Toward Highly Trustable Miniaturized Semiconductor Gas Sensors

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Directed supramolecular assembly is blazing a new trial for promoting the consistency level of micro- and nanoscale chemical sensing devices as well as their derived data quality.

Solid-state gas sensors have exponentially evolved since their invention in 1962 by Seiyama and coworkers. Resistive changes in sensitive materials when exposed to target agents have now been the most commonly utilized fundamental principle. Early systems were derived from primitive Taguchi-type sensors with subsequent iterations moving to sophisticated low power micro/nano-electro-mechanical-systems (MEMS/NEMS) compatible with complementary metal oxide semiconductor (CMOS). Gold standards between the 1970s and 2000s were based on ceramic substrate oxide sensors, which occupy sizable market share owing to their robustness of the technology, easy for batch manufacturing and low cost. These systems typically suffer from large power dissipation (~0.5-1 W) because many metal oxide semiconductors that are used as gas responding elements require elevated temperatures (150~350 ℃) to activate the carrier mediated sensing mechanism, thus restricting their usage in battery-driven applications. Such limitations have been circumvented by micromachined silicon substrate technologies, where suspended thermal isolation structure design has reduced

the heat conduction and radiation, facilitating milliwatt level power consumption. The post monolithic integration of CMOS transducing circuitry further forms the best performance-power tradeoff and makes such a platform ideal for portable gas sensory systems, thus offering much wider applicability.

With the popularity of the Internet of things (IoT) in civilian national security, healthcare and real-time environmental monitoring, especially the dangerous chemical industry, the fast-growing scale of gas sensing network promote current on-chip systems to be new treasures in the market. However, the explosive demand has not been accompanied by persistent research enthusiasm and large profit. Figure 1 displays the timeline showing the milestones and device evolutionary process related to semiconductor gas sensors. Remarkably, judging from the number of publications, the attention heat of this field showed a downwards trend. Meanwhile, in the last few years, the procurement of MEMS-based semiconductor gas sensors in the leakage accident prone industry of China, announced by SINOPEC-CNPC-CNOOC Emergency Headquarters, has always been low, less spectacular and not much of a surprise. It seems that things fall short of expectation, and front-line workers do not recognize this so-called revolutionary technique.

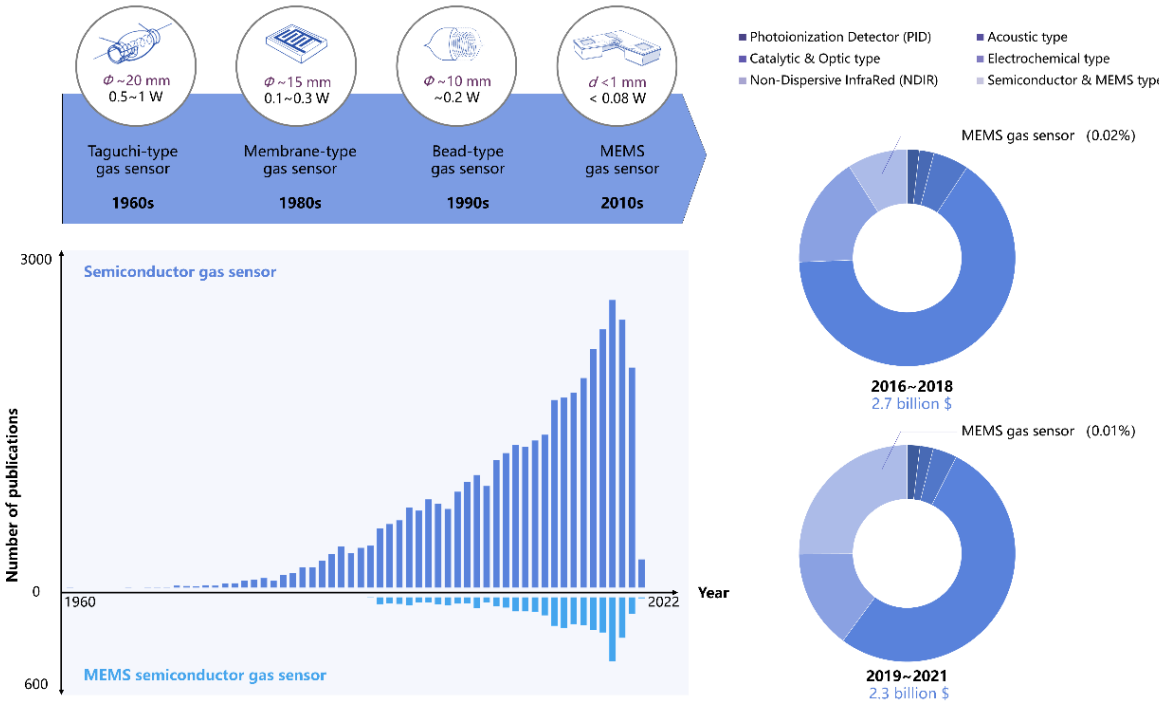

Figure 1. Academic and regional market developing trends of semiconductor gas sensors.

