizing mono- to tri-layer MoS₂ and determining crystal orientation, crystal domain size and layer stacking.^{63, 64}

Optical second-harmonic studies show retention of the bulk lattice symmetry in few-layer MoS₂. Few-layer MoS₂ with an even number of layers retains inversion symmetry but odd-layered MoS₂ does not.⁶⁵ This has been confirmed by strong enhancement of optical second harmonic intensity in the odd-layered samples. MoS₂ has 4 Raman-active modes (E_{1g}, E_{2g}¹, A_{1g} and E_{2g}²) and 2 IR-active modes (A_{2u} and E_{1u}) (see Fig 2a).^{48, 60-62} Raman spectroscopy is very popularly used to study crystal quality as well as accurately identify the layer number of MoS₂ flakes. The E_{2g}¹ is an in-plane mode resulting from the opposite vibration of two S atoms with respect to the Mo in between them while the A_{1g} mode is attributed to the out-of-plane vibration of only S atoms in opposite directions. From mono-layer to bulk, the E_{2g}¹ mode undergoes a red-shift while the A_{1g} mode undergoes a blue shift (see Fig 2c).^{42, 61, 66} The E_{2g}¹ mode is believed to be affected by the long range inter-layer Coulombic interaction between molybdenum atoms with increasing layer number due to the increase in the dielectric tensor. The A_{1g} mode on the other hand is less affected by inter-layer interactions.⁶⁷ The A_{1g} mode is very sensitive to adsorbates on the MoS₂ surface⁶⁸ and electron doping⁶⁹. Due to stronger electron-phonon-coupling of the A_{1g} mode, it shows a red shift and an increase in the peak width with increasing doping level. The frequency or frequency-shift difference between these two modes on the Raman spectrum can be used to determine the layer number of few-layer flakes.⁴²

MoS₂ belongs to a unique class of layered materials^{40, 46, 49} known as transition metal dichalcogenides (TMDCs) whose bandgaps vary with the number of layers. Bulk MoS₂ has an indirect bandgap of 1.29eV (see Figs 3a and 3b).^{40, 43, 46} The valence band maximum is located at the Γ point while the conduction band minimum is located almost halfway along Γ -K direction, which constitutes the indirect bandgap transition.^{43, 76, 77} With the layer number decreasing, the lowest band in the conduction band moves upwards, increasing the overall bandgap. As the conduction band states at the K point are mainly due to the d-orbitals of the molybdenum atoms and are relatively unaffected by inter-layer interactions, the direct bandgap at the K point only increases by about 0.05~0.1eV (See Fig 3b).^{49, 77} The states near the Γ point on the conduction band are due to hybridization between p_z-orbitals of sulphur atoms and the d-orbitals of molybdenum atoms and are affected by inter-layer interactions. Thus the bands at Γ are more affected by a decrease in layer number.^{49, 75} In the monolayer the indirect transition gap is larger than the direct transition gap, and the smallest bandgap is thus the direct bandgap at K point of about 1.9eV. This transition from an indirect to a direct bandgap semiconductor is very interesting and reflects inter-layer interaction, quantum confinement and long-range Coulomb effects.^{40, 43, 46, 75-78} Substrate interaction is also predicted to have a pronounced effect on the properties of few-layer MoS₂.⁷⁶ Due to the indirect to direct bandgap transition observed in few-layer MoS₂ along with further band structure variations as a function of layer number, band calculations and material physics^{76, 77, 79-87} are now receiving more attention as this phenomenon is quite unique from previously known materials and provides a whole new host of physics and applications.

2.3 Carrier Physics

The effective mass for electrons at the K point is calculated to be $0.48m_e$ ⁸⁸, which is much higher than that in graphene ($0.012m_e$)⁸⁹. Carrier mobility and the carrier scattering processes in MoS₂ are dominated by interactions with acoustic phonons at lower temperatures (<100K) and optical phonons at higher temperatures.^{27, 88} Under the strong effect of optical phonons on the mobility of electrons in single layer MoS₂, first principle calculations predict a mobility drop from $\sim 2450 \text{ cm}^2/\text{Vs}$ in the acoustic phonon dominated low temperature regime to $\sim 400 \text{ cm}^2/\text{Vs}$ at room temperature in the optical phonon dominated higher temperature regime.⁸⁸ Strong electron-phonon interactions have also been suggested to be the reason for superconductivity in MoS₂.⁹⁰⁻⁹² A recent study of the temperature dependence of the mobility shows two distinct regimes which border at 200K.⁹³ Quenching of the less dominating homopolar mode by the use of high- κ dielectric oxides could increase the carrier mobility.^{88, 93, 94} It is noted that the experimentally determined mobilities are significantly smaller than theoretically predicted values. The difference may be due to charge impurities. MoS₂ also displays the presence of graphene-like ripples which may have a negative effect on carrier mobility.⁹⁵ A vertical electric field exerted to few-layer MoS₂ is found to be an efficient way of bandgap engineering.^{47, 82} The bandgap of bilayer MoS₂ could be tuned to zero with an electric field of about $1.0 - 1.5 \text{ V/\AA}$.⁹⁶

Under optical pumping, a carrier lifetime of $\sim 100 \pm 10 \text{ ps}$, a carrier diffusion coefficient of $20 \pm 10 \text{ cm}^2/\text{s}$ and a substantially higher mobility of $800 \text{ cm}^2/\text{Vs}$ were achieved.⁹⁷ The higher mobility was attributed to the ambipolar nature of carrier diffusion due to optical injection where the electron-hole pairs move as an almost charge-neutral pair and are less susceptible to Coulomb scattering which could be the

origin of the strong degradation of carrier mobilities seen in MoS₂. Employment of high- κ dielectrics may provide charge screening by decreasing Coulomb scattering,^{88, 93, 94, 98} and allow for greater carrier mobilities in MoS₂ devices. In addition, high- κ dielectrics are also predicted to decrease the monolayer bandgap and exciton binding energy closer to those seen in bulk MoS₂.⁸³ Most MoS₂ field effect transistors (FETs) are predominantly n-type^{94, 99-109}, while some are p-type^{110, 111} or ambipolar^{57, 112-114}. A recent ab-initio study¹¹⁵ suggested that substrates may play strong roles in the doping MoS₂ due to the presence of surface states, impurities and defects that may be present on the substrate surface. Such a doping behaviour cannot be attributed to the defects in MoS₂ itself as such defects could create deep states which do not have strong doping effects. The substrate induced doping may also be an alternative way of doping MoS₂.

2.4 Band Structure Engineering

Band structure engineering methods are desired in order to tailor the electronic properties of few-layer MoS₂ for specific applications. The application of strain is a very straightforward method of band engineering in which the crystal structure dimensions are altered through the application of force across specific axes. Theoretical work¹¹⁶ predicts a bandgap reduction under uniaxial compressive strain across the c-axis of the crystal structure of MoS₂, with both the conduction band maximum as well as valence band minimum moving towards each other. Biaxial tensile strain on the other hand causes the conduction band minimum at the point of indirect band transition to move upwards while the conduction band at the K point moves downwards with no shift seen in the valence band at the Γ point (see Fig 4b).

Band structure redesign under tensile strain is predicted to lower the electron effective mass and consequently improve electron mobility.¹¹⁷ Applied strain could also cause band degeneracy which can be used for better spin-related properties and research in MoS₂.^{116, 118, 119} Practical strain experiments^{118, 120-122} have shown results consistent with theoretical predictions, i.e., up to ~300meV change in bandgap per 1% applied strain¹²⁰. A strain was found to cause a split in the E_{2g}¹ peak of the Raman spectrum coupled with a shift in the PL and absorbance spectrum (see Fig 4a, 4c and 4d) congruent with bandgap change along with a large increase in PL intensity.^{118, 123} The impact of a strain on MoS₂ FET devices has also been theoretically modelled for and predicted substantial improvement in the device performance.¹¹⁹

Figure 2.4 Variation of Band Structure Properties With Strain (a, c, d), Shift of absorbance and photoluminescence peaks with application of uniaxial tensile strain.¹²¹ (b), evolution of the band structure of monolayer MoS₂ under various values of biaxial strain and consequent lattice constants as measured using different calculation models (DFT-PBE, G0W0, SCGW0).¹¹⁷ Reprinted with permission from (a, c, d) ref. 121,

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A material level method for band engineering is to grow alloys of MoS₂ and other TMDCs. As TMDCs have identical crystal structures with comparable bond lengths, it is theoretically feasible¹²⁴ to grow stable and miscible alloys of TMDCs including MoS₂ allowing precise bandgap engineering over a much wider range and enabling the tuning of electronic and optical properties of the material. Mo_{1-x}W_xS₂ alloys were recently grown and studied.¹²⁵ The photoluminescence and Raman spectra showed the characteristics from both parent materials, and the bandgap could be quite accurately tuned suggesting a bowing effect like most other semiconductor alloys. Although much study is still required in such alloyed materials, this method shows promise in engineering tailored material properties.

Figure 2.5 Optical Characterization (a), Photoluminescence spectra for monolayer and bilayer MoS₂. (b), Normalized photoluminescence spectra of MoS₂ with increasing number of layers, showing evolution of A and B excitons as well as the I-peak of indirect transition. (c), Evolution of bandgap with layer number of MoS₂.

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2.5 Optical Physics

The direct optical bandgap in single-layer MoS₂ opens up a whole new host of possibilities in optical properties and optoelectronic devices^{51, 83, 123, 126-132}. Photoluminescence studies show a very high quantum yield for monolayer MoS₂ and also affirm the optical transition bandgap at around 1.9eV (see Fig 5a).^{43, 52, 75} Photoluminescence tests along with Raman tests are frequently used in MoS₂ characterization and determination of the quality of MoS₂ growth, especially for monolayer-growth quality and crystallinity^{52, 75, 100, 101, 104, 109, 133-136}. Although the direct bandgap in MoS₂ does exist even in the bulk structure, photoluminescence in the bulk is non-existent due to excitonic absorption. But in the monolayer regime where the direct band gap is dominant, direct band radiative recombination becomes the principle method for excitonic recombination.⁷⁵ Direct as well as indirect exciton transition in mono-, bi- and tri-layer MoS₂ is found to be entirely a product of in-plane excitons¹²⁹, and may help in understanding exciton-phonon interactions. Photoluminescence quantum yields for monolayer MoS₂ were found to be about 3 orders greater than multi-layer MoS₂ due to radiative recombination across the direct band gap. A greater difference of 4 orders was obtained when monolayer MoS₂ was suspended⁴³. Substrate contact and interface quality also has a substantial effect on photoluminescence tests and by extension may have effects on material performance.¹³⁷ Excess charge transfer through adsorbed liquids or gases has been

shown to suppress electrostatic screening causing up to two orders of increase in the quantum yield of light emission from MoS₂.¹³⁸ Control of gas pressure provides accurate and reversible control of molecular adsorption on MoS₂ surface at room temperature, thus controlling the amount of charge transfer and the resulting electrostatic screening. Few-layer MoS₂ is predicted to show a photothermoelectric effect with a very widely tuneable Seebeck coefficient.¹³⁹

The photoluminescence spectra for MoS₂ show two exciton peaks (see Fig 5b) called exciton A (~1.92eV) and B (~2.08eV) at the K point^{43, 75} and are predicted to exist due to spin-orbit band splitting (145 meV⁴⁹) in the valence band. This band splitting is the largest at the K point of the entire upper valence band, thus making two possible transitions available for excitons to the doubly degenerate conduction band.^{49, 75, 140} These two excitons have high binding energies due to the low dielectric screening in monolayer MoS₂.¹⁴⁰ The introduction of excess electrons with the application of gate voltage shows a split in the absorption and photoluminescence spectra for exciton A (see Fig 6), found to be due to the existence of negative trions with high binding energies¹³² which exist even at room temperatures. A large control was shown over the trion emission helicity by control of the polarization of incident light. The ability to affect trion movement through the application of electric fields could be of great use in optoelectronics towards better control of such devices. The I-peak (1.59eV) shown in the PL spectrum could result from the indirect gap luminescence⁴³ and showed a blue-shift with decreasing layer number consistent with the associated widening of the indirect bandgap.

Bandgap engineering through applied strain is very useful for tailoring the optical properties of materials as well. As mentioned earlier, MoS₂ could be elastically

deformed up to 11% without breaking the material.^{53, 56} A study by Feng et al.¹⁴¹ took strain engineering a step further in proposing the use of strain on MoS₂ to create a broadband optical funnel. The concept was to continuously vary strain across a sheet of monolayer MoS₂ causing a continuous variation of the optical bandgap, allowing not only the capture of photons across a wide range of the solar spectrum but also

Figure 2.6 Trion Behaviour With Gate-Induced Doping (a), Absorbance and photoluminescence spectra of A excitons and A⁻ trions with variation of indicated gate voltages. (b), Threshold energies of the trions ω_{A^-} (black dots) and neutral exciton ω_A (red dots) plotted against gate voltage (above) and Fermi energy (below). (c), Plot of difference in energies between trions and excitons ($\omega_A - \omega_{A^-}$) as a function of Fermi energy. Reproduced with permission from Macmillan Publishers Ltd: [Nature Materials](#), ref. 132, copyright © 2012.

Figure 2.7 Strain-Induced Optical Funnel (a, b), Illustrations of the possible physical set-ups of a varying strain system. **(c),** Spectra of the band transition peaks with varying strain. **(d),** Variation of band structure with applied strain. Reproduced with permission from Macmillan Publishers Ltd: [Nature Photonics](#), ref. 141, copyright © 2012.

guidance of the resulting generated excitons towards contacts. An implementation of such a structure could be a monolayer of MoS_2 suspended and anchored to form one contact over a circular hole while the centre of the sheet over the hole is stretched downwards and anchored at a point to another contact, literally taking the shape of a

funnel (see Fig 7). The smoothly varied strain across the monolayer sheet from the edge of the hole to the stretched centre of the monolayer to the contact below could result in a smooth narrowing of bandgap. This is a very appealing concept and requires extensive practical experimentation to realize. A recent strain-engineered experiment¹²² did show signs of a funnelling effect of excitons in MoS₂.

Figure 2.8 Valley Polarization (a), Illustration of the K (or K+, shown in red) and – K (or K_, shown in teal) valleys in the bottom of conduction band (purple) and top of the valence band (blue). η is the k-resolved degree of optical polarization between the top of the valence bands and the bottom of the conduction bands. (b), Data points of observed out-of-plane right (black) or left (red) polarized luminescence from monolayer MoS₂ when incident with correspondingly polarized light, where $P_{\sigma+}$ is the degree of right-circular polarization and $P_{\sigma-}$ is the degree of left-circular polarization. Reproduced with permission from Macmillan Publishers Ltd: (a) [Nature Communications](#), ref. 142, copyright © 2012 (b) [Nature Nanotechnology](#), ref. 51, copyright © 2012.

