Science Challenges and Research Opportunities for Plasma Applications in Microelectronics

David B. Graves[1,12], Catherine B. Labelle[2], Mark J. Kushner[3], Eray S. Aydil[4], Vincent M. Donnelly[5], Jane P. Chang[6], Peter Mayer[7], Lawrence Overzet[8], Steven Shannon[9], Shahid Rauf[10] and David N. Ruzic[11]

[1] Department of Chemical and Biological Engineering, Princeton University, Princeton, New Jersey 08540
[2] Intel Corporation, 1600 Rio Rancho Blvd SE, Rio Rancho, NM 87124
[3] Department of Electrical Engineering and Computer Science, University of Michigan, Ann Arbor, MI 48109-2122, mjkush@umich.edu
[4] Department of Chemical and Biomolecular Engineering, Tandon School of Engineering, New York University, New York 11201
[5] William A. Brookshire Department of Chemical and Biomolecular Engineering, University of Houston, Houston, Texas 77204
[6] Department of Chemical and Biomolecular Engineering, University of California Los Angeles, Los Angeles, California 90095
[7] ASML, 17075 Thornmint Court, San Diego, CA 92127
[8] Department of Electrical and Computer Engineering, The University of Texas at Dallas, Richardson, Texas 75080
[9] Department of Nuclear Engineering, North Carolina State University, Raleigh, North Carolina 27695-7909
[10] Applied Materials, Inc., 3333 Scott Blvd., Santa Clara, CA 95054, United States of America
[11] Department of Nuclear, Plasma, and Radiological Engineering, Center for Plasma-Material Interactions, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801
[12] Author to whom correspondence should be addressed.

Abstract

Low-temperature plasmas are essential to manufacturing devices in the semiconductor industry, from creating extreme ultraviolet photons used in the most advanced lithography to thin film etching, deposition, and surface modifications. It is estimated that 40-45% of all process steps needed to manufacture semiconductor devices use low-temperature plasmas (LTPs) in one form or another. LTPs have been an enabling technology in the multi-decade progression of the shrinking of device dimensions, often referred to as Moore's Law. New challenges in circuit and device design, novel materials, and increasing demands to achieve environmentally benign processing technologies require advances in plasma technology beyond the current state-of-the-art. The Department of Energy Office of Science Fusion Energy Sciences (FES) held a workshop titled *Plasma Science for Microelectronics Nanofabrication* in August 2022 to discuss the plasma science challenges and technical barriers that need to be overcome to continue to develop the innovative plasma technologies required to support and advance the semiconductor industry. One of the key outcomes of the workshop was identifying a set of Priority Research Opportunities (PROs) to focus attention on the most strategic plasma science challenges to address to benefit the semiconductor industry. For each PRO, scientific challenges and recommended strategies to address those challenges were identified. This article summarizes the PROs identified by the workshop participants.

1. Introduction

Low-temperature plasmas (LTPs) are used extensively in the manufacture of devices in the semiconductor industry, from creating extreme ultraviolet photons used in the most advanced lithography to thin film etching, deposition, and surface modifications. It is estimated that 40-45% of all process steps in this industry use low-temperature plasmas in one form or another. Plasma has been an enabling technology in the multi-decade progression in device critical dimension shrinking, colloquially known as 'Moore's law.' New challenges in circuit and device design, novel materials, and increasing demands to achieve environmentally benign processing technologies require advances in the current state-of-the-art in plasma technology.

The Department of Energy (DOE) Office of Fusion Energy Sciences (FES) held a workshop titled "Plasma Science for Microelectronics Nanofabrication" in August 2022 to discuss the scientific and technical barriers for meeting the challenges of developing innovative plasma technology needed to support and advance the semiconductor industry. One of the key outcomes of the workshop was to identify a set of Priority Research Opportunities (PROs) to meet these goals. For each PRO, scientific challenges and a recommended set of actions to address those challenges were identified.