The pain points

An important challenge holding back the practical applications of micro/nano gas sensors is their inevitable run-to-run and device-to-device variations in the sensing performance. Unlike fully mechanical transducers, combo gas sensors consist of not only physical units but also a large number of interfacial materials that are sensitive to molecule-specific interactions, which need to be integrated with physical components for comprehensive monitoring of the environment. As the feature size shrinks to the micro- and nanoscale, the accurate loading of sensing materials onto the device electrodes at desired locations becomes colossally difficult. Any concomitant systemic, random and dynamic small changes in the configuration or layout could bring adverse effects, resulting in unsteady sensing signals[1]. For instance, the resistance, conductance, threshold voltage, etc., often decline or drift from one sensing cycle to the next, from one device to another, making the detection response unrepeatable even under the same analyte concentration. These variations distort the classical sensitivity formula and negatively affect the quantitative analysis reliability. The generated chaos seriously hampers the subsequent data mining.

For a long period, great majority of microsensor studies neatly sidestepped this inconvenient dilemma, intentionally or unintentionally, instead they are accustomed to focus primarily on new material/device design for achieving preferable individual performance that may be lack of reliability and repeatability in large scale applications. The comprehensive considerations on correlations between on-chip sensing materials and mini-devices, *i.e.*, micro to nanoscale heterogeneous integration issues, have yet to be taken seriously. During the novelty retrieval *via* the Web of Science search engine, we set “semiconductor gas sensor” and “micro semiconductor gas sensor AND on chip integration” as search topics, which shows that the number of publications is dramatically reduced from 38615 down to 35. Actually, the same thing is happening in contemporary MEMS chemiresistor industrialization.

Current strategies

In the last few years, we have visited several local enterprises that specialized in manufacturing complete sets of semiconductor gas sensors. It was an impressive scenario: hundreds of assembly workers used tiny brushes to paint the sensing materials onto the

electrode substrate. The qualified rate of samples is heavily dependent on artificial skills, generating waste products easily. Even if they attain the standard of leave factory on the performance criterion, one-by-one and time-consuming sensitivity calibration remains inescapable.

State-of-the-art automatic parallel inkjet printing, flesh imprinting and dip-pen nanolithography provide efficient paths for the precise manipulation and placement of sensing materials in circuits[2]. These tools significantly lower the degree of human participation and improve the lot-to-lot consistency, with the coefficient of variation (CV=τ/υ, defined as the ratio of standard deviation τ and mean υ) dropping from more than 60% to under 15%. However, elsewhere, chemical additives that reduce the solute slurry viscosity to suppress the coffee-ring effect are still disturbing the intrinsic structural integrity of the materials as well as bringing contaminants. Furthermore, the limited pattern resolution of printed dots or lines with feature sizes of tens or even hundreds of micrometers is another important issue for ink-based integration protocols.

To achieve more uniform sensitive layer with CV below 5%, some fledgling tech startups and foundry vendors are inclined to adopt optical lithography patterning coupled with physical sedimentation procedures[3], such as atomic vapor deposition and magnetron sputtering, which are most suitable for the current MEMS chip processing line. However, compared with prevalent wet-chemical fabrication methods, micromachining film integration generates relatively limited categories of sensitive layer architectures. In addition, as the three-dimensional (3D) texture features become more sophisticated and the dimension size continues to evolve from 100 nm to 50 nm and sub10 nm, the process technology approaches the physical limit. Then, not only is the technology more difficult to implement and the required equipment more complex, but the cost of developing chips is also increasing rapidly. The latest systems reportedly cost more than 100 million dollars for 16 nm node chip manufacturing. Obviously, the economic benefit that performance doubles or more every two years at the same price will no longer exist, which is produced by Moore's law.

Emerging opportunities

The self-assembly of block copolymers (BCPs) brings the hope of offering sub 10 nm

resolution without the need for lithographic guidance and thus enhancing process flexibility. BCP consists of two or more chemically distinct monomer chains, which repel each other and result in microphase separation to form periodic patterns with periods of just a few nanometers. The self-assembled membrane structure may have a diverse library of topographies, involving intercalated lamellae, cylinder or sphere arrays, gyroids, and complex iterative multilayer structures. The block Flory-Huggins χ (polymer-to-polymer interaction) parameter and their volume fraction contribute to the assembly dynamics and morphology. Additionally, incorporating external influences (*e.g.*, annealing by elevated temperature or exposure to a solvent vapor environment) or constraints imposed by a prepatterned substrate could bring more variety to textures.