Chapter 3 | Fabrication and Growth

3.1 Exfoliation

Although the existence of layered bulk crystalline materials has been known for many years, scientists had believed that the single-layer crystalline forms of such materials would be too unstable for use or study.² Novoselov et al.² were among the first to use mechanical exfoliation or the “Scotch Tape method” to obtain few- or even single-layer graphite, or graphene. Soon after that, other atomic thick 2D materials have been fabricated from layered materials like MoS₂, boron nitride and many more. In the mechanical exfoliation process a small high quality natural bulk MoS₂ crystal is adhered to a stretch of adhesive tape, repeatedly exfoliated followed by being adhered on a substrate. This causes ultra-thin material layers to be left on the substrate.²

To observe the monolayer or few-layer MoS₂ flakes on the substrate, a specific thick dielectric layer coated substrate is needed as the exfoliated monolayer or few-layer MoS₂ must have an excellent optical contrast to be easily identified under an optical microscope.² Silicon oxide is the most commonly used substrate. The ideal silicon oxide thickness for the optical identification of single- to few-layers of MoS₂ has been studied by several groups (see Fig 9a).¹⁴³⁻¹⁴⁶ 270-300 micron thick SiO₂ has been most commonly used for the purpose of direct observation.^{93, 94, 106, 113, 147-151}

Figure 3.1 Exfoliation of MoS₂ (a) optical and (b) AFM height image of multi-layer sections of an MoS₂ flake on a 285nm silicon oxide substrate. (c), height profile of MoS₂ flake measured along the dotted line in (b). (d) Chemically exfoliated MoS₂ flakes, roughly segregated according to flake size at different RPM through centrifugation. (e), Illustration of controlled lithiation and subsequent exfoliation using an electrochemical set-up. Reproduced with permission from (a, b, c) ref. 66, copyright © 2012 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim (d) ref. 152, copyright © 2012 American Chemical Society (e) ref. 153, copyright © 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

MoS₂ flakes obtained through mechanical exfoliation are usually preferred for research as they possess perfect crystalline structure and pristine quality. However, the yield of this process is extremely low. Most few-layer flakes obtained using this method range from a few microns to few tens of microns in size. A modified version

of mechanical exfoliation, using wafer anodic bonding¹⁵⁴, was reported to have a higher yield and better control over the number of layers. By placing a bulk crystalline MoS₂ on a piece Pyrex glass, contacting an anode to the MoS₂ crystal and a cathode to the back surface of the Pyrex glass, a voltage (200 ~1500V) applied to the anode and cathode at 130~200°C facilitated anodic bonding. Lastly, an adhesive tape was used to mechanically peel away the bonded crystal, leaving very thin flakes on the glass substrate.

Another class of exfoliation used to separate crystalline MoS₂ layers is so called chemical exfoliation, which has been known much earlier than mechanical exfoliation.^{32, 155} Chemical exfoliation has recently gained huge interest due to the new physics and applications of layered materials. There are two basic approaches: ion-intercalation and solvent-based exfoliation.

An ion-intercalation method was first used in 1986 by Joensen et al.³², also referred to as the Morrison method. The ion-intercalation method uses the concept of ion insertion in the gaps between the MoS₂ layers, widening the layer gaps. As lithium ions are very small, n-butyl lithium in hexane is a commonly used solution as a source of lithium ions. After Li ion intercalation, water is introduced and it vigorously reacts with the intercalated lithium ions to form hydrogen gas between the MoS₂ layers. The released hydrogen gas forces the MoS₂ layers apart, resulting in mostly single-layer sheets in the suspension. Methanol, ethanol, isopropanol or rapid heating in vacuum at around 600°C can also be used to release MoS₂ layers instead of water³². Some difficulties with this process are the relatively high temperatures required (100°C) and lengthy reaction time (around 3 days). There is also little control over the extent of intercalation. A low level of intercalation results in a low yield of single-layer sheets

while excess intercalation causes decomposition of MoS₂ into metal nanoparticles along with the generation of Li₂S. Ion intercalation also causes MoS₂'s crystalline structure to convert from 2H (hexagonal, semiconducting) to 1T-MoS₂ (octahedral, metallic)^{32, 52, 153}. This is unwanted from an electronic point of view as the semiconducting properties of MoS₂ are preferred for electronic use.

Zeng et al.'s¹⁵³ method further improved the chemical exfoliation process through an electrochemical process. Instead of using n-butyl lithium in hexane, they used MoS₂ as the cathode and a lithium foil as an anode; with the whole set-up placed in a galvanic cell (see Fig 9e). A measured galvanic discharge controlled the extent of lithiation and provided a better control over the extent of intercalation. This method was conducted at room temperature and required only a few hours instead of days. It yielded about 92% of single-layer MoS₂ sheets. A study conducted by Eda et al.⁵² addressed the problem of the crystalline structure transformation due to ion-intercalation in greater detail. Their study showed that 1T-MoS₂ almost completely (95%) reverted back to 2H-MoS₂ upon annealing at 300°C.

Solvent-based exfoliation method is relatively new. It was initially proposed by Coleman et al. in 2011 and is often referred to as the Coleman method.¹⁵⁶ They began with introducing bulk MoS₂ crystals into organic solvents like N-methyl-pyrrolidone (NMP) and isopropanol (IPA). The bulk crystals were found to separate into single- and few-layer sheets of MoS₂. The organic solvents were used as they decrease the energy required for layer separation and exfoliation. This method is sometimes also preferred as use of the organic solvents preserves the 2H-MoS₂ (hexagonal) crystal structure, the semiconducting structure of MoS₂, unlike ion-intercalation which tends to render metallic MoS₂ with 1T-MoS₂ (octahedral) crystal structure. The Coleman

method was further improved through using an aqueous surfactant followed by high power sonification which yielded higher suspension concentration in the solvent.¹⁵⁷ Despite the advantages of this method, there were still a few drawbacks like the low yield of single-layer sheets and low MoS₂ flake concentration in the solution (0.25 to 0.3 mg/mL).^{52, 156}

An improvement to the solvent-based exfoliation was proposed by Yao et al.¹⁵⁸ who used a sodium-dodecyl sulphate water solution as a surfactant in combination with ball milling of the bulk MoS₂ flakes before introducing into the solution. Their process had a much higher yield of mono- and bi-layer sheets, and a higher material concentration of about 0.8 ~ 4 mg/mL. A further in-depth study of the effects and duration of sonification on obtained sheet size was conducted by O'Neill et al.¹⁵², resulting in better control of flake size and an even higher reported flake concentration of about 40mg/mL.

Although chemical exfoliation has much higher yields than mechanical exfoliation, the sonification process does cause scission and tearing of the 2D material sheets, reducing their dimensions down to a few thousand nanometres or even smaller^{32, 52, 152, 153, 156, 158-160}. Small sized MoS₂ flakes are not easily utilized for electronic devices that are directly built on them. However, they can be assembled into MoS₂ thin films, used as colloidal suspensions and even for flexible devices and sensors.^{159, 160}

A few unconventional methods have been reported which can loosely be categorized as exfoliation methods. Both laser thinning¹⁶¹ and thermal anneal thinning¹⁶² use heat directly or indirectly to sublime and thin MoS₂ flakes down to few layers or a single layer. In laser thinning, a laser from a Raman system was systematically scanned over a thick flake of MoS₂ at a higher power.¹⁶¹ In thermal anneal thinning, MoS₂ flakes on

a substrate were annealed at 650°C in an inert argon environment causing sublimation of roughly one layer of MoS₂ per hour.¹⁶² Both these methods caused higher surface roughness due to defect generation, incomplete sublimation of layers or creation of pinholes in the top layers of the final flakes. Thermal anneal thinning also showed a decrease in flake area along with layer number, indicating sublimation from the flake edges as well. Layer thinning using argon plasma¹⁶³ demonstrated lower surface roughness than the formerly mentioned two methods and could be controlled through the time of exposure to the plasma. This method can also be used with lithographic techniques to pattern MoS₂ heterostructures.

3.2 Material Growth

Despite the unique and interesting properties of few-layer MoS₂ flakes, their full potential cannot be realized until the material is possibly obtained on a wafer-scale. Exfoliation techniques have flake size and yield limitations and they cannot be adopted for large-scale applications like integrated circuit fabrication or other advanced uses. The methods for growing high quality large area few-layer MoS₂ crystalline flakes are in high demand towards large-scale implementation of such a unique material.

Till now, thin MoS₂ could be primarily grown from one of three precursors: ammonium thiomolybdate [(NH₄)₂MoS₄] solution^{101, 135}, a thin deposition of elemental molybdenum^{104, 110} or molybdenum tri-oxide [MoO₃] powder^{100, 107-109, 133,}

¹³⁴.

The first precursor, ammonium thiomolybdate, was usually dissolved in dimethylformamide (DMF) and used in solution form.^{101, 135} This solution was then either coated on a substrate as a thin film or used in vapour form by passing through a bubbler (see Fig 10a). Liu et al.¹⁰¹ dipped their substrate in an ammonium thiomolybdate solution and then pulled the substrate out vertically at a constant low rate in order to obtain a uniform thin film. After the substrate was annealed in a quartz tube with flowing Ar/H₂ at 500°C and a low pressure of 1 Torr, a second anneal at 1000°C at a higher pressure of 500 Torr was followed. During the annealing processes, ammonium thiomolybdate was decomposed into MoS₂, S, H₂S and NH₃ gases; and MoS₂ was deposited onto the substrate. Sulphur in powder form could also be added to the quartz tube during the second anneal to protect against oxidation of the as-forming film. The final film appeared to be very uniform and consisted of mostly 3 layers with a few areas having 2 layers. Although the crystal grain sizes were larger than 160nm, they were still significantly smaller than those found in exfoliated sheets which are of the order of a few microns. Annealing in a sulphur environment yielded a much higher crystallinity of MoS₂ layers. In addition, MoS₂ grown on sapphire substrates showed better quality and larger grains than those grown on SiO₂. FETs fabricated on the grown MoS₂ typically had n-type behaviour with an on/off ratio of about $\sim 10^5$ and a field-effect mobility of 6 cm²/Vs.

Shi et al.¹³⁵ took a different approach in terms of substrate choice and used single-layer CVD-Graphene on Cu foil in order to facilitate van der Waals epitaxy of MoS₂. Graphene was chosen as the growth substrate as its surface is free of dangling bonds and could prove a better growth substrate. MoS₂ was then grown on the substrate using low pressure CVD at around 400°C. The precursor was bubbled with argon gas which

was then introduced into the LPCVD chamber to be adsorbed onto the substrate surface. MoS₂ then nucleated at wrinkles on the graphene surface and began to form hexagonal islands of a few hundred nanometres to several micrometres. Increasing the precursor dose was found to result in the islands expanding and coalescing to form complete sheets, with further islands growing on the sheets. It was found that graphene did influence the growth process. In sharp contrast, bare Cu did not show hexagonal MoS₂ island growth. The thickness of the final growth was around 2nm to 5nm and depended on the precursor dose. Another similar work by Liu et al.¹⁰¹ reported on the crystal grain size of about 160nm laterally.

Figure 3.2 Growth Techniques MoS₂ growth using (a) ammonium thiomolybdate, (b) elemental molybdenum and (c) molybdenum trioxide as the precursors. Reproduced with permission from (a) ref. 101, copyright © 2012 American Chemical Society (b) ref. 104, copyright © 2013, AIP Publishing LLC (c) [ref. 109](#), copyright © The Royal Society of Chemistry.

The second method precursor consisted of a very thin layer of molybdenum which was evaporated onto a substrate, followed by sulphurization at a high temperature under inert conditions (see Fig 10b).^{104, 110} It was found that a higher process temperature resulted in higher quality of grown crystalline MoS₂ layers which seemed to cover the entire substrate.^{104, 110} Zhan et al.¹¹⁰ used lower temperatures of up to 750°C to grow MoS₂ on SiO₂ substrate. The grain sizes were found to be 10 ~ 30 nm and the devices fabricated with this grown MoS₂ displayed p-type behaviour with field effect mobilities between 0.004 to 0.04 cm²/Vs. Laskar et al.¹⁰⁴ on the other hand grew MoS₂ on a crystalline sapphire substrate at up to 1000°C. Their devices based on this MoS₂ showed n-type behaviour with significantly higher mobilities of 10 to 14 cm²/Vs. In addition, vertically aligned edge terminated MoS₂ sheets was reported.¹⁶⁴ A ~5nm thick Mo layer was evaporated on a different substrates. The substrate was kept at the centre of a quartz tube furnace having a temperature of 550°C. Sulphur was placed at an upstream location in the quartz tube, heated to ~220°C, with flowing argon gas at a pressure of 100m Torr and a flow rate of 100 sccm. Argon flow is continued during the natural cooling of the sample to facilitate vertical growth. The vertically aligned edge terminated MoS₂ sheets was found to be unique and they could be used for catalyst and sensing purposes due to the active edges of the MoS₂ sheets being exposed.

The third choice of precursor, MoO₃ (molybdenum tri-oxide) has been the most popular for MoS₂ growth.^{100, 107-109, 133, 134} All the reports reviewed here have used MoO₃ along with sulphur to grow crystalline MoS₂ layers on a substrate in a quartz tube furnace (see Fig 10c). Balendhran et al.¹³³ were among the first to use this technique. They annealed their substrate in the presence of powdered MoO₃ kept in a

crucible and found that the highest quality samples were obtained from the annealing at 830°C for 180 min, although it was not known if the substrate was uniformly coated with MoS₂ layers. Lee et al.¹⁰⁷ next reported using PTAS (perylene-3,4,9,10-tetracarboxylic acid tetrapotassium salt), PTCDA (perylene-3,4,9,10-tetracarboxylic dianhydride) and rGO (reduced graphene oxide) as seed crystals for MoS₂ growth. Aqueous solutions of PTAS, PTCDA or rGO were spin coated upon SiO₂ substrates and annealed in N₂ environment at 650°C. Star shaped MoS₂ crystals were found to grow around the seed crystals which coalesced to form mono-layer to few-layer areas. The rGO-seeded growth was the most uniform with the crystal domain sizes of around 160nm. FET devices based on the as-prepared MoS₂ flakes were n-type with an on/off ratio of $\sim 10^4$ and a field-effect mobility of 0.02cm²/Vs. Lin et al.¹⁰⁹ employed a two-step process with the first anneal at 500°C in a reducing environment of argon and hydrogen, followed by a second anneal at 1000°C in a sulphur environment. The two-step process was preferred for higher electron mobility of the grown MoS₂. The few-layer MoS₂ film obtained uniformly covered the entire sapphire substrate with a grain size of 160nm, yielding n-type MoS₂ FET devices with an on/off ratio of $\sim 10^5$ and a field-effect mobility of 0.8cm²/Vs. Mann et al.¹⁰⁰ used a single anneal process at 600°C in nitrogen atmosphere, but turned off the heating 3 min after the sulphur melted. Although the resultant films did not cover the whole substrate, there were long strips of deposited films that seemed to follow the direction of nitrogen gas flow over the substrate. The films obtained were hundreds of microns long with mono- to bi-layer areas and had relatively larger grain sizes of 3-5 micron. Fabricated FET devices were n-type with a field-effect mobility of 0.26cm²/Vs. Ji et al.¹³⁴ grew few-layer MoS₂ on a mica substrate which has a very small lattice mismatch with MoS₂ ($\sim 2.7\%$)

and could result in epitaxial growth of MoS₂. Compressively strained single-layer films were found to be deposited at 700°C which covered most of the substrate.

Apart from these three commonly used precursors, some other precursors have been used as well. Wu et al.¹³⁶ used powdered MoS₂ the precursor which was heated at 900°C and transported using flowing Ar to the substrate at 650°C. The grown MoS₂ flakes were triangular in shape up to 25 micron in size with high crystallinity. It was found that higher density was easily grown on sapphire substrates as compared to silicon oxide substrates. Yu et al.¹⁶⁵ used MoCl₅ and elemental sulphur as the precursors, depositing uniform and high quality monolayer and bilayer MoS₂ on different substrates with grain sizes ranging from tens to hundreds of nanometres at above 800°C. The layer number of the grown MoS₂ flakes can be controlled accurately by control of the amount of MoCl₅ used and the growth pressure.