Since the 1960s, the model for semiconductor innovation has been conceptually simple: double the number of transistors on a chip every 1.5-2 years with an ever-increasing performance-to-cost ratio. LTPs played and continue to play an enabling role in this 'Moore's Law' progression by enabling thin film deposition, precision etching, and surface modification across entire wafer diameters. Plasmas, in some cases exceeding the usual boundaries of LTPs, also played key roles in generating photons for lithography.

Due to physical limits, shrinking the critical dimensions of microelectronics devices is increasingly more challenging and expensive, prompting the search for new designs and architectures. These new devices and architectures will require new materials and new methods of fabrication, 3D heterogeneous integration, and fabrication at the atomic scale. The goal is to continue to achieve steady improvements in device performance/cost ratios, to reduce energy consumption in both manufacture and operation and to minimize other environmental impacts such as greenhouse gas emissions.

Maintaining a robust microelectronics supply chain is typically couched in terms of major new investments in chip manufacturing capacity. However, these investments rely on advances in several fields of science and technology. One of the most important enabling technologies in microelectronics manufacturing is rooted in plasma science and the associated materials and surface science that plasma-activated processes enable. In turn, plasma science relies on robust and readily accessible fundamental data for modeling and diagnostics, which requires strong support from the basic atomic and molecular physics sciences.

The DOE Office of Science 2018 Basic Research Needs (BRN) study on Microelectronics [1] cited the challenges associated with continuing to improve computing power in the manner driven by Moore's Law. As the report cites, achieving this goal will require new materials, synthesis technologies, and circuit architectures and algorithms, all developed using co-design principles. To address the challenges and key questions discussed in the BRN, the plasma-based fabrication techniques that underpin the industry and the majority of materials synthesis processes must be integrated into the co-design process. The "Plasma Science for Microelectronics Nanofabrication" workshop prioritized the science challenges that must be addressed to enable that integration.

It is in this context that the present article on plasma science for microelectronics fabrication is offered. Low-temperature plasma science has proven to be essential for scalable, economical, and ultra-precise fabrication over the decades. This article outlines the nature of the emerging challenges and suggests a set of priorities in LTP science research to meet the industry's challenges with new generations of plasma-based technologies. A workforce trained in these intrinsically multidisciplinary, plasma-focused fields will be essential in advancing this indispensable technology.

Participants in the workshop aimed to define the role of the DOE Office of Science, and Fusion Energy Sciences in particular, in advancing the LTP science required for new plasma-based semiconductor nanofabrication technologies. The major outcome of the workshop is a set of prioritized research opportunities (PROs) that can inform future research efforts in plasma-associated semiconductor nanofabrication science and build a community of next-generation researchers in this multidisciplinary area. The PROs are listed below, each with a representative key question. The rest of this article explores each PRO in more detail. The full DOE FES report is available on the DOE FES Reports website (https://science.osti.gov/-/media/fes/pdf/2023/DOE_FES_PlasmaScience_Semiconductors_Final.pdf). [2]

PRO 1: Develop sustainable device manufacturing at extreme scales with integrated efforts in plasma science, reactor technology, process engineering, and plasma chemistry

Key question: *How can plasma-based manufacturing processes support the fabrication of cutting-edge devices while consuming less power and resources, and while eliminating the use and generation of global warming species?*

PRO 2: Advance understanding, characterization, and control of plasma-surface interactions down to the atomic scale to enable materials and device structures required for future microelectronics and semiconductor fabrication

Key question: *How do we independently optimize plasma-generated species fluxes and energies at wafer surfaces to control plasma-surface interactions at the atomic scale?*

PRO 3: Develop fundamental data and centralized databases to enable comprehensive low-temperature plasma diagnostics and modeling

Key question: *How can the appropriate fundamental data for plasma modeling and diagnostics be rapidly produced to reduce plasma process development time?*

PRO 4: Enable experimentally validated, predictive, and integrated modeling of fundamental low-temperature plasma physics, chemistry, and surface interactions to enable next-generation semiconductor plasma processing