Thus, strategies to infiltrate, deposit and simultaneously co-assemble with inorganic material precursors by using subtle BCP surface topography open a powerful paradigm to integrate ordered semiconductors on chips in the microcosmic regime at low prices. The feasibility of employing this concept to the fabrication of gas sensing devices has been forecasted and verified during the past years[4]. A typical, recent case was from Deng and coworkers in 2020[5]. By manipulating the interfacial electrostatic assembly of amphiphilic poly(ethylene oxide)-block-polystyrene (PEO-*b*-PS) and hydrated silicotungstic acid ($H_4SiW_{12}O_{40}\cdot 15H_2O$), a 3D WO_3 semiconductor nanowire stack framework with equal spacing and orthogonal arrangement can be directly synthesized.

Nonetheless, this was just the beginning of a trend in BCP-templated sensing nanostructure research. Current academic achievement requires separate multi-steps for the growth, harvesting and transfer of semiconducting materials for subsequent functionalities. How to develop a rapid, *in situ*, precise positioning and high-resolution integration method for neat microdomain patterns within sensing films in localized space on a microcosmic device electrode is still a challenge. For high product conformity, controlling the long-range regularity of BCP-based routes is also the most significant concern during industrialization. Even in the manufacturing of micro/nano gas sensor chips, the defectivity (mainly disclinations and dislocations) required for a responsive membrane structure is not as stringent as that required for fin field-effect transistors (FinFETs) and computing devices.

In this regard, directed co-assembly (DCA) has been gradually raised. The most recent efforts

by means of synergetic integration with aqueous metal reduction, sequential infiltration and metal-salt inclusion based on shear alignment and/or boundary epitaxy supplemented thermal annealing process have been made to enhance uptake and overall uniformity for inorganic combination[6]. Unfortunately, high-fidelity nanodomains with desired arrangements over an arbitrarily large area have not yet been demonstrated to a great extent. The critical issue is due to the retarded equilibrium structure formation because of strong inter-block segregation when subjected to conventional hot-zone annealing processes, which commonly leads to poly-grain structures with high defect density. Improving grain size *via* annihilation of BCP assembly defects becomes a key to the eventual success of the DCA approach.

In principle, assembled stripe pattern coarsening processes follow a power law[7]: $\xi=At^{\alpha}$, where ξ is the correlation distance associated with grain size, t is annealing time, and the exponential order of α experimentally varies from 0.2 to 0.5 for thin films. The pre-factor A is generally considered to be Arrhenius-like, with a kinetic activation energy related to the defect barrier (E_b) to combine, *i.e.*, $A\sim D_0\exp(-E_b/k_BT)$. The Boltzmann factor $\exp(-E_b/k_BT)$ dominates the defect removal rate, and the diffusion coefficient D_0 depends on BCP chain diffusivity. Accordingly, the shorter the annealing duration is, the lower the energy barrier for polymer reorganization and the higher the treatment temperature approaching the tolerable upper limit of the order-to-disorder transition (T_{ODT}), making it possible to heal more defects per unit time. Briefly, the shear rates must be fast enough to break through the inherent polymer relaxation time scales.

The introduction of a field during annealing could enhance the anisotropy of grains to achieve high degrees of order in BCP thin films. Among the existing methodologies, light-induced DCA, especially laser writing based on a cold zone annealing (LZA) mechanism, with respect to electric, magnetic and shear-directed epitaxy, is an effective and versatile route to promote chain mobility for polymer self-assembly[8]. It can easily force a single grain orientation at levels close to the theoretical enthalpy minimum state. This benefits from extreme thermal gradients ($>10^3$ °C/mm) and high peak temperatures generated by local photoheating. The sharp heating gradient profiles at the disorder/order boundaries allow access to immense shear forces and massive kinetic acceleration by orders of magnitude. Motivated by the innate advantages, LZA processing enables continuous inorganic materials phase transformations at highly confined

desired locations and high compatibility with other chemically/physically lithography processes, allowing "rapid *in situ* imprint" for MEMS industrial viability. For the wafer-level large-scale continuous processing of nanostructures, parallel scanning with beam arrays or slit beams can also be supplemented.