Almost all studies report on the initial growing crystals having a triangular shape. The grains grow to join neighbouring MoS₂ crystals at the boundaries and thus form complete films. The grain sizes of grown MoS₂ seem to be much smaller than those obtained using exfoliation techniques. MoS₂ grown on sapphire has consistently higher crystallinity and field-effect mobility than when grown on other substrates like SiO₂. Najmaei et al.¹⁰⁸ recently attempted to provide an explanation of a possible growth model for MoS₂. In this study, MoO₃ nanoribbons along with sulphur were heated to 850°C in a nitrogen environment. Sulphur concentration and chamber pressure were found to play vital roles in the formation of continuous crystalline MoS₂ films. They suggest two possible growth mechanisms: triangular grains either stop growing once their boundaries meet neighbouring grain edges, or a new crystal is nucleated above the current film at the grain boundaries. This boundary-nucleated growth may lead to a

completely new independent crystal above the currently formed layer or it may be an overlapping extension of a grain of the same layer over an adjacent grain.

In this sense, it becomes important to consider the possible defects in CVD grown MoS₂, their effects on the crystal quality and electrical properties. Well acceptable knowledge of defects could help understand the possible reasons for CVD-grown MoS₂ being inferior to exfoliated MoS₂ and possibly shed some light on where new improvements in growth techniques should be focused. A study by Zhou et al.¹⁶⁶ theoretically considered possible defects in CVD-grown MoS₂ depending on the growth conditions. Mo-rich or S-rich growth conditions made the respective defects more energetically favourable, for example Mo-atom replacement by S-atoms in the crystal lattice is more favourable in a sulphur rich condition. Single sulphur vacancies could have the lowest formation energy and most commonly be expected. Single or columnar sulphur vacancies may create unoccupied energy levels about 0.6eV below the conduction band minimum, which are expected to act as compensation centres in n-type MoS₂. Filling up these vacancies is very likely to improve the material conductivity, being consistent with the higher electrical performance seen in samples annealed in sulphur-rich conditions. Vacancies are also predicted to increase the material sensitivity of MoS₂ based gas sensors. Electron irradiation could be used to generate such vacancies. The possibility of filling vacancies with atoms of other elements to facilitate doping is also an interesting prospect. The grain boundary defects were also theoretically studied.^{166, 167} Some common grain boundaries behave like metallic wires and tend to disrupt electrical pathways, negatively affecting field-effect mobilities of CVD-MoS₂ flakes.^{50, 167} MoS₂ edges are rich in unsaturated bonds which can be useful for gas and chemical sensors. MoS₂ grown in Mo-rich growth

conditions are predicted to have Mo-terminated states showing a ferromagnetic ground state.¹⁶⁸

3.3 Doping

Fine-tuning of a material's electronic properties can be achieved through successful doping. As MoS₂ is a quite new material for electronic applications, several theoretical studies¹⁶⁹⁻¹⁷² have provided possible doping strategies and doping species. Two main categories of doping were considered for few-layer MoS₂: substitutional doping and surface adsorption doping. Substitution of either S atoms or Mo atoms by commonly used species creates deep states in the conduction or valence bands and may not play a role of doping of the material in any way. Nb, V, Ta and Re could be the only species which create shallow energy levels in MoS₂.^{169, 170, 172} Nb, V and Ta are predicted to be acceptors, while Re as a donor. S atom substitution could occur when dopant atoms fill up S atom vacancies. However, the doping may not be ineffective due to the generation of deep states.^{170, 173} In contrast, surface adsorption doping has high potential as it shows lower energy requirement.¹⁷⁰ Alkali metals have predicted strong donor doping characteristics if adsorbed dopants would be used.^{170, 174} Potassium has already been successfully used as a surface dopant to degenerately dope few-layer MoS₂.¹⁷⁵ Ionic liquids were predicted¹⁷⁰ as well as experimentally confirmed to donate or accept electrons to/from MoS₂ efficiently as well.^{57, 112, 114}

Chapter 4 | Electronic Devices

4.1 FET Variants and Circuits

As compared to graphene which is a semi-metal with a zero bandgap, MoS₂ is a semiconductor having a much wider indirect (1.29eV^{40, 46, 133}) as well as direct (~1.9eV^{40, 46, 75, 133}) bandgap in the bulk and monolayer regimes respectively. The presence of an appreciable bandgap makes MoS₂ a viable candidate for next generation electronic devices. The direct large direct bandgap in monolayer MoS₂ also opens up a whole new scope in optoelectronic devices.

Simulations and theoretical studies predict MoS₂ devices to have good electron mobilities of ~200 to ~400 cm²/Vs,^{88, 176, 177} very high on/off ratios of >10¹⁰¹⁷⁶ and large transconductance of 4.4 ms/μm¹⁷⁶. MoS₂ devices showed very high current carrying capabilities of about 5 x 10⁷ A/cm²¹⁷⁸ and small subthreshold swing of about 70 mV/dec¹⁷⁷. Most MoS₂ FETs have shown n-type behaviour. A comparison of silicon devices with MoS₂ devices in line with the ITRS guidelines for low operating power technologies suggests the numerous advantages in favour of MoS₂ devices in terms of higher on/off ratios, much lower power consumption and current leakage and good switching delay.¹⁷⁷ Due to its 2D structure MoS₂ is much more resistant to short channel effects as compared to silicon showing excellent Drain Induced Barrier Lowering (DIBL) of about 10 mV/V¹⁷⁶, making it theoretically possible to drive down channel length in MoS₂ FETs to sub-10 nm dimensions while having respectable on/off

ratios and low current leakage^{147, 177}. Conductance of MoS₂ devices scale with their channel width and with a shift in the threshold voltage from negative to positive signifying a transition from the depletion mode to enhancement mode by varying the channel width.¹⁷⁹ Significant improvement is still required in contact engineering in order to extract the best performance from practical MoS₂ devices¹⁴⁷.

Figure 4.1 MoS₂ Device And Performance (a), Illustration of a top-gate monolayer MoS₂ FET with a high- κ HfO₂ gate dielectric. I_{ds} - V_g device characteristics measured using (b) top gate and (c) back gate. (d), I_{ds} - V_{ds} characteristics plot.⁹⁴ Reproduced with permission from Macmillan Publishers Ltd: [Nature Nanotechnology](#), ref. 94, copyright © 2011.

Figure 4.2 Current Through Multi-Layer Systems And Other Device Structures (a,c,d), Movement of conduction “hot-spot” in multilayer MoS₂ devices with variation of gate voltage. **(b),** Illustration of series-parallel resistor-model for multilayer MoS₂ devices. **(e),** Illustration of MoS₂/graphene flash memory cell. **(f)** Illustration of a flexible MoS₂ device fabricated on a flexible substrate. Reproduced with permission from (a - d) ref. 181, copyright © 2013 American Chemical Society, (e) ref. 182, copyright © 2013 American Chemical Society (f) ref. 183, copyright © 2013 American Chemical Society

The effective mass of carriers in MoS₂ is relatively higher than that of silicon.¹⁷⁷ Higher electron mass allows for thinner channel potential barrier in the off state as well as lower potential barrier in the on state resulting in increased drive current capabilities and higher on/off ratios. It also allows for greater doping without pushing the Fermi level into the conduction or valence bands. Due to its ultra-thin structure and lower density of states, higher gate control is expected.¹⁷⁷ The absence of dangling

bonds promotes a very clean surface interface with almost no recombination centres. Also, the ultra-thin structure results in the inversion layer charge being closer to the surface as compared to silicon devices.¹⁸⁰ The use of thinner gate oxides should help to gain better gate control. A model developed by Das et al.¹⁸¹ attempted to explain the current flow patterns in layered materials such as MoS₂. The model took each layer in a stacked layered material as a resistor. The van der Waals gap between the layers was also treated as a resistor and the current tunnels through layers to travel across layers. The simulation predicted the presence of a “hot spot”, i.e. a particular layer or set of adjacent layers through which most of the flowing current was concentrated as the gate voltage was varied, (see Figure 12a-d) and predicted that the “hot spot” moved toward the upper layers of the stacked structure and farther away from the back gate as the gate voltage was increased.

A major issue with fabricated MoS₂ devices is the extremely low mobility. Thus, improvement of real-life mobility has been the focus of multiple studies^{94, 102, 103, 105, 106, 112, 114, 176, 180, 183-188}. High- κ gate dielectrics and dielectric engineering in general have been proposed⁹⁸ to suppress Coulomb scattering in MoS₂ channels. There have been multiple device studies using various dielectrics. The general prediction was that higher mobilities could be obtainable through high- κ dielectrics^{57, 94, 103, 105, 106, 112-114, 183, 188}. The very first few-layer MoS₂ FET with SiO₂ as the gate dielectric layer made by Novoselov et al.² were of very low mobilities in the range of 0.5-3 cm²/Vs. A significant improvement in the device performance was achieved by Radisavljevic et al.⁹⁴ with the use of a HfO₂ high- κ gate dielectric (see Fig 11). The top-gated MoS₂ FETs demonstrated a large jump in the mobility up to about 200cm²/Vs along with an on/off ratio of 10⁸. This achievement was attributed to suppression of Coulomb

scattering and modification of phonon dispersion. Al_2O_3 as a high- κ dielectric has been applied to MoS_2 FETs, leading to high mobilities of $\sim 100 \text{ cm}^2/\text{Vs}$ for the bottom gated structure¹⁸⁶, $\sim 170 \text{ cm}^2/\text{Vs}$ for the top gated structure¹⁰⁶ and $517 \text{ cm}^2/\text{Vs}$ for the dual gated structure¹⁸⁸. The use of ionic liquids as a dielectric material resulted in an ambipolar characteristics and suggest an improvement in the mobility attributed to the dielectric properties as well as a reduction in the Schottky barrier at the metal/ MoS_2 contacts.^{112, 114} Polymer gated MoS_2 FETs have been also presented.^{105, 113} Poly(ethylene oxide) used with lithium perchlorate (LiClO_4)¹⁰⁵ was found to promote a three-order improvement in the mobility from ~ 0.1 to $\sim 150 \text{ cm}^2/\text{Vs}$, attributed partially due to the dielectric effect of the polymer and partially through reduction of contact resistance. Polymethyl methacrylate (PMMA)¹¹³ was used as the gate dielectric as well as the substrate of MoS_2 FETs, resulting in ambipolar device characteristics and a large mobility of $470 \text{ cm}^2/\text{Vs}$. This large enhancement in the mobility was explained to be due to the smooth PMMA substrate with no chemical bonding.¹¹³

This is quite interesting as it brings up two possible causes of lower mobility in MoS_2 : substrate effects and contact effects. The importance of selection of the substrate has already been seen in the crystal as well as electrical quality of few-layer MoS_2 obtained via growth processes. Substrate interactions with MoS_2 flakes have also been important issues in study of the 2D MoS_2 . Factors like surface roughness and sheet ripples strongly affect mobility, while dangling bonds have been shown to introduce deep energy states to the energy structure of MoS_2 . The field effect mobility of devices was recently found to be an order of magnitude greater when placed on hexagonal boron nitride substrates, having inert surfaces relatively free of dangling bonds, as compared to mobilities measured when on silicon oxide substrates which

have a high density of dangling bonds on the surface.¹⁸⁹ MoS₂ was found to be sensitive even to atmospheric humidity, which could adsorb on the material surface and resulted in a hysteresis in the transfer characteristics.¹⁴⁹

Studying the contact effects on MoS₂ and engineering contact barriers is another push to practically realize the theoretically predicted field effect mobilities of MoS₂. An ab initio study by Popov et al.¹⁸⁵ compared gold and titanium contacts to MoS₂. It was suggested that gold, a common metal for electrodes in many electronic devices, is not an ideal contact metal material for MoS₂ for multiple reasons. Due to the material geometries of MoS₂ flakes, gold and titanium, there is physically less space between Ti atoms and the S atoms of MoS₂ and thus there is a greater overlap of titanium's atomic orbitals with MoS₂ as compared to that with gold. Also for better charge transfer, the electronic states at the Fermi level of the contact metal must strongly overlap and align with that of MoS₂. Gold turns out to be less aligned with MoS₂ as compared to titanium, resulting in poor electrical contact properties. Also, metal-MoS₂ contacts cannot be completely ohmic as a Schottky barrier always exists. As the barrier width was greater for gold as compared to titanium owing to greater work function differences along with the above reasons, there is a reduced amount of charge transfer to MoS₂. Titanium was thus predicted to be a better contact material to MoS₂ as compared to gold.¹⁸⁵ Scandium has a lower work function which could match the density of states in MoS₂ much better than Au and other metals. Scandium/MoS₂ contacts were found to be of small contact resistance and the reported mobility of 700cm²/Vs¹⁰³ was the highest reported so far. Potassium doped contacts for MoS₂ devices¹⁷⁵ demonstrated ohmic behaviour, suggesting that a low work function metal is better than a high work function metal as the electrodes in MoS₂ devices.

Many application-oriented devices based on MoS₂ have been developed. Taking advantage of the flexible and transparent nature of few-layer MoS₂, Chang et al reported¹⁹⁰ on MoS₂ FETs with high- κ dielectrics fabricated on flexible substrates, which had a typical on/off ratio of 10^7 , subthreshold slope of $\sim 82\text{mV/dec}$ and a low field mobility of $30\text{cm}^2/\text{Vs}$ and could be bent to a radius of 1mm with stable performance (see figure 12(f)).

Integrated circuits based on mono-layer¹⁹¹ and bi-layer¹⁹² MoS₂ were successfully demonstrated, although they were only in the proof-of-concept stage. Hybrid devices using MoS₂ along with other materials have been studied as well as reported. A density functional theory (DFT) study of stacked monolayer graphene-MoS₂ heterostructures¹⁹³ predicted an introduction of a small bandgap in graphene due to MoS₂ and significantly higher mobilities in MoS₂ due to graphene. This would make a very interesting practical device. An inverter with p-type carbon nanotube and an n-type MoS₂ FETs was fabricated with a reported gain of 1.3.¹⁹⁴ A non-volatile memory cell with monolayer MoS₂ as the channel semiconductor and single layer graphene as the floating gate showed very stable operation and was estimated to be able to retain 30% of the initial stored charge even after 10 years (see Figure 12f).¹⁸²

4.2 Sensors

The 2D structure of MoS₂ flakes provides not only new electronic and optoelectronic avenues but also high surface-to-area ratios. These unique merits make few-layer MoS₂ flakes excellent sensing elements to many adsorbates. A first-principle study¹⁹⁵ examined the adsorption and diffusion of gaseous hydrogen on the MoS₂

surface and revealed monolayer MoS₂ to have a high sensing ability and a preferential bonding of hydrogen to sulphur atoms or in sulphur vacancies on MoS₂ surface. An applied strain could lower the energy barrier to adsorption on MoS₂ surface. Two studies used MoS₂ in aqueous suspensions to sense NO₂ with sensitivities as high as 20 ppb¹⁹⁶ and 2 ppb¹⁹⁷ (using reduced graphene oxide and Pt nanoparticles). MoS₂ sensors in NO environment¹⁹⁸ displayed a very high sensitivity (0.3 to 2 ppm). Monolayer MoS₂ NO sensor performance was found to be unstable despite being faster, while bi- to quad-layer sensors had stable performance. Another report¹⁹⁹ on NO₂, NH₃ and humidity MoS₂ sensors presented a higher sensitivity of five-layer MoS₂ flake than that of the two-layer samples, with unstable performance of monolayer samples. Sensitivity to gases was found to be tunable through gate voltage (for the FET structure), enhancing sensitivity for NO₂ and decreasing sensitivity for NH₃ with application of positive back gate voltage. This was explained by the electron donor and acceptor natures of NH₃ and NO₂ respectively. It was found that electron donor gases caused higher sensitivity than electron acceptor gases.

Exposure to light was also observed to increase device sensitivity and decrease recovery time, depending on the gas being sensed. MoS₂ has also shown sensitivity towards triethylamine²⁰⁰, a decomposition product of a nerve gas agent. Triethylamine is a strong electron donor and exposure of MoS₂ to triethylamine increases its conductivity with increasing gas concentration.