Key question*: What fundamental modeling and experimental validation capabilities, including new plasma diagnostics, are needed to enable predictive modeling of complex transient and multi-step plasma processing to reduce plasma process development time and complexity?*

PRO 5: Understand and control low-temperature plasma generation of radiation, radiation transport, and materials interactions in semiconductor processing systems

Key question: *How can plasma-generated photons be used with minimal damage to advance nanofabrication objectives in advanced lithography and processing?*

PRO 6: Develop novel institutional structures to meet emerging challenges of the field

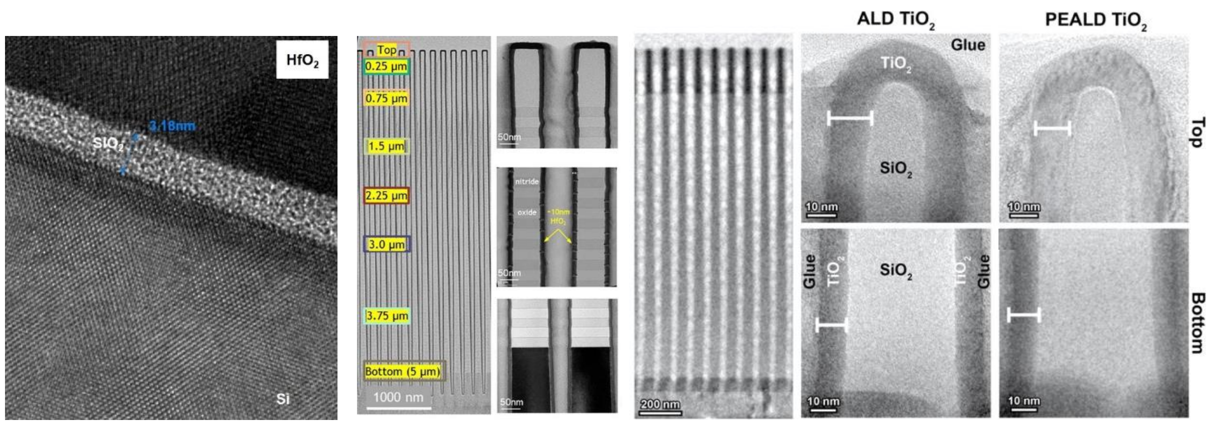
Key question: *How can we develop new plasma technologies with both fundamental scientific and commercialization challenges while producing a workforce for U.S. industry that is knowledgeable about plasmas and their applications?*

2. Priority Research Opportunities (PROs)

PRO 1: Enable sustainable device manufacturing at extreme scales with integrated efforts in plasma science, reactor technology, process engineering, and plasma chemistry.

Sustainable fabrication of cutting edge nanoelectronic devices requires plasma assisted processes that can construct these devices with features manufactured at the atomic level alongside features that are hundreds of atoms wide and tens of thousands of atoms deep (cf. Fig 1). To manufacture devices at these extreme scales at the historic pace of innovation for the industry defined by Gordon Moore, basic plasma science, plasma chemistry, reactor technology, and process engineering must converge to formulate new plasma source and chamber design concepts and accelerate their deployment to volume manufacturing. Exploration of new methods of plasma generation, new chamber components, and new process gases are essential for the fabrication of advanced devices. These process advances must be achieved while reducing their impact on the planet by reducing current trends in process energy consumption and minimizing environmental burden generated through the consumption of scare consumables and emission of harmful process byproducts. Toward these goals, an integrated research effort that extends from basic plasma science to advanced manufacturing technologies that enables co-design of hardware with manufacturing processes and lowers the barrier for industry collaboration with research institutions is needed to rapidly advance basic plasma science concepts to plasma reactor systems and manufacturing lines.

The equipment that carries out plasma assisted manufacturing for critical semiconductor processes is complex, expensive, energy intensive, and requires exotic feedstocks that include numerous greenhouse gases. Despite these drawbacks it is also the most easily scalable and economical technology for the fabrication of atomic scale and high aspect ