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James R. Engstrom ; Andrew C. Kummel

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Preface: Special Topic on Atomic and Molecular Layer Processing: Deposition, Patterning, and Etching

James R. Engstrom[1] and Andrew C. Kummel[2]
[1]*Robert F. Smith School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, New York 14853, USA*
[2]*Department of Chemistry and Biochemistry, University of California, 9500 Gilman Dr., La Jolla, San Diego, California 92093, USA*

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Thin film processing technologies that promise atomic and molecular scale control have received increasing interest in the past several years, as traditional methods for fabrication begin to reach their fundamental limits. Many of these technologies involve at their heart phenomena occurring at or near surfaces, including adsorption, gas-surface reactions, diffusion, desorption, and re-organization of near-surface layers. Moreover many of these phenomena involve not just reactions occurring under conditions of local thermodynamic equilibrium but also the action of energetic species including electrons, ions, and hyperthermal neutrals. There is a rich landscape of atomic and molecular scale interactions occurring in these systems that is still not well understood. In this Special Topic Issue of *The Journal of Chemical Physics*, we have collected recent representative examples of work that is directed at unraveling the mechanistic details concerning atomic and molecular layer processing, which will provide an important framework from which these fields can continue to develop. These studies range from the application of theory and computation to these systems to the use of powerful experimental probes, such as X-ray synchrotron radiation, probe microscopies, and photoelectron and infrared spectroscopies. The work presented here helps in identifying some of the major challenges and direct future activities in this exciting area of research involving atomic and molecular layer manipulation and fabrication. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4975141]

This Special Topic Issue concerns fundamental aspects of issues related to what are perhaps the three most important operations used to fabricate modern microelectronic and related devices: the deposition of thin films, defining a microstructure where material is to be added or removed (patterning), and etching of thin films and/or the substrate itself. Thin film deposition encompasses a wide variety of techniques, which can be thermal or make use of plasmas, also covering a wide range of operating pressures from high vacuum to ambient and temperatures from room temperature to 1000 °C. Patterning is most often achieved using optical photolithography, employing UV light and photolithographic masks to expose light sensitive polymeric thin films, which are subsequently developed to expose a substrate in selected areas. Etching of thin films, similar to deposition, can be either thermal or make use of plasmas, and the latter is strongly preferred when fidelity is important since the plasma process can produce a directional etch, nearly perfectly reproducing the pattern defined by lithography.

The basis for most of the Si-based microelectronics, which still represents the state-of-the-art in microfabrication, can be traced to activities in or around 1959. That year Jack Kilby filed a patent describing an integrated, all-solid circuit, which was quickly followed by filings by Jean Hoerni and Robert Noyce that described a planar process that could be used to manufacture monolithic integrated circuits. These developments launched high volume Si-based microelectronics, eventually leading to the continuous innovations captured by Moore's law. That same year, Richard Feynman presented his lecture "There is plenty more room at the bottom." This celebrated lecture, largely ignored for almost 30 years, laid out a vision for where microfabrication could ultimately lead. For example, he suggests, conservatively, that storing a bit of information might "require a little cube of atoms $5 \times 5 \times 5$ that is 125 atoms" and also suggests that wires in a computing device "should be 10 to 100 atoms in diameter, and the circuits should be a few thousand Å across." He also poses a challenge, "What would happen if we could arrange the atoms one by one the way we want them," and suggests one possible route to do exactly this: "chemical synthesis," possibly "inspired by the biological phenomena in which chemical forces are used in repetitious fashion." These length scales, and indeed smaller, are where the microelectronics industry would like to go over the next several years. Many of the techniques that will be developed to reach these goals will likely be of a chemical nature, taking advantage of phenomena such as self-assembly, self-aligned, and self-limited processes. Moreover, many of these techniques, once developed, can contribute to a variety of technologies including optoelectronics, photovoltaics, displays and micro-electromechanical systems, and possibly areas such as batteries, fuel cells, and supercapacitors.

Atomic layer deposition (ALD) represents the most mature form of atomic and molecular layer processing, and it is used in the modern day manufacturing of microelectronic devices, including logic and memory. ALD experienced a substantial increase in activity, both technological and scientific, starting about in the year 2000, and it sprang directly from atomic layer epitaxy, a technique developed in the 1970s. At its heart, ALD involves sequential gas-surface reactions that go to completion as the rates of irreversible adsorption approach zero, either due to the formation of an adsorbed layer that is no longer reactive to the gas phase species, or where conditions are such that multilayer adsorption cannot occur. Thus, ALD holds strong conceptual similarities to a multitude of fields where chemisorption is important, such as heterogeneous catalysis, oxidation, and corrosion phenomena. ALD typically involves sequential exposures of a substrate to a metal or semiconducting element containing gas phase species (*aka* the thin film precursor), and a co-reactant designed to form an oxide (e.g., H_2O and O_2), a nitride (e.g., NH_3), or other compound, or possibly an elemental thin film (e.g., H_2, O_2). In some cases, the co-reactant step involves the use of plasma excitation, often to generate more reactive species such as H and O. Control of substrate temperature is important in ALD, to balance providing sufficient thermal energy for gas-surface reactions, while not promoting desorption of adsorbed species that could lead to continuous decomposition and uncontrolled growth, particularly concerning the thin film precursor. ALD has been used to deposit successfully a great variety of thin films, including oxides, nitrides, sulfides, elemental metal thin films, and many others.