Chapter 5 | Kelvin Probe Force Microscopy

5.1 Atomic Force Microscopy

Characterization tools are essential in order to study a material's structure and properties. Some popularly used characterization tools are optical microscopes, Raman spectrometers, x-ray diffraction spectrometers, x-ray photoelectron spectrometers, scanning tunnelling microscopes, etc. One such important characterization tool is the atomic force microscope (AFM), which was the primary tool used for this study.

Figure 5.1 Schematic of AFM And Frequency Curve Shift (a), Schematic of a modern AFM. (b), Shift of cantilever beam's fundamental frequency from ω_0 to ω_0' due to tip-sample interaction force. Resonance curve shift can be interpreted as a frequency or amplitude change. Reproduced with permission from (a) ref. 201, copyright © The Royal Society of Chemistry (b) ref. 202, copyright © 1991, AIP Publishing LLC.

An AFM is used to study the surface profile and properties of a material. It is most commonly used to extract a height profile image of a material surface. The concept of the AFM was first proposed in 1986 by Binnig et al. to overcome the drawbacks of the scanning tunnelling microscope (STM).^{203, 204} Unlike an optical microscope which uses an optical image sensor to capture photons reflected from a sample in order to build an image, an AFM uses an atomically sharp tip attached to the end of a cantilever beam to scan a material's surface. Variations of the material surface profile are sensed through force interactions between the material surface and AFM tip to form a 3D height profile image of the surface as the sample is moved below the sensing tip using the x, y and z piezo crystal vibrations.^{203, 205-207} A schematic of the basic structure of a modern AFM is shown in the Fig 5.1. Tip movement is sensed by monitoring the deflection of a narrow laser beam off the cantilever beam, whose shift is detected by a four-quadrant photodiode.^{205, 208, 209}

There are two methods of performing atomic force microscopy: non-contact atomic force microscopy and contact atomic force microscopy.^{205, 206} Contact AFMs gain topography through physical contact of the cantilever tip and the material surface, while non-contact (NC) AFMs position the cantilever tip at a certain height above the material surface while scanning. An AFM has two basic modes of operation: static and dynamic.^{205, 206} In static mode, the cantilever beam is held steadily while scanning a material surface. The forces acting between the material surface and the AFM tip cause the cantilever beam to bend, depending on the material surface height and consequently the force exerted, until equilibrium is reached. The cantilever beam in this case is viewed as a spring with spring constant k , and the extent of cantilever beam deformation is used to gain sample surface topography data.^{203, 205, 206} In

dynamic mode, the cantilever beam is continually oscillated at or near its resonant frequency. Interactive forces between the cantilever beam tip and the material surface being scanned causes a shift in the cantilever beam's resonant frequency curve.^{205, 206, 210-212} The static and dynamic modes have two further sub-divisions of operation: equiforce and variable deflection; variable gradient and constant gradient respectively.²⁰⁶

Under the static equiforce mode, the height of the sample is continually adjusted to maintain the constant repulsive forces between the tip and sample surface. The height variations made at every point of sampling is interpreted as the sample height profile at that point.²⁰⁶ Under the variable deflection mode, the sample height is kept constant and the change in force felt by the AFM tip through the cantilever beam is measured and used to interpret the sample's surface height profile.²⁰⁶ Under the dynamic variable gradient scheme there is no feedback from the cantilever beam, similar to the static variable deflection mode and the shift in resonance frequency curve is interpreted.^{205, 206, 210} On the other hand, the constant gradient technique uses a feedback loop and varies sample height in order to maintain constant cantilever beam oscillation amplitude (Amplitude Modulation [AM-AFM]) or constant beam oscillation frequency (Frequency Modulation [FM-AFM]).^{205, 206, 210}

Figure 5.2 Force-distance Plot For An AFM. Reproduced with permission from ref. 213 with kind permission from Springer Science and Business Media.

Figure 5.3 Working Principles For Dynamic AFM (a), Monitoring change in oscillation amplitude in AM AFM. (b), Monitoring change in oscillation frequency in FM AFM. Reprinted with permission from ref 208, copyright © 2011 Elsevier.

The operating principles of the AFM rely on the interpretation of the physical forces felt by the AFM tip, which can be detected through changes in the cantilever beam's mechanical motion.^{203, 205-207, 210, 211, 214, 215} It is thus essential to have a brief overview of the operating forces between an AFM tip and the sample surface being scanned. The force-distance curve shown in Fig 5.2 is illustrative of the interactive forces felt by the AFM tip with respect to distance from the sample to be measured. As the tip is brought close to a sample surface, the overall force felt is attractive and keeps increasing in strength till an inflection point beyond which the overall force felt rapidly evolves into a repulsive one.^{205, 206, 214} Dynamic AFM modes are operated in the “Non-contact” and “Intermittent contact” regimes shown while static modes are operated in the “Contact” regime. The forces felt by an AFM tip can roughly be divided into long range forces like van der Waals type forces, short range and contact forces between atoms and molecules, and other forces like electrostatic forces and capillary forces.^{205-207, 210, 214, 216} For dynamic mode AFM operation, a repulsive force increases the spring-like oscillating cantilever beam and increases its resonance frequency, while an attractive force does the opposite.²⁰⁶ This understanding coupled when applied in conjunction with the force-distance curve makes it clear that any change in the height of a sample's surface topography being scanned would result in a change in the separation gap between the oscillating tip and the sample surface and consequently a change in the force felt by the AFM tip. This change in force is quantified in terms of change in oscillation amplitude (AM-AFM) or frequency (FM-AFM) due to a shift in the cantilever beam's resonance curve²⁰⁵⁻²⁰⁷ as seen in Fig 5.1 and Fig 5.3.

Early AFMs were operated in the static mode, but suffered from many limitations.²⁰⁵ For high sensitivity, the cantilever spring constant k had to be lower than that of the atomic bonds being measured. This strongly limited cantilever design and material choice. Also, low frequency noise would strongly interfere with the scanning signal resulting in noisy scans. Long range attractive forces like van der Waals forces would cause the tip to “jump to” or “snap to” the sample material surface, making continuous operation unstable at times. These challenges led to the development of dynamic operation modes which allowed for higher k values and provided higher frequency scan signals which could easily be separated from low frequency noise signals.^{205, 206,}

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Atomic force microscopes can be used for much more than just topography scans through the application of a potential to conductive AFM tip giving rise to various applications like EFM²¹⁷, MFM²¹⁸, KFM²⁰⁸, etc.

5.2 Fundamentals of Kelvin Probe Force Microscopy

Kelvin probe force microscopy (KPFM), also called Kelvin force microscopy (KFM) or scanning Kelvin probe microscopy (SKPM), allows the use of an AFM to measure the contact potential difference (CPD) between the AFM tip and the sample surface over the entirety of the scanning area with high sensitivity^{208, 219-221}. The working principle for KPFM is derived from the Kelvin method or the vibrating capacitor method.²²² When the AFM is far from the material surface, their vacuum energy levels are aligned but their Fermi levels are not aligned (see fig 5.3).^{208, 223} When the tip is brought close enough to the material surface for electrons to tunnel

through the gap between them, the Fermi levels of the tip and material align causing misalignment in their vacuum levels. At every point of measurement during a scan, the AFM control system applies a DC voltage V_{DC} to the tip to realign the vacuum energy levels of tip and sample. This applied voltage is the contact potential difference and can be linked to the work functions of tip and sample material^{208, 223} by $V_{DC} = V_{CPD} = (\Phi_t - \Phi_s)/e$

Figure 5.4 Tip-Sample Interaction (a), Tip far from sample. (b), Tip-sample Fermi level align with decreased distance. (c), Application of external V_{DC} to align vacuum levels of tip and sample materials. Reprinted with permission from ref 208, copyright © 2011 Elsevier.

Where Φ_t is the tip work function and Φ_s is the sample material's work function. Mapping out V_{CPD} at every point of the scanning area generates the KPFM image. If the work function of the tip is known, the work function map of the scanned area can easily be calculated giving a high resolution surface work function topography image. The electrostatic forces between the tip and sample surface are generated by

application of both AC voltage (V_{AC}) and DC voltage (V_{DC}). V_{AC} of frequency ω generates a sinusoidal varying component of the applied electric field while V_{DC} is variably applied by the control system to nullify the varying electric field component due to the CPD between tip and sample.^{208, 220, 221}

KPFM is mostly implemented along with dynamic (AM and FM) AFM operational modes.^{208, 223, 224} AM mode KPFM determines the tip-sample electrostatic force from the cantilever's vibrational amplitude at a particular V_{DC} and V_{AC} with set electrical frequency ω . V_{DC} is varied until the measured amplitude is nullified, at which point its value is recorded as the CPD at that point of measurement. FM mode KPFM on the other hand detects the shift in frequency from V_{AC} 's set electrical excitation frequency ω and varies V_{DC} to cancel out that shift.²⁰⁸ A topography scan is usually generated along with a surface potential scan. This is handled differently for AM and FM modes. In AM mode, the fundamental resonance peak frequency is chosen for mechanical resonance while the second resonance peak frequency is chosen for electrical resonance. This allows for better signal separation aiding in accurate signal detection and consequently allowing for simultaneous topography and CPD scans.^{208, 224} Another solution is to use the first resonance peak frequency for both mechanical as well as electrical excitation but scan each alternately. This means that each scanned line is scanned twice; once for a topography scan followed by a return scan at a fixed delta height Δz above the sample during which the surface potential is scanned.²²³ This method is slower but has the advantage of being able to utilize the stronger fundamental resonance peak for greater sensitivity. In FM mode V_{AC} is used to modulate the tip-sample electrostatic force at a frequency ω while the tip is mechanically excited at its resonant frequency f_0 . The oscillating force due to the

applied V_{AC} modulates the cantilever's resonant mechanical frequency f_0 giving two sub-bands, $f_0 - \omega$ and $f_0 + \omega$. These two sub-bands are sensitive to the force gradient felt by the tip which provides greater spatial resolution than AM KPFM. The amplitudes of the sub-bands are monitored as V_{DC} is varied in order to determine the CPD.^{208, 223, 225}

Chapter 6 | Study of Surface Potential Shift in MoS₂ Due to Moisture Adsorption

6.1 Experimental Setup

Roughly 1cm x 1cm squares were cut from heavily p-doped 4-inch silicon wafers with thermally grown 285nm silicon oxide as substrates. The square wafer samples were then cleaned by ultrasonication in acetone and isopropyl alcohol solutions for 15 minutes each followed by cleaning in standard 1:3 (H₂SO₄:H₂O₂) Piranha solution for 15 minutes. The samples were then rinsed in DI water and dried under a dry nitrogen flow. MoS₂ sample flakes were obtained by exfoliating natural MoS₂ crystals using adhesive tape onto wafer samples, followed by optical identification of few-layered samples suitable for further study. Sample flake layer thicknesses were characterized using AFM scans.

The AFM used was the Asylum Cypher. The AFM tip used was Nanoworld's EFM tip which is conductively coated with Cr/Pt/Ir. The tip had a resonant frequency was 75 kHz, a force constant of 2.8 N/m and a radius of curvature of less than 25nm at its apex.

The humidity control system was a custom setup using two dry N₂ gas lines combined and introduced into the sealed AFM chamber with one line passing through a bubbler containing DI water. Relative humidity levels were controlled by varying the gas flow rates through the individual gas lines. A Testo hygrometer with an error of

less than 3% was used to measure the relative humidity levels in the AFM chamber. Tests were conducted at 300K and at atmospheric pressure.

6.2 Method

For this experiment, the AFM was operated in AM KPFM mode with the mechanical vibrational frequency was tuned to 5% below the cantilever beam's fundamental resonance frequency while the electrical excitation frequency was set at the cantilever's fundamental resonance frequency. The scan mode was a two-pass scan, wherein the system generates a topography scan during the first pass of a scan line and in the subsequent pass the work function scan is conducted with the tip at a height of 50nm above the first scan's trajectory. The scan rate was set at 0.5Hz per scan line.

The custom humidity setup allowed humidity levels to be set and held at levels ranging from RH 3% to RH 70% with greater than 95% accuracy. Higher levels were not attempted as the AFM's control electronics were not meant to be operated at relative humidity levels higher than RH 70%. Before commencing experimental scans, the AFM chamber was first pumped with pure dry N₂ till it reached and was maintained at a relative humidity level of about 3% in order to evacuate other components of atmospheric gases to which MoS₂ may be sensitive. Once the chamber was thus prepared, the relative humidity level would be increased from 10% to 70% and then subsequently decreased to 10% in steps of 10% to observe hysteresis effects if any. Upon reaching a particular humidity level, KPFM scans would be taken at 1 min, 5 min, 10 min, 20 min and 30 min durations. Scans were performed upon

repeated cycling through the relative humidity range in both directions as well as testing at in-between values of relative humidity at random to observe for any hysteresis effects. Samples were even kept under set humidified conditions over the span of days, followed by repeated scanning and testing. Scan results were calibrated against gold deposited on silicon oxide samples as gold's work function was shown to vary by only about 3% under changing humidity conditions.²²⁶

6.3 Results and Discussion

Figure 6.1 Optical And KPFM Scan Images. (a, b, c), Optical images of some of the scanned samples. (d, e, f), SKPM scans of the respective samples.

Surface potential scans of MoS₂ samples under the described methods and conditions showed a consistent decrease in surface potential by $145 \pm 5\text{mV}$ with increasing relative humidity from RH 10% to RH 70%. Such a decrease in surface potential, or increase in work function, is indicative of p-type doping induced by the adsorbed water. This is consistent with other theoretical²²⁷ and experimental reports¹⁹⁹. MoS₂ was predicted²²⁷ to be very sensitive to adsorbed gases including H₂O which was expected to be an electron acceptor with respect to MoS₂. This was consistent with the findings of this experiment. The same report²²⁷ also calculates an absorption energy of -234meV for H₂O being preferentially adsorbed on MoS₂'s crystal surface at the centre of hexagonal ring of MoS₂'s crystal structure as seen from Fig 6.3.

Figure 6.2 Contact Potential Difference Plot. Plot of relative contact potential change with variation of relative humidity level from 10% to 70%.

The rate of surface potential decrease with increase in relative humidity is initially high but then slows down and saturates as the humidity level reaches 70%. This could be attributed to the saturation of sample surfaces by the adsorbed water molecules. While the measured surface potentials were found to be constant across flakes with different thicknesses, consistent with a previous report²²⁸, even the surface potential variation with humidity was found to be constant across flakes of different thicknesses. While KPFM only allows the study of surface potentials, limiting any comments on any effects on bulk energy levels, it could be argued that the consistency of surface potentials irrespective of flake thickness suggests this to be only a surface phenomenon as a redistribution of charges from the surface to the bulk would be expected to alter the surface potential. By extension, this argument could be extended to suggest that the crystal bulk is not strongly affected by surface adsorption or at least points to a potential gradient from the modified surface potential to a less shifted or almost un-shifted potential within the bulk depending on material thickness and applied external electric field if any, suggesting that single-layer flakes may show the most current or resistance variation and thus higher sensitivity as a sensor. This possibility would require further detailed study.