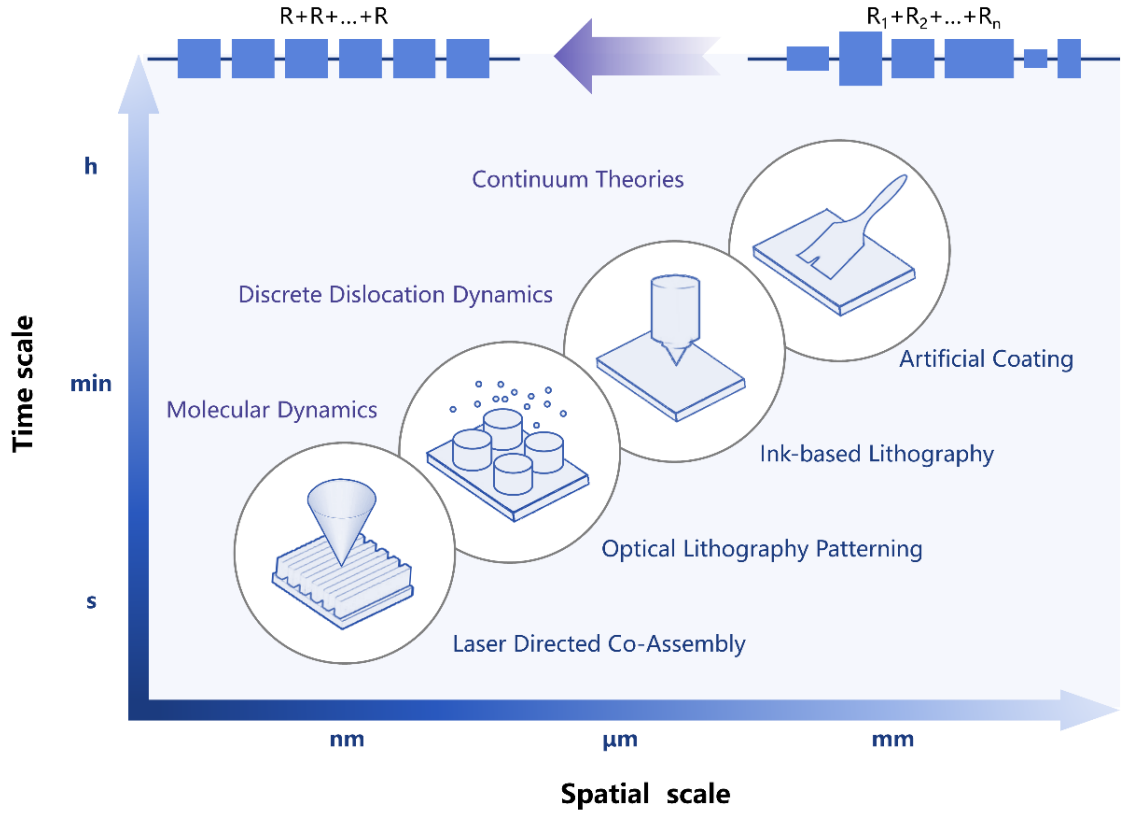

Figure 2. Evolution of materials/device integration methodologies.

The way forward

Predictably, laser-directed BCP assembly presents a golden opportunity for bridging the considerable gap between the fundamental research of miniaturized gas sensing devices and their widespread practical applications. It is believed to give a high level of control over the synergistic deviation of integrated sensing chips and help to boost data quality. Moreover, there are also opportunities for such a unique approach beyond its use in semiconductor resistors for gas detection. Area-selective nanopatterns based on laser writing could be further applied to any electrical device constructed by exceptionally low defect high-volume manufacturing-relevant architectures at scales below 10 nm, including but not limited to photonic meta-surfaces/waveguides, photovoltaics, catalysts, electronic skin and logic FETs.

In the near future, exciting avenues surrounding laser-induced BCP assembly in the fabrication of functional nanostructures will continue. Several considerable unsolved issues need to be more deeply explored: (i) energy model for capturing field response mechanisms of directed BCP co-assembly phase, including the interplay between the final inorganic semiconducting membrane morphology and interbedded residual strain during iterative assembly process; (ii) direct study of extreme near-field relaxation phenomena and dynamics of organic/inorganic co-assembly down to gaps as small as nanometers; (iii) the ability to precisely control spontaneous defect annihilation by mutual coupling to accelerate cold-zone annealing; (iv) novel synthesis strategies and architectures based on the interfacial co-assembly of BCPs, semiconductor precursors and doping elements, etc. Knowledge gained from such studies will be critical for the ultimate application of DCA to the mass production of next-generation IoT solutions.

Acknowledgements

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