Atomic layer etching (ALE—it supplanted epitaxy) and molecular layer deposition (MLD) represent more recent developments in atomic and molecular layer processing. The former technique has some similarities to ALD, but it is not the reverse of ALD in any real sense. ALE often involves a step where the thin film or substrate is exposed to a species that is often used in more conventional etching (e.g., a halogen-containing species), which forms a saturated adlayer. This adlayer is subsequently exposed, typically, to a plasma tuned to produce a flux of ions that can remove the topmost layer of the thin film via a mechanism akin to collision induced desorption or "chemical sputtering." To date, there are only a handful of examples of a purely thermal ALE process, the most notable and numerous from Steve George's group. In MLD, the goal is to use bifunctional small organic molecules to build an organic superlattice, one layer at a time, in a process similar to polymerization or to combine this chemistry with inorganic thin film precursors to construct inorganic-organic hybrids. One final example of atomic and molecular layer processing involves the deposition of thin films of small molecule organics, particularly small molecule organic semiconductors. This is also a field where there is considerable scientific and technological activity. Here, the conceptual connection with ALD is not as great, as the forces that hold these materials together are primarily van der Waals interactions. The goals remain the same however. These materials, whose building blocks are molecules, also hold promise for the formation of functional thin films in the form of ultrathin layers, superlattices, and other microstructures successfully employed with inorganic semiconductors. Learning how to control the microstructure of these materials to the molecular level can greatly enhance their opportunities to contribute to a variety of technologies, including some of those mentioned above.

This Special Topic Issue represents a snapshot of the current work in the areas of atomic and molecular layer processing, with examples that fit into the traditional areas of emphasis in *The Journal of Chemical Physics*. These include, obviously, an examination of the molecular scale phenomena occurring in these processes, which include the dynamics of chemical reactions, including adsorption, reactions between species on the surface, and diffusion including interlayer and intralayer transport. Spectroscopic techniques, including the use of probe microscopies with atomic scale resolution, can provide important details concerning the composition of the adlayers following each half cycle, such as the concentration and thermal stability of adsorbed species, which can affect the final microstructure and composition of the thin film. These processes are also in great need of molecular scale simulations to better understand a variety of phenomena, including the detailed mechanisms of the gas-surface reactions between the thin film precursor and the co-reactants with the adlayers formed after each half cycle. Atomic layer etching, in particular, can be aided greatly by simulations detailing the effects of adlayer composition and the role in incident ion energy, identity (e.g., mass), and flux concerning the thin film etching process. Ion-molecule interactions are a traditional area of emphasis in the field of chemical physics.

Technologically, the future of atomic and molecular layer processing is bright and will be even more so if improvements continue to be made. For example, concerning ALD, the worldwide market for ALD system tools grew from ~\$200 M in 2009 to \$1200 M in 2015. Some of this growth in ALD is due to the introduction of new materials, while a significant component is associated with applications in patterning, namely, self-aligned double and quadruple patterning. Semiconductor applications continue to dominate the market for ALD tools, capturing about 90%. A large driver for ALD is the introduction of truly 3D features in microelectronic devices, such as fin-FETs, wrap-around gates, and 3D NAND (non-volatile flash memory). Concerning thin film deposition tools, ALD has a unique capability to deposit thin films uniformly over complex 3D structures and will continue to be in high demand for such applications. Selective area ALD, where one deposits a thin film on one area of a substrate, but not another, defined by their chemical composition, will also enable a variety of applications but is still in need of considerable research and development. Atomic layer etching is another area that will require additional research. For example, and as we discussed above, unlike ALD, ALE often requires the use of a plasma and its associated directed flux of ions. This directionality is often desirable, except in cases where one might wish to etch a 3D feature equally, independent of the orientation of the various surfaces. Here, further development of truly thermal ALE processes is required.

The articles we have solicited for the Special Topic Issue give an excellent picture of some of the current areas of research on atomic and molecular layer processing. We hope these articles will inspire future work on this important area of technology that continues to expand, employing the techniques of the chemical physicist to help provide further understanding and develop new and exciting approaches.