While samples showed an even work function distribution on the exposed 2D crystal surfaces, flake edges were found to have potentials lower than the surface by about 30mV which is in agreement with a previous report²²⁸. This potential difference was consistent throughout the humidity measurement range giving a graph identical to the one in Fig 6.2 but displaced downwards by about 30mV. This is expected to be due to the presence of open bonds at flake edges. MoS₂ edges can be expected to thus show similar potential variation as a sensor but may be more sensitive due to its lower

energy level compared to the crystal surface. Absorption at flake or crystal edges may thus have even greater absorption energy, leading to preferential attachment of gaseous molecular species. With this understanding, MoS₂ edges may be an important factor in the design of sensors as greater edge exposure could result in higher sensitivity. One such reported MoS₂ sensor¹⁹⁷ was fabricated using chemically exfoliated micron-size MoS₂ flakes as the device, channel resulting in higher edge exposure in the sensing channel, and showed response to NO₂ even at very low concentrations of 2 ppb. The study also found a decrease in device sensitivity with increasing channel thickness, attributed to a decrease in surface-to-volume ratios. Apart from edges, other surface features like wrinkles and folds also showed a lower potential in our observations, but the extent of potential difference from the standard surface potential was not consistent and could depend on other factors such as the degree of strain at those points.

Figure 6.3 H₂O Adsorption on MoS₂. (a), Top and side views of the charge distribution of an H₂O molecule on MoS₂ crystal surface. The red volume region indicates charge accumulation while the green volume region indicates charge depletion. 0.012e is the amount of charge transfer involved. Reproduced with permission from ref. 227 under Creative Commons Licence.

While most devices and sensors show a hysteresis effect, surprisingly no evidence of a hysteresis effect was found in our experiments. Varying humidity levels from 10% to 70% and subsequently back to 10% or even setting to random values yielded almost identically consistent surface potentials in every scan. Also, surface potential measurements upon leaving samples at a set humidity level for even 30 minutes showed no significant difference from immediately scanned samples. While no definitive comment can be made on MoS₂'s sensing speed as KPFM scans take time, even the quickest partial scans made about within a few seconds after reaching a particular humidity level yielded stable and consistent surface potential levels with scans taken after longer durations at the same level of humidity. Bringing the humidity level back to 10% also showed reproducible and consistent levels. This suggests the adsorption of H₂O being of a purely physisorbed nature with no chemisorption involved. As H₂O molecules share only a fraction of an electron's charge from MoS₂ ($0.012e$)²²⁷ instead of a complete unit of charge (electron/hole) being transferred, desorption should be quick which would explain the fast material response as well as hysteresis-free repeatability observed. This quick and repeatable sensing behaviour by MoS₂ to H₂O and even O₂ was also observed by Tongay *et al.*¹³⁸ in the form of change of the strength of photoluminescence from observed monolayer flakes. They found the photoluminescence (PL) peak strength from monolayer MoS₂ varied quite linearly and consistently with the change in the gas pressure of the introduced H₂O or O₂. The PL intensity was observed to consistently recover to its initial value upon decreasing the gas pressure of H₂O. They also found that the speed of change of PL intensity was limited only by the speed of their testing setup. These observations correspond with our own observations of quick material response with no hysteresis due to quick physisorption.

Chapter 7 | Conclusions and Recommendations

7.1 Conclusion

While theoretical studies have predicted p-type doping of MoS₂ due to H₂O adsorption, this work has experimentally confirmed the theoretical calculations to a great degree. It has also been observed that the MoS₂ surface potential shifts downward by 145 ± 5 mV when humidity is increased from RH 10% to RH 70%, once again consistent with theoretical expectations. This phenomenon is expected to be a result of H₂O adsorption induced doping. The effects of surface adsorption of H₂O are observed to be completely reversible and surprisingly devoid of any hysteresis, suggesting that H₂O adsorption is of a physisorbed nature and does not form any permanent chemical bonds. The surface potential shift was consistently observed irrespective of sample thickness, time of exposure and condition reversal or repetition. The surface potential shift was also found to be quite consistent with no significant hysteresis effect, and appeared to have short response times. The independence as well as consistent hysteresis-free readings of the surface potential observations with respect to the time before subsequent readings (<1 min to few days) suggests a quick, stable and predictable physisorption mechanism for H₂O molecule attachment to the MoS₂ surface. Such physisorbed behaviour coupled with rapid response rates is highly desirable in gas sensors. The effect of such gas adsorption on the material's optical response, as shown in other works, makes MoS₂ a viable candidate for high-speed and high-sensitivity gas sensors.

The speed and consistency of surface potential observations as well as the independence of tested values from the thickness of the various samples tested strongly suggests that the physisorption of H_2O and its effects may be entirely surface phenomena which, by extension, also hints at the possibility that the bulk material may be unaffected by such surface disturbances. While further study is required to more concretely determine the isolation of effects of such molecular physisorption to the material surface, it could be an important factor in designing capable and reliable gas sensors. Restriction of adsorption effects to the surface may also be an important factor in the study of surface doping techniques which currently seem more viable and effective as compared to substitution doping techniques. MoS_2 Edges have been found to have a lower potential than the exposed crystalline surfaces, highlighting edges to be preferential adsorption sites, which is expected to be the reason for the high sensitivity and performance of sensors fabricated using liquid exfoliated MoS_2 flake channels having a larger edge-to-surface ratio.

The observations and conclusions drawn above point to MoS_2 having high potential as the active material in a range of sensing devices. It is also indicative of the immense avenues of research into the physics of MoS_2 as well as other 2D crystalline materials.

7.2 Recommendations for Further Research

While the surface potential behaviour under varying humidity levels has been studied, it is still unclear if similar behaviour exists within the bulk crystal. Understanding the extent of such surface effects could even extend the understanding of MoS₂'s interaction with substrates like silicon dioxide, helping to improve not just sensor performance but the electronic and optoelectronic device performance as well which is believed to be severely limited due to substrate interactions. Some theoretical studies suggest surface doping methods may be more effective for MoS₂ as compared to substitutional doping. An understanding of the extent to which such surface doping and surface-adsorption affects the surface as well as bulk energy bands may help improve doping techniques as well as performance for MoS₂ devices as well. Testing of suspended-channel devices in different gaseous environments would provide an interesting comparison of device sensitivity between devices having a single exposed surface and those having both surfaces exposed.

Due the limiting nature of an AFM on the possible choices of gaseous environments, only H₂O could be used. Testing with other gases could be done with Raman spectroscopy tools. A custom transparent enclosure of glass or other such inert material could be created to envelope and seal the samples to be tested. A gas inlet and outlet would be included to allow any gas to be safely tested. Such a setup would help test not only the material's response to a larger spectrum of gaseous species but also open the doors to including the effects of other factors such as incident light, doping factors and gate voltage. As Raman spectroscopy is a faster system as compared to an AFM, material response times could be determined over a range of less than a few seconds.

List of Publications

International Journal

1. Rudren Ganatra, Qing Zhang, “Few Layer MoS₂ – A Promising Layered Semiconductor”, *ACS Nano* (2014).

Bibliography

1. Schwierz, F. Nanoelectronics: Flat transistors get off the ground. *Nat Nanotechnol* 2011, 6, 135-6.
2. Novoselov, K. S.; Jiang, D.; Schedin, F.; Booth, T. J.; Khotkevich, V. V.; Morozov, S. V.; Geim, A. K. Two-dimensional atomic crystals. *Proc Natl Acad Sci U S A* 2005, 102, 10451-3.
3. Christy, R. I. Sputtered MoS₂ lubricant coating improvements. *Thin Solid Films* 1980, 73, 299-307.
4. Fleischauer, P. D.; Bauer, R. Chemical and Structural Effects on the Lubrication Properties of Sputtered MoS₂Films. *Tribology Transactions* 1988, 31, 239-250.
5. Wahl, K. J.; Singer, I. L. Quantification of a lubricant transfer process that enhances the sliding life of a MoS₂ coating. *Tribology Letters* 1995, 1, 59-66.
6. Wu, C.; Hou, S. X.; Zhang, H. Q.; Jia, X. M. Study and Evaluation on Dispersion of Molybdenum Disulfide in Aqueous Solution. *Advanced Materials Research* 2013, 750-752, 2175-2178.
7. Ripoll, M. R.; Simič, R.; Brenner, J.; Podgornik, B. Friction and Lifetime of Laser Surface-Textured and MoS₂-Coated Ti6Al4V Under Dry Reciprocating Sliding. *Tribology Letters* 2013, 51, 261-271.
8. Feng, X.; Tang, Q.; Zhou, J.; Fang, J.; Ding, P.; Sun, L.; Shi, L. Novel mixed-solvothermal synthesis of MoS₂nanosheets with controllable morphologies. *Crystal Research and Technology* 2013, 48, 363-368.

9. Park, T. Y.; Nam, I.-S.; Kim, Y. G. Kinetic Analysis of Mixed Alcohol Synthesis from Syngas over K/MoS₂Catalyst. *Industrial & Engineering Chemistry Research* 1997, 36, 5246-5257.
10. Del Valle, M.; Cruz-Reyes, J.; Avalos-Borja, M.; Fuentes, S. *Catalysis Letters* 1998, 54, 59-63.
11. Faye, P.; Payen, E.; Bougeard, D. Cluster Approach of Active Sites in an MoS₂ Catalyst. *Journal of Molecular Modeling* 1999, 5, 63-71.
12. Tye, C. T.; Smith, K. J. Catalytic Activity of Exfoliated MoS₂ in Hydrodesulfurization, Hydrodenitrogenation and Hydrogenation Reactions. *Topics in Catalysis* 2006, 37, 129-135.
13. Wu, Z.; Fang, B.; Wang, Z.; Wang, C.; Liu, Z.; Liu, F.; Wang, W.; Alfantazi, A.; Wang, D.; Wilkinson, D. P. MoS₂Nanosheets: A Designed Structure with High Active Site Density for the Hydrogen Evolution Reaction. *ACS Catalysis* 2013, 2101-2107.
14. Yun, J.-M.; Noh, Y.-J.; Yeo, J.-S.; Go, Y.-J.; Na, S.-I.; Jeong, H.-G.; Kim, J.; Lee, S.; Kim, S.-S.; Koo, H. Y.; Kim, T.-W.; Kim, D.-Y. Efficient work-function engineering of solution-processed MoS₂ thin-films for novel hole and electron transport layers leading to high-performance polymer solar cells. *Journal of Materials Chemistry C* 2013, 1, 3777.
15. Fontana, M.; Deppe, T.; Boyd, A. K.; Rinzan, M.; Liu, A. Y.; Paranjape, M.; Barbara, P. Electron-hole transport and photovoltaic effect in gated MoS₂ Schottky junctions. *Scientific reports* 2013, 3, 1634.
16. Bernardi, M.; Palummo, M.; Grossman, J. C. Extraordinary Sunlight Absorption and 1 nm-Thick Photovoltaics using Two-Dimensional Monolayer Materials. *Nano Letters* 2013, 130610122620006.

17. Shanmugam, M.; Durcan, C. a.; Yu, B. Layered semiconductor molybdenum disulfide nanomembrane based Schottky-barrier solar cells. *Nanoscale* 2012, 4, 7399-405.
18. Jamieson, I.; Jakovidis, G. Thin Film Texture of Layered Molybdenum Disulphide for Photovoltaic Cells. In *Conference on Optoelectronic and Microelectronic Materials and Devices, 2004.*, IEEE: 2004; pp 117-120.
19. Kwon, J.-H.; Ahn, H.-J.; Jeon, M.-S.; Kim, K.-W.; Ahn, I.-S.; Ahn, J.-H.; Wang, G.; Ryu, H.-S. The electrochemical properties of Li/TEGDME/MoS₂ cells using multi-wall carbon nanotubes as a conducting agent. *Research on Chemical Intermediates* 2010, 36, 749-759.
20. Zhang, C.; Wu, H. B.; Guo, Z.; Lou, X. W. D. Facile synthesis of carbon-coated MoS₂ nanorods with enhanced lithium storage properties. *Electrochemistry Communications* 2012, 20, 7-10.
21. Liu, H.; Su, D.; Zhou, R.; Sun, B.; Wang, G.; Qiao, S. Z. Highly Ordered Mesoporous MoS₂ with Expanded Spacing of the (002) Crystal Plane for Ultrafast Lithium Ion Storage. *Advanced Energy Materials* 2012, 2, 970-975.
22. Chang, K.; Chen, W. In situ synthesis of MoS₂/graphene nanosheet composites with extraordinarily high electrochemical performance for lithium ion batteries. *Chemical communications (Cambridge, England)* 2011, 47, 4252-4.
23. Fang, X.; Guo, X.; Mao, Y.; Hua, C.; Shen, L.; Hu, Y.; Wang, Z.; Wu, F.; Chen, L. Mechanism of lithium storage in MoS₂ and the feasibility of using Li₂S/Mo nanocomposites as cathode materials for lithium-sulfur batteries. *Chemistry, an Asian journal* 2012, 7, 1013-7.

24. Guo, G.; Hong, J.; Cong, C.; Zhou, X. Molybdenum disulfide synthesized by hydrothermal method as anode lithium rechargeable battery. *Journal of materials science* 2005, 40, 2557-2559.
25. Zhang, C.; Wang, Z.; Guo, Z.; Lou, X. W. Synthesis of MoS₂-C One-Dimensional Nanostructures with Improved Lithium Storage Properties. *ACS Appl Mater Interfaces* 2012, 2-5.
26. Frindt, R. F. Single Crystals of MoS₂ Several Molecular Layers Thick. *Journal of Applied Physics* 1966, 37, 1928.
27. Fivaz, R.; Mooser, E. Mobility of Charge Carriers in Semiconducting Layer Structures. *Physical Review* 1967, 163, 743-755.
28. Kasowski, R. Band Structure of MoS₂ and NbS₂. *Physical Review Letters* 1973, 30, 1175-1178.
29. Mattheiss, L. Energy Bands for 2H-NbSe₂ and 2H-MoS₂. *Physical Review Letters* 1973, 30, 784-787.
30. Mattheiss, L. Band Structures of Transition-Metal-Dichalcogenide Layer Compounds. *Physical Review B* 1973, 8, 3719-3740.
31. Bronsema, K.; De Boer, J.; Jellinek, F. On the structure of molybdenum diselenide and disulfide. *Zeitschrift für anorganische und allgemeine Chemie* 1986, 540, 15-17.
32. Joensen, P.; Frindt, R. F.; Morrison, S. R. Single-layer MoS₂. *Materials Research Bulletin* 1986, 21, 457-461.
33. Coehoorn, R.; Haas, C.; de Groot, R. Electronic structure of MoSe₂, MoS₂, and WSe₂. II. The nature of the optical band gaps. *Physical Review B* 1987, 35, 6203-6206.

34. Coehoorn, R.; Haas, C.; Dijkstra, J.; Flipse, C. J. F.; de Groot, R. A.; Wold, A. Electronic structure of MoSe_2 , MoS_2 , and WSe_2 . I. Band-structure calculations and photoelectron spectroscopy. *Physical Review B* 1987, 35, 6195-6202.
35. Miremadi, B. K.; Cowan, T.; Morrison, S. R. New structures from exfoliated MoS_2 . *Journal of Applied Physics* 1991, 69, 6373.
36. Wypych, F.; Schöhlhorn, R. 1T- MoS_2 , a new metallic modification of molybdenum disulfide. *Journal of the Chemical Society, Chemical Communications* 1992, 1386.
37. Byskov, L.; Hammer, B.; Nørskov, J. Sulfur bonding in MoS_2 and Co-Mo-S structures. *Catalysis letters* 1997, 47, 177-182.
38. Wypych, F.; Weber, T.; Prins, R. Scanning Tunneling Microscopic Investigation of 1T- MoS_2 . *Chemistry of Materials* 1998, 10, 723-727.
39. Helveg, S.; Lauritsen, J.; Laegsgaard, E.; Stensgaard, I.; Nørskov, J.; Clausen, B.; Topsoe, H.; Besenbacher, F. Atomic-scale structure of single-layer MoS_2 nanoclusters. *Physical review letters* 2000, 84, 951-4.
40. Böker, T.; Severin, R.; Müller, A.; Janowitz, C.; Manzke, R.; Voß, D.; Krüger, P.; Mazur, A.; Pollmann, J. Band structure of MoS_2 , MoSe_2 , and α - MoTe_2 : Angle-resolved photoelectron spectroscopy and ab initio calculations. *Physical Review B* 2001, 64, 235305.
41. Lauritsen, J. V.; Kibsgaard, J.; Helveg, S.; Topsoe, H.; Clausen, B. S.; Laegsgaard, E.; Besenbacher, F. Size-dependent structure of MoS_2 nanocrystals. *Nat Nanotechnol* 2007, 2, 53-8.
42. Lee, C.; Yan, H.; Brus, L.; Heinz, T.; Hone, J.; Ryu, S. Anomalous lattice vibrations of single-and few-layer MoS_2 . *ACS nano* 2010, 4, 2695-2700.

43. Mak, K. F.; Lee, C.; Hone, J.; Shan, J.; Heinz, T. F. Atomically Thin MoS₂: A New Direct-Gap Semiconductor. *Physical Review Letters* 2010, 105, 136805.
44. Wypych, F.; Schöllhorn, R. 1T-MoS₂, a new metallic modification of molybdenum disulfide. *Journal of the Chemical Society, Chemical Communications* 1992, 1386-1388.
45. Ramakrishna Matte, H. S. S.; Gomathi, A.; Manna, A. K.; Late, D. J.; Datta, R.; Pati, S. K.; Rao, C. N. R. MoS₂ and WS₂ Analogues of Graphene. *Angewandte Chemie* 2010, 122, 4153-4156.
46. Ataca, C.; Şahin, H.; Ciraci, S. Stable, Single-Layer MX₂Transition-Metal Oxides and Dichalcogenides in a Honeycomb-Like Structure. *The Journal of Physical Chemistry C* 2012, 116, 8983-8999.
47. Qi, J.; Li, X.; Qian, X.; Feng, J. Bandgap engineering of rippled MoS₂ monolayer under external electric field. *Applied Physics Letters* 2013, 102, 173112.
48. Ataca, C.; Topsakal, M.; Aktürk, E.; Ciraci, S. A Comparative Study of Lattice Dynamics of Three- and Two-Dimensional MoS₂. *The Journal of Physical Chemistry C* 2011, 115, 16354-16361.
49. Kadantsev, E. S.; Hawrylak, P. Electronic structure of a single MoS₂ monolayer. *Solid State Communications* 2012, 152, 909-913.
50. Le, D.; Rahman, T. S. Joined edges in MoS₂: metallic and half-metallic wires. *Journal of physics. Condensed matter : an Institute of Physics journal* 2013, 25, 312201.
51. Zeng, H.; Dai, J.; Yao, W.; Xiao, D.; Cui, X. Valley polarization in MoS₂ monolayers by optical pumping. *Nature nanotechnology* 2012, 7, 490-3.

52. Eda, G.; Yamaguchi, H.; Voiry, D.; Fujita, T.; Chen, M.; Chhowalla, M. Photoluminescence from chemically exfoliated MoS₂. *Nano Lett* 2011, 11, 5111-6.
53. Castellanos-Gomez, A.; Poot, M.; Steele, G. a.; van der Zant, H. S. J.; Agraït, N.; Rubio-Bollinger, G. Elastic properties of freely suspended MoS₂ nanosheets. *Advanced materials* 2012, 24, 772-775.
54. Wagner, P.; Ivanovskaya, V. V.; Rayson, M. J.; Briddon, P. R.; Ewels, C. P. Mechanical properties of nanosheets and nanotubes investigated using a new geometry independent volume definition. *Journal of physics. Condensed matter : an Institute of Physics journal* 2013, 25, 155302.
55. Li, T. Ideal strength and phonon instability in single-layer MoS. *Physical Review B* 2012, 85, 235407.
56. Bertolazzi, S.; Brivio, J.; Kis, A. Stretching and breaking of ultrathin MoS₂. *ACS Nano* 2011, 5, 9703-9.
57. Pu, J.; Yomogida, Y.; Liu, K.-K.; Li, L.-J.; Iwasa, Y.; Takenobu, T. Highly flexible MoS₂ thin-film transistors with ion gel dielectrics. *Nano letters* 2012, 12, 4013-7.
58. Duerloo, K.-A. N.; Ong, M. T.; Reed, E. J. Intrinsic Piezoelectricity in Two-Dimensional Materials. *The Journal of Physical Chemistry Letters* 2012, 3, 2871-2876.
59. Lee, J.; Wang, Z.; He, K.; Shan, J.; Feng, P. X.-L. High Frequency MoS₂ Nanomechanical Resonators. *ACS nano* 2013.
60. Zhao, Y.; Luo, X.; Li, H.; Zhang, J.; Araujo, P. T.; Gan, C. K.; Wu, J.; Zhang, H.; Quek, S. Y.; Dresselhaus, M. S.; Xiong, Q. Interlayer breathing and shear modes in few-trilayer MoS₂ and WSe₂. *Nano letters* 2013, 13, 1007-15.

61. Molina-Sánchez, A.; Wirtz, L. Phonons in single-layer and few-layer MoS₂ and WS₂. *Physical Review B* 2011, 84, 155413.
62. Sahoo, S.; Gaur, A. P. S.; Ahmadi, M.; Guinel, M. J. F.; Katiyar, R. S. Temperature-Dependent Raman Studies and Thermal Conductivity of Few-Layer MoS₂. *The Journal of Physical Chemistry C* 2013, 117, 9042-9047.
63. Malard, L. M.; Alencar, T. V.; Barboza, A. P. M.; Mak, K. F.; de Paula, A. M. Observation of intense second harmonic generation from MoS₂ atomic crystals. *Physical Review B* 2013, 87, 1-5.
64. Kumar, N.; Najmaei, S.; Cui, Q.; Ceballos, F.; Ajayan, P. M.; Lou, J.; Zhao, H. Second harmonic microscopy of monolayer MoS₂. *Physical Review B* 2013, 87, 161403.
65. Li, Y.; Rao, Y.; Mak, K. F.; You, Y.; Wang, S.; Dean, C. R.; Heinz, T. F. Probing Symmetry Properties of Few-Layer MoS and h-BN by Optical Second-Harmonic Generation. *Nano Lett* 2013, 13, 3329-3333.
66. Li, H.; Zhang, Q.; Yap, C. C. R.; Tay, B. K.; Edwin, T. H. T.; Olivier, A.; Baillargeat, D. From Bulk to Monolayer MoS₂: Evolution of Raman Scattering. *Advanced Functional Materials* 2012, 22, 1385-1390.
67. Chakraborty, B.; Matte, H. S. S. R.; Sood, a. K.; Rao, C. N. R. Layer-dependent resonant Raman scattering of a few layer MoS₂. *Journal of Raman Spectroscopy* 2013, 44, 92-96.
68. Zhang, W.; Huang, J.-K.; Chen, C.-H.; Chang, Y.-H.; Cheng, Y.-J.; Li, L.-J. High-Gain Phototransistors Based on a CVD MoS₂ Monolayer. *Advanced materials* 2013, n/a-n/a.

69. Chakraborty, B.; Bera, A.; Muthu, D. V. S.; Bhowmick, S.; Waghmare, U. V.; Sood, A. K. Symmetry-dependent phonon renormalization in monolayer MoS₂ transistor. *Physical Review B* 2012, 85, 161403.
70. Zeng, H.; Zhu, B.; Liu, K.; Fan, J.; Cui, X.; Zhang, Q. M. Low-frequency Raman modes and electronic excitations in atomically thin MoS₂ films. *Physical Review B* 2012, 86, 241301.
71. Plechinger, G.; Heydrich, S.; Eroms, J.; Weiss, D.; Schüller, C.; Korn, T. Raman spectroscopy of the interlayer shear mode in few-layer MoS₂ flakes. *Applied Physics Letters* 2012, 101, 101906.
72. Lanzillo, N. A.; Birdwell, A. G.; Amani, M.; Crowne, F. J.; Shah, P. B.; Najmaei, S.; Liu, Z.; Ajayan, P. M.; Lou, J.; Dubey, M.; Nayak, S. K.; Regan, T. P. O. Temperature-dependent phonon shifts in monolayer MoS₂. *arXiv preprint arXiv:1307.2447* 2013, 1-4.
73. Najmaei, S.; Liu, Z.; Ajayan, P. M.; Lou, J. Thermal effects on the characteristic Raman spectrum of molybdenum disulfide (MoS₂) of varying thicknesses. *Applied Physics Letters* 2012, 100, 013106.
74. Wang, Y.; Cong, C.; Qiu, C.; Yu, T. Raman Spectroscopy Study of Lattice Vibration and Crystallographic Orientation of Monolayer MoS₂ under Uniaxial Strain. *Small* 2013, 9, 2857-61.
75. Splendiani, A.; Sun, L.; Zhang, Y.; Li, T.; Kim, J.; Chim, C.-Y.; Galli, G.; Wang, F. Emerging photoluminescence in monolayer MoS₂. *Nano letters* 2010, 10, 1271-5.
76. Ellis, J. K.; Lucero, M. J.; Scuseria, G. E. The indirect to direct band gap transition in multilayered MoS₂ as predicted by screened hybrid density functional theory. *Applied Physics Letters* 2011, 99, 261908.

77. Kuc, a.; Zibouche, N.; Heine, T. Influence of quantum confinement on the electronic structure of the transition metal sulfide TS2. *Physical Review B* 2011, 83, 245213.
78. Ataca, C.; Ciraci, S. Functionalization of Single-Layer MoS2 Honeycomb Structures. *The Journal of Physical Chemistry C* 2011, 115, 13303-13311.
79. Kang, J.; Tongay, S.; Zhou, J.; Li, J.; Wu, J. Band offsets and heterostructures of two-dimensional semiconductors. *Applied Physics Letters* 2013, 102, 012111.
80. Zahid, F.; Liu, L.; Zhu, Y.; Wang, J.; Guo, H. A generic tight-binding model for monolayer, bilayer and bulk MoS2. *AIP Advances* 2013, 1-4.
81. Kormányos, A.; Zólyomi, V. Monolayer MoS2: trigonal warping, "\ Gamma-valley", and spin-orbit coupling effects. *arXiv preprint arXiv: ...* 2013, 1-7.
82. Rostami, H.; Moghaddam, A.; Asgari, R. Effective lattice Hamiltonian for monolayer MoS2: Tailoring electronic structure with perpendicular electric and magnetic fields. *arXiv preprint arXiv:1302.5901* 2013, 3, 1-7.
83. Komsa, H.-P.; Krasheninnikov, A. V. Effects of confinement and environment on the electronic structure and exciton binding energy of MoS from first principles. *Physical Review B* 2012, 86, 241201.
84. Kumar, A.; Ahluwalia, P. K. Tunable dielectric response of transition metals dichalcogenides MX2 (M=Mo, W; X=S, Se, Te): Effect of quantum confinement. *Physica B: Condensed Matter* 2012, 407, 4627-4634.
85. Han, S. W.; Cha, G.-B.; Frantzeskakis, E.; Razado-Colambo, I.; Avila, J.; Park, Y. S.; Kim, D.; Hwang, J.; Kang, J. S.; Ryu, S.; Yun, W. S.; Hong, S. C.; Asensio, M. C. Band-gap expansion in the surface-localized electronic structure of MoS2(0002). *Physical Review B* 2012, 86, 115105.

86. Mahatha, S. K.; Menon, K. S. R. Inhomogeneous band bending on MoS₂(0001) arising from surface steps and dislocations. *Journal of physics. Condensed matter : an Institute of Physics journal* 2012, 24, 305502.
87. Salmani-Jelodar, M.; Tan, Y.; Klimeck, G. Single layer MoS₂ band structure and transport. 2011, 6, 1-2.
88. Kaasbjerg, K.; Thygesen, K. S.; Jacobsen, K. W. Phonon-limited mobility in n-type single-layer MoS₂ from first principles. *Physical Review B* 2012, 85, 115317.
89. Tiras, E.; Ardali, S.; Tiras, T.; Arslan, E.; Cakmakyapan, S.; Kazar, O.; Hassan, J.; Janzén, E.; Ozbay, E. Effective mass of electron in monolayer graphene: Electron-phonon interaction. *Journal of Applied Physics* 2013, 113, 043708.
90. Taniguchi, K.; Matsumoto, A.; Shimotani, H.; Takagi, H. Electric-field-induced superconductivity at 9.4 K in a layered transition metal disulphide MoS₂. *Applied Physics Letters* 2012, 101, 109902.
91. Roldan, R.; Cappelluti, E.; Guinea, F. Interactions and superconductivity in heavily doped MoS₂. *arXiv preprint arXiv:1301.4836* 2013, 1-5.
92. Ge, Y.; Liu, A. Y. Phonon-mediated superconductivity in electron-doped single-layer MoS₂: A first-principles prediction. *Physical Review B* 2013, 87, 241408.
93. Radisavljevic, B.; Kis, A. Mobility engineering and a metal–insulator transition in monolayer MoS₂. *Nature Materials* 2013, 12, 1-6.
94. Radisavljevic, B.; Radenovic, A.; Brivio, J.; Giacometti, V.; Kis, A. Single-layer MoS₂ transistors. *Nat Nanotechnol* 2011, 6, 147-50.
95. Brivio, J.; Alexander, D. T.; Kis, A. Ripples and layers in ultrathin MoS₂ membranes. *Nano Lett* 2011, 11, 5148-53.

96. Liu, Q.; Li, L.; Li, Y.; Gao, Z.; Chen, Z.; Lu, J. Tuning Electronic Structure of Bilayer MoS₂ by Vertical Electric Field: A First-Principles Investigation. *The Journal of Physical Chemistry C* 2012, 116, 21556-21562.
97. Wang, R.; Ruzicka, B. a.; Kumar, N.; Bellus, M. Z.; Chiu, H.-Y.; Zhao, H. Ultrafast and spatially resolved studies of charge carriers in atomically thin molybdenum disulfide. *Physical Review B* 2012, 86, 045406.
98. Jena, D.; Konar, A. Enhancement of Carrier Mobility in Semiconductor Nanostructures by Dielectric Engineering. *Physical Review Letters* 2007, 98, 136805.
99. Qiu, H.; Pan, L.; Yao, Z.; Li, J.; Shi, Y.; Wang, X. Electrical characterization of back-gated bi-layer MoS₂ field-effect transistors and the effect of ambient on their performances. *Applied Physics Letters* 2012, 100, 123104.
100. Mann, J.; Sun, D.; Ma, Q.; Chen, J.-R.; Preciado, E.; Ohta, T.; Diaconescu, B.; Yamaguchi, K.; Tran, T.; Wurch, M.; Magnone, K.; Heinz, T. F.; Kellogg, G. L.; Kawakami, R.; Bartels, L. Facile growth of monolayer MoS₂ film areas on SiO₂. *The European Physical Journal B* 2013, 86, 226.
101. Liu, K.-K.; Zhang, W.; Lee, Y.-H.; Lin, Y.-C.; Chang, M.-T.; Su, C.-Y.; Chang, C.-S.; Li, H.; Shi, Y.; Zhang, H.; Lai, C.-S.; Li, L.-J. Growth of large-area and highly crystalline MoS₂ thin layers on insulating substrates. *Nano letters* 2012, 12, 1538-44.
102. Wu, W.; De, D.; Chang, S.-C.; Wang, Y.; Peng, H.; Bao, J.; Pei, S.-S. High mobility and high on/off ratio field-effect transistors based on chemical vapor deposited single-crystal MoS₂ grains. *Applied Physics Letters* 2013, 102, 142106.

103. Das, S.; Chen, H.-Y.; Penumatcha, A. V.; Appenzeller, J. High performance multilayer MoS₂ transistors with scandium contacts. *Nano letters* 2013, 13, 100-5.
104. Laskar, M. R.; Park, P. S.; Krishnamoorthy, S.; Nath, D. N.; Lu, W.; Wu, Y.; Rajan, S. Large Area Single Crystal (0001) Oriented MoS₂ Thin Films. *arXiv preprint arXiv:1302.3177* 2013, 1, 1-23.
105. Lin, M.-W.; Liu, L.; Lan, Q.; Tan, X.; Dhindsa, K. S.; Zeng, P.; Naik, V. M.; Cheng, M. M.-C.; Zhou, Z. Mobility enhancement and highly efficient gating of monolayer MoS₂ transistors with polymer electrolyte. *Journal of Physics D: Applied Physics* 2012, 45, 345102.
106. Min, S. W.; Lee, H. S.; Choi, H. J.; Park, M. K.; Nam, T.; Kim, H.; Ryu, S.; Im, S. Nanosheet thickness-modulated MoS₂ dielectric property evidenced by field-effect transistor performance. *Nanoscale* 2013, 5, 548-51.
107. Lee, Y. H.; Zhang, X. Q.; Zhang, W.; Chang, M. T.; Lin, C. T.; Chang, K. D.; Yu, Y. C.; Wang, J. T.; Chang, C. S.; Li, L. J.; Lin, T. W. Synthesis of large-area MoS₂ atomic layers with chemical vapor deposition. *Advanced materials* 2012, 24, 2320-5.
108. Najmaei, S.; Liu, Z.; Zhou, W.; Zou, X.; Shi, G.; Lei, S.; Yakobson, B. I.; Idrobo, J. C.; Ajayan, P. M.; Lou, J. Vapour phase growth and grain boundary structure of molybdenum disulphide atomic layers. *Nat Mater* 2013, 12, 754-9.
109. Lin, Y. C.; Zhang, W.; Huang, J. K.; Liu, K. K.; Lee, Y. H.; Liang, C. T.; Chu, C. W.; Li, L. J. Wafer-scale MoS₂ thin layers prepared by MoO₃ sulfurization. *Nanoscale* 2012, 4, 6637-41.

110. Zhan, Y.; Liu, Z.; Najmaei, S.; Ajayan, P. M.; Lou, J. Large-area vapor-phase growth and characterization of MoS₂ atomic layers on a SiO₂ substrate. *Small (Weinheim an der Bergstrasse, Germany)* 2012, 8, 966-71.
111. Nam, H.; Wi, S.; Rokni, H.; Chen, M.; Priessnitz, G.; Lu, W.; Liang, X. MoS₂ Transistors Fabricated via Plasma-Assisted Nanoprinting of Few-Layer-MoS₂ Flakes into Large-Area Arrays. *ACS Nano* 2013, 130622103851005.
112. Zhang, Y.; Ye, J.; Matsushashi, Y.; Iwasa, Y. Ambipolar MoS₂ thin flake transistors. *Nano letters* 2012, 12, 1136-40.
113. Bao, W.; Cai, X.; Kim, D.; Sridhara, K.; Fuhrer, M. S. High mobility ambipolar MoS₂ field-effect transistors: Substrate and dielectric effects. *Applied Physics Letters* 2013, 102, 042104.
114. Perera, M.; Lin, M.; Chuang, H. Improved Carrier Mobility in Few-Layer MoS₂ Field-Effect Transistors with Ionic-Liquid Gating. *ACS ...* 2013.
115. Dolui, K.; Rungger, I.; Sanvito, S. Origin of the n-type and p-type conductivity of MoS₂ monolayers on a SiO₂ substrate. *Physical Review B* 2013, 87, 165402.
116. Peelaers, H.; Van de Walle, C. G. Effects of strain on band structure and effective masses in MoS₂. *Physical Review B* 2012, 86, 241401.
117. Shi, H.; Pan, H.; Zhang, Y.-W.; Yakobson, B. I. Quasiparticle band structures and optical properties of strained monolayer MoS₂ and WS₂. *Physical Review B* 2013, 87, 155304.
118. Conley, H.; Wang, B.; Ziegler, J. Bandgap Engineering of Strained Monolayer and Bilayer MoS₂. *arXiv preprint arXiv: ...* 2013, 1-4.
119. Mohammad Tabatabaei, S.; Noei, M.; Khaliji, K.; Pourfath, M.; Fathipour, M. A first-principles study on the effect of biaxial strain on the ultimate

- performance of monolayer MoS₂-based double gate field effect transistor. *Journal of Applied Physics* 2013, 113, 163708.
120. Hui, Y. Y.; Liu, X.; Jie, W.; Chan, N. Y.; Hao, J.; Hsu, Y.-T.; Li, L.-J.; Guo, W.; Lau, S. P. Exceptional Tunability of Band Energy in Compressively Strained Tri-Layer MoS₂ Sheet. *ACS nano* 2013.
 121. He, K.; Poole, C.; Mak, K. F.; Shan, J. Experimental Demonstration of Continuous Electronic Structure Tuning via Strain in Atomically Thin MoS₂. *Nano letters* 2013, 13, 2931-2936.
 122. Castellanos-Gomez, A.; Roldán, R. Local strain engineering in atomically thin MoS₂. *arXiv preprint arXiv: ...* 2013, 1-16.
 123. Wang, G.; Zhu, C.; Liu, B.; Marie, X. Strain tuning of optical emission energy and polarization in monolayer and bilayer MoS₂. *arXiv preprint arXiv: ...* 2013, 1-5.
 124. Komsa, H.-P.; Krasheninnikov, A. V. Two-Dimensional Transition Metal Dichalcogenide Alloys: Stability and Electronic Properties. *The Journal of Physical Chemistry Letters* 2012, 3, 3652-3656.
 125. Chen, Y.; Xi, J.; Dumcenco, D. O.; Liu, Z.; Suenaga, K.; Wang, D.; Shuai, Z.; Huang, Y. S.; Xie, L. Tunable band gap photoluminescence from atomically thin transition-metal dichalcogenide alloys. *ACS Nano* 2013, 7, 4610-6.
 126. Tsai, D.-S.; Liu, K.-K.; Lien, D.-H.; Tsai, M.-L.; Kang, C.-F.; Lin, C.-A.; Li, L.-J.; He, J.-H. Few-Layer MoS₂ with High Broadband Photogain and Fast Optical Switching for Use in Harsh Environments. *ACS nano* 2013.
 127. van der Zande, A.; Hone, J. Optical materials: Inspired by strain. *Nature Photonics* 2012, 6, 804-806.

128. Gaur, A. P. S.; Sahoo, S.; Ahmadi, M.; Guinel, M. J.-F.; Gupta, S. K.; Pandey, R.; Dey, S. K.; Katiyar, R. S. Optical Properties and Raman Studies of Partially Edge Terminated Vertically Aligned Nanocrystalline MoS₂ Thin Film. *arXiv preprint arXiv: ...* 2013, 1-19.
129. Schuller, J. A.; Karaveli, S.; Schiros, T.; He, K.; Yang, S.; Kymissis, I.; Shan, J.; Zia, R. Orientation of luminescent excitons in layered nanomaterials. *Nat Nanotechnol* 2013, 8, 271-6.
130. Sallen, G.; Bouet, L.; Marie, X.; Wang, G.; Zhu, C. R.; Han, W. P.; Lu, Y.; Tan, P. H.; Amand, T.; Liu, B. L.; Urbaszek, B. Robust optical emission polarization in MoS₂ monolayers through selective valley excitation. *Physical Review B* 2012, 86, 081301.
131. Alkis, S.; Oztas, T.; Aygun, L. E.; Bozkurt, F.; Okay, A. K.; Ortac, B. Thin film MoS₂ nanocrystal based ultraviolet photodetector. *Optics express* 2012, 20, 21815-20.
132. Mak, K. F.; He, K.; Lee, C.; Lee, G. H.; Hone, J.; Heinz, T. F.; Shan, J. Tightly bound trions in monolayer MoS₂. *Nat Mater* 2013, 12, 207-11.
133. Balendhran, S.; Ou, J. Z.; Bhaskaran, M.; Sriram, S.; Ippolito, S.; Vasic, Z.; Kats, E.; Bhargava, S.; Zhuiykov, S.; Kalantar-Zadeh, K. Atomically thin layers of MoS₂ via a two step thermal evaporation-exfoliation method. *Nanoscale* 2012, 4, 461-6.
134. Ji, Q.; Zhang, Y.; Gao, T.; Zhang, Y.; Ma, D.; Liu, M.; Chen, Y.; Qiao, X.; Tan, P.-H.; Kan, M.; Feng, J.; Sun, Q.; Liu, Z. Epitaxial Monolayer MoS₂ on Mica with Novel Photoluminescence. *Nano Letters* 2013, 13, 3870-3877.
135. Shi, Y.; Zhou, W.; Lu, A. Y.; Fang, W.; Lee, Y. H.; Hsu, A. L.; Kim, S. M.; Kim, K. K.; Yang, H. Y.; Li, L. J.; Idrobo, J. C.; Kong, J. van der Waals

- epitaxy of MoS(2) layers using graphene as growth templates. *Nano Lett* 2012, 12, 2784-91.
136. Wu, S.; Huang, C.; Aivazian, G.; Ross, J. S. J.; Cobden, D. H.; Xu, X. Vapor-solid growth of high optical quality MoS₂ monolayers with near-unity valley polarization. *ACS nano* 2013, 7, 2768-2772.
 137. Sercombe, D.; Schwarz, S.; Del Pozo-Zamudio, O.; Liu, F.; Robinson, B. J.; Chekhovich, E. A.; Tartakovskii, I. I.; Kolosov, O.; Tartakovskii, A. I. Optical investigation of the natural electron doping in thin MoS₂ films deposited on dielectric substrates. *arXiv preprint arXiv:1304.7221* 2013, 11.
 138. Tongay, S.; Zhou, J.; Ataca, C.; Liu, J.; Kang, J. S.; Matthews, T. S.; You, L.; Li, J.; Grossman, J. C.; Wu, J. Broad-Range Modulation of Light Emission in Two-Dimensional Semiconductors by Molecular Physisorption Gating. *Nano letters* 2013.
 139. Buscema, M.; Barkelid, M.; Zwiller, V.; van der Zant, H. S. J.; Steele, G. a.; Castellanos-Gomez, A. Large and tunable photothermoelectric effect in single-layer MoS₂. *Nano letters* 2013, 13, 358-63.
 140. Ramasubramaniam, A. Large excitonic effects in monolayers of molybdenum and tungsten dichalcogenides. *Physical Review B* 2012, 86, 115409.
 141. Feng, J.; Qian, X.; Huang, C.-W.; Li, J. Strain-engineered artificial atom as a broad-spectrum solar energy funnel. *Nature Photonics* 2012, 6, 866-872.
 142. Cao, T.; Wang, G.; Han, W.; Ye, H.; Zhu, C.; Shi, J.; Niu, Q.; Tan, P.; Wang, E.; Liu, B.; Feng, J. Valley-selective circular dichroism of monolayer molybdenum disulphide. *Nature communications* 2012, 3, 887.
 143. Li, H.; Lu, G.; Yin, Z.; He, Q.; Li, H.; Zhang, Q.; Zhang, H. Optical identification of single- and few-layer MoS(2) sheets. *Small* 2012, 8, 682-6.

144. Late, D. J.; Liu, B.; Matte, H. S. S. R.; Rao, C. N. R.; Dravid, V. P. Rapid Characterization of Ultrathin Layers of Chalcogenides on SiO₂/Si Substrates. *Advanced Functional Materials* 2012, 22, 1894-1905.
145. Wang, Y. Y.; Gao, R. X.; Ni, Z. H.; He, H.; Guo, S. P.; Yang, H. P.; Cong, C. X.; Yu, T. Thickness identification of two-dimensional materials by optical imaging. *Nanotechnology* 2012, 23, 495713.
146. Benameur, M. M.; Radisavljevic, B.; Heron, J. S.; Sahoo, S.; Berger, H.; Kis, A. Visibility of dichalcogenide nanolayers. *Nanotechnology* 2011, 22, 125706.
147. Liu, H.; Neal, A. T.; Ye, P. D. Channel length scaling of MoS₂ MOSFETs. *ACS nano* 2012, 6, 8563-9.
148. Wu, S.; Ross, J. S.; Liu, G.-B.; Aivazian, G.; Jones, A.; Fei, Z.; Zhu, W.; Xiao, D.; Yao, W.; Cobden, D.; Xu, X. Electrical tuning of valley magnetic moment through symmetry control in bilayer MoS₂. *Nature Physics* 2013, 9, 149-153.
149. Late, D. J.; Liu, B.; Matte, H. S. S. R.; Dravid, V. P.; Rao, C. N. R. Hysteresis in single-layer MoS₂ field effect transistors. *ACS nano* 2012, 6, 5635-41.
150. Lee, H. S.; Min, S.-W.; Park, M. K.; Lee, Y. T.; Jeon, P. J.; Kim, J. H.; Ryu, S.; Im, S. MoS₂ nanosheets for top-gate nonvolatile memory transistor channel. *Small (Weinheim an der Bergstrasse, Germany)* 2012, 8, 3111-5.
151. Yin, Z.; Li, H.; Li, H.; Jiang, L.; Shi, Y.; Sun, Y.; Lu, G.; Zhang, Q.; Chen, X.; Zhang, H. Single-layer MoS₂ phototransistors. *ACS Nano* 2012, 6, 74-80.
152. O'Neill, A.; Khan, U.; Coleman, J. N. Preparation of High Concentration Dispersions of Exfoliated MoS₂ with Increased Flake Size. *Chemistry of Materials* 2012, 24, 2414-2421.

153. Zeng, Z.; Yin, Z.; Huang, X.; Li, H.; He, Q.; Lu, G.; Boey, F.; Zhang, H. Single-layer semiconducting nanosheets: high-yield preparation and device fabrication. *Angewandte Chemie* 2011, 50, 11093-7.
154. Gacem, K.; Boukhicha, M.; Chen, Z.; Shukla, A. High quality 2D crystals made by anodic bonding: a general technique for layered materials. *Nanotechnology* 2012, 23, 505709.
155. Dines, M. B. Intercalation in layered compounds. *Journal of Chemical Education* 1974, 51, 221.
156. Coleman, J. N.; Lotya, M.; O'Neill, A.; Bergin, S. D.; King, P. J.; Khan, U.; Young, K.; Gaucher, A.; De, S.; Smith, R. J.; Shvets, I. V.; Arora, S. K.; Stanton, G.; Kim, H.-Y.; Lee, K.; Kim, G. T.; Duesberg, G. S.; Hallam, T.; Boland, J. J.; Wang, J. J.; Donegan, J. F.; Grunlan, J. C.; Moriarty, G.; Shmeliov, A.; Nicholls, R. J.; Perkins, J. M.; Grieveson, E. M.; Theuwissen, K.; McComb, D. W.; Nellist, P. D.; Nicolosi, V. Two-Dimensional Nanosheets Produced by Liquid Exfoliation of Layered Materials. *Science* 2011, 331, 568-571.
157. Smith, R. J.; King, P. J.; Lotya, M.; Wirtz, C.; Khan, U.; De, S.; O'Neill, A.; Duesberg, G. S.; Grunlan, J. C.; Moriarty, G. Large-Scale Exfoliation of Inorganic Layered Compounds in Aqueous Surfactant Solutions. *Advanced materials* 2011, 23, 3944-3948.
158. Yao, Y.; Lin, Z.; Li, Z.; Song, X.; Moon, K.-S.; Wong, C.-p. Large-scale production of two-dimensional nanosheets. *Journal of Materials Chemistry* 2012, 22, 13494.

159. King, L. A.; Zhao, W.; Chhowalla, M.; Riley, D. J.; Eda, G. Photoelectrochemical properties of chemically exfoliated MoS₂. *Journal of Materials Chemistry A* 2013, 1, 8935.
160. Liu, J.; Zeng, Z.; Cao, X.; Lu, G.; Wang, L. H.; Fan, Q. L.; Huang, W.; Zhang, H. Preparation of MoS₂ -Polyvinylpyrrolidone Nanocomposites for Flexible Nonvolatile Rewritable Memory Devices with Reduced Graphene Oxide Electrodes. *Small* 2012, 3517-3522.
161. Castellanos-Gomez, a.; Barkelid, M.; Goossens, a. M.; Calado, V. E.; van der Zant, H. S. J.; Steele, G. a. Laser-thinning of MoS₂: on demand generation of a single-layer semiconductor. *Nano letters* 2012, 12, 3187-92.
162. Lu, X.; Utama, M. I. B.; Zhang, J.; Zhao, Y.; Xiong, Q. Layer-by-Layer Thinning of MoS₂ by Thermal Annealing. *Nanoscale* 2013.
163. Liu, Y.; Nan, H.; Wu, X.; Pan, W.; Wang, W.; Bai, J.; Zhao, W.; Sun, L.; Wang, X.; Ni, Z. Layer-by-Layer Thinning of MoS₂ by Plasma. *ACS nano* 2013.
164. Kong, D.; Wang, H.; Cha, J. J.; Pasta, M.; Koski, K. J.; Yao, J.; Cui, Y. Synthesis of MoS₂ and MoSe₂ films with vertically aligned layers. *Nano Lett* 2013, 13, 1341-7.
165. Yu, Y.; Li, C.; Liu, Y.; Su, L.; Zhang, Y.; Cao, L. Controlled Scalable Synthesis of Uniform, High-Quality Monolayer and Few-layer MoS₂ Films. *Scientific reports* 2013, 3, 1866.
166. Zhou, W.; Zou, X.; Najmaei, S.; Liu, Z.; Shi, Y.; Kong, J.; Lou, J.; Ajayan, P. M.; Yakobson, B. I.; Idrobo, J. C. Intrinsic structural defects in monolayer molybdenum disulfide. *Nano Lett* 2013, 13, 2615-22.

167. Zou, X.; Liu, Y.; Yakobson, B. I. Predicting dislocations and grain boundaries in two-dimensional metal-disulfides from the first principles. *Nano Lett* 2013, 13, 253-8.
168. Zhou, W.; Zou, X.; Najmaei, S.; Liu, Z.; Shi, Y.; Kong, J.; Lou, J.; Ajayan, P. M.; Yakobson, B. I.; Idrobo, J.-C. Intrinsic Structural Defects in Monolayer Molybdenum Disulfide. *Nano letters* 2013.
169. Ivanovskaya, V.; Zobelli, A.; Gloter, A.; Brun, N.; Serin, V.; Colliex, C. Ab initio study of bilateral doping within the MoS₂-NbS₂ system. *Physical Review B* 2008, 78, 134104.
170. Dolui, K.; Rungger, I. Ab-initio study on the possible doping strategies for MoS₂ monolayers. *arXiv preprint arXiv: ...* 2013, 1-9.
171. Chang, J.; Larentis, S.; Tutuc, E.; Register, L. F.; Banerjee, S. K. Atomistic simulation of doping by adatoms in monolayer MoS₂. *arXiv preprint arXiv:1305.7162* 2013, 1-13.
172. Noh, J.-y.; Park, M.; Kim, Y.-s.; Kim, H. Stability and dopability of native defects and group-V and -VII impurities in single-layer MoS₂. 2013, 1-12.
173. Sun, Q.-Q.; Li, Y.-J.; He, J.-L.; Yang, W.; Zhou, P.; Lu, H.-L.; Ding, S.-J.; Wei Zhang, D. The physics and backward diode behavior of heavily doped single layer MoS₂ based p-n junctions. *Applied Physics Letters* 2013, 102, 093104.
174. Chang, J.; Register, L.; Banerjee, S. Atomistic Full-Band Simulations of Monolayer MoS₂ Transistors. *arXiv preprint arXiv:1304.2990* 2013, 1, 13-15.
175. Fang, H.; Tosun, M.; Seol, G.; Chang, T. C.; Takei, K.; Guo, J.; Javey, A. Degenerate n-Doping of Few-Layer Transition Metal Dichalcogenides by Potassium. *Nano letters* 2013, 13, 1991-5.

176. Yoon, Y.; Ganapathi, K.; Salahuddin, S. How good can monolayer MoS₂ transistors be? *Nano letters* 2011, 11, 3768-73.
177. ALAM, K.; LAKE, R. Monolayer MoS₂ Transistors Beyond the Technology Road Map. *IEEE transactions on electron devices* 2012, 59, 3250-3254.
178. Lembke, D.; Kis, A. Breakdown of high-performance monolayer MoS₂ transistors. *ACS nano* 2012, 6, 10070-5.
179. Liu, H.; Gu, J.; Ye, P. MoS₂ Nanoribbon Transistors: Transition from Depletion-mode to Enhancement-mode by Channel Width Trimming. *arXiv preprint arXiv:1206.1020* 2012, 2-4.
180. Liu, L.; Kumar, S. B.; Ouyang, Y.; Guo, J. Performance Limits of Monolayer Transition Metal Dichalcogenide Transistors. *IEEE Transactions on Electron Devices* 2011, 58, 3042-3047.
181. Das, S.; Appenzeller, J. Where Does the Current Flow in Two-Dimensional Layered Systems? *Nano Lett* 2013, 13, 3396-3402.
182. Bertolazzi, S.; Krasnozhon, D.; Kis, A. Nonvolatile memory cells based on MoS₂/graphene heterostructures. *ACS Nano* 2013, 7, 3246-52.
183. Chang, H.-Y.; Yang, S.; Lee, J.; Tao, L.; Hwang, W.-S.; Jena, D.; Lu, N.; Akinwande, D. High-Performance, Highly Bendable MoS₂ Transistors with High-K Dielectrics for Flexible Low-Power Systems. *ACS nano* 2013, 7, 5446-5452.
184. Jariwala, D.; Sangwan, V. K.; Late, D. J.; Johns, J. E.; Dravid, V. P.; Marks, T. J.; Lauhon, L. J.; Hersam, M. C. Band-like transport in high mobility unencapsulated single-layer MoS₂ transistors. *Applied Physics Letters* 2013, 102, 173107.

185. Popov, I.; Seifert, G.; Tománek, D. Designing Electrical Contacts to MoS₂ Monolayers: A Computational Study. *Physical Review Letters* 2012, 108, 156802.
186. Kim, S.; Konar, A.; Hwang, W.-S.; Lee, J. H.; Lee, J.; Yang, J.; Jung, C.; Kim, H.; Yoo, J.-B.; Choi, J.-Y.; Jin, Y. W.; Lee, S. Y.; Jena, D.; Choi, W.; Kim, K. High-mobility and low-power thin-film transistors based on multilayer MoS₂ crystals. *Nature communications* 2012, 3, 1011.
187. Radisavljevic, B.; Kis, A. Mobility engineering and a metal-insulator transition in monolayer MoS₂. *Nature materials* 2013.
188. Liu, H.; Ye, P. MoS₂ dual-gate mosfet with atomic-layer-deposited Al₂O₃ as top-gate dielectric. *arXiv preprint arXiv:1112.4397* 2011, 33, 546-548.
189. Chan, M. Y.; Komatsu, K.; Li, S. L.; Xu, Y.; Darmawan, P.; Kuramochi, H.; Nakaharai, S.; Aparecido-Ferreira, A.; Watanabe, K.; Taniguchi, T.; Tsukagoshi, K. Suppression of thermally activated carrier transport in atomically thin MoS₂ on crystalline hexagonal boron nitride substrates. *Nanoscale* 2013, 5, 9572-6.
190. Chang, H.-Y.; Yang, S.; Lee, J.; Tao, L.; Hwang, W.-S.; Jena, D.; Lu, N.; Akinwande, D. High-Performance, Highly Bendable MoS₂ Transistors with High-K Dielectrics for Flexible Low-Power Systems. *ACS Nano* 2013, 7, 5446-5452.
191. Radisavljevic, B.; Whitwick, M. B.; Kis, A. Integrated circuits and logic operations based on single-layer MoS₂. *ACS nano* 2011, 5, 9934-8.
192. Wang, H.; Yu, L.; Lee, Y.-H.; Shi, Y.; Hsu, A.; Chin, M. L.; Li, L.-J.; Dubey, M.; Kong, J.; Palacios, T. Integrated circuits based on bilayer MoS₂ transistors. *Nano letters* 2012, 12, 4674-80.

193. Ma, Y.; Dai, Y.; Guo, M.; Niu, C.; Huang, B. Graphene adhesion on MoS₂ monolayer: an ab initio study. *Nanoscale* 2011, 3, 3883-7.
194. Huang, J.; Somu, S.; Busnaina, A. A molybdenum disulfide/carbon nanotube heterogeneous complementary inverter. *Nanotechnology* 2012, 23, 335203.
195. Keong Koh, E. W.; Chiu, C. H.; Lim, Y. K.; Zhang, Y.-W.; Pan, H. Hydrogen adsorption on and diffusion through MoS₂ monolayer: First-principles study. *International Journal of Hydrogen Energy* 2012, 37, 14323-14328.
196. Cantalini, C.; Giancaterini, L.; Donarelli, M. NO₂ response to few-layers MoS₂. *Tagungsband* 2012, 1656-1659.
197. He, Q.; Zeng, Z.; Yin, Z.; Li, H.; Wu, S.; Huang, X.; Zhang, H. Fabrication of flexible MoS₂ thin-film transistor arrays for practical gas-sensing applications. *Small (Weinheim an der Bergstrasse, Germany)* 2012, 8, 2994-9.
198. Li, H.; Yin, Z.; He, Q.; Li, H.; Huang, X.; Lu, G.; Fam, D. W. H.; Tok, A. I. Y.; Zhang, Q.; Zhang, H. Fabrication of single- and multilayer MoS₂ film-based field-effect transistors for sensing NO at room temperature. *Small (Weinheim an der Bergstrasse, Germany)* 2012, 8, 63-7.
199. Late, D. J.; Huang, Y. K.; Liu, B.; Acharya, J.; Shirodkar, S. N.; Luo, J.; Yan, A.; Charles, D.; Waghmare, U. V.; Dravid, V. P.; Rao, C. N. Sensing behavior of atomically thin-layered MoS₂ transistors. *ACS Nano* 2013, 7, 4879-91.
200. Perkins, F. K.; Friedman, a. L.; Cobas, E.; Campbell, P. M.; Jernigan, G. G.; Jonker, B. T. Chemical vapor sensing with monolayer MoS₂. *Nano letters* 2013, 13, 668-73.
201. Averett, L. E.; Schoenfisch, M. H. Atomic force microscope studies of fibrinogen adsorption. *The Analyst* 2010, 135, 1201-9.

202. Albrecht, T. R.; Grütter, P.; Horne, D.; Rugar, D. Frequency modulation detection using high-Q cantilevers for enhanced force microscope sensitivity. *Journal of Applied Physics* 1991, 69, 668.
203. Binnig, G.; Quate, C. F.; Gerber, C. Atomic force microscope. *Phys Rev Lett* 1986, 56, 930-933.
204. Binnig, G. K. Atomic force microscope and method for imaging surfaces with atomic resolution. Google Patents: 1988.
205. Giessibl, F. J. Advances in atomic force microscopy. *Reviews of Modern Physics* 2003, 75, 949-983.
206. Meyer, E. Atomic force microscopy. *Progress in Surface Science* 1992, 41, 3-49.
207. García, R.; San Paulo, A. Attractive and repulsive tip-sample interaction regimes in tapping-mode atomic force microscopy. *Physical Review B* 1999, 60, 4961-4967.
208. Melitz, W.; Shen, J.; Kummel, A. C.; Lee, S. Kelvin probe force microscopy and its application. *Surface Science Reports* 2011, 66, 1-27.
209. Meyer, G.; Amer, N. M. Novel optical approach to atomic force microscopy. *Applied Physics Letters* 1988, 53, 1045.
210. García, R. Dynamic atomic force microscopy methods. *Surface Science Reports* 2002, 47, 197-301.
211. Giessibl, F. Forces and frequency shifts in atomic-resolution dynamic-force microscopy. *Physical Review B* 1997, 56, 16010-16015.
212. Goodman, F.; Garcia, N. Roles of the attractive and repulsive forces in atomic-force microscopy. *Physical Review B* 1991, 43, 4728-4731.
213. Chasiotis, I. *Atomic Force Microscopy in Solid Mechanics*. 2008; p 409-444.

214. Cappella, B.; Dietler, G. Force-distance curves by atomic force microscopy. *Surface Science Reports* 1999, 34, 1-104.
215. Weisenhorn, a. L.; Hansma, P. K.; Albrecht, T. R.; Quate, C. F. Forces in atomic force microscopy in air and water. *Applied Physics Letters* 1989, 54, 2651.
216. Ohnesorge, F.; Binnig, G. True atomic resolution by atomic force microscopy through repulsive and attractive forces. *Science (New York, N.Y.)* 1993, 260, 1451-6.
217. Valdrè, G. Electric Force Microscopy. *Imaging & Microscopy* 2006, 8, 44-46.
218. Hartmann, U. Magnetic Force Microscopy. *Annual Review of Materials Science* 1999, 29, 53-87.
219. Weaver, J. M. R. High resolution atomic force microscopy potentiometry. *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures* 1991, 9, 1559.
220. Yasutake, M.; Aoki, D.; Fujihira, M. Surface potential measurements using the Kelvin probe force microscope. *Thin Solid Films* 1996, 273, 279-283.
221. Nonnenmacher, M.; O'Boyle, M. P.; Wickramasinghe, H. K. Kelvin probe force microscopy. *Applied Physics Letters* 1991, 58, 2921.
222. Blott, B. H.; Lee, T. J. A two frequency vibrating capacitor method for contact potential difference measurements. *Journal of Physics E: Scientific Instruments* 1969, 2, 785-788.
223. Berger, R.; Butt, H.-J.; Retschke, M. B.; Weber, S. a. L. Electrical modes in scanning probe microscopy. *Macromolecular rapid communications* 2009, 30, 1167-78.

224. Glatzel, T.; Sadewasser, S.; Lux-Steiner, M. C. Amplitude or frequency modulation-detection in Kelvin probe force microscopy. *Applied Surface Science* 2003, 210, 84-89.
225. Loppacher, C.; Zerweck, U.; Teich, S.; Beyreuther, E.; Otto, T.; Grafström, S.; Eng, L. M. FM demodulated Kelvin probe force microscopy for surface photovoltage tracking. *Nanotechnology* 2005, 16, S1-S6.
226. Guo, L. Q.; Zhao, X. M.; Bai, Y.; Qiao, L. J. Water adsorption behavior on metal surfaces and its influence on surface potential studied by in situ SPM. *Applied Surface Science* 2012, 258, 9087-9091.
227. Yue, Q.; Shao, Z.; Chang, S.; Li, J. Adsorption of gas molecules on monolayer MoS₂ and effect of applied electric field. *Nanoscale Res Lett* 2013, 8, 425.
228. Hao, G.; Huang, Z.; Liu, Y.; Qi, X.; Ren, L.; Peng, X.; Yang, L.; Wei, X.; Zhong, J. Electrostatic properties of few-layer MoS₂ films. *AIP Advances* 2013, 3, 042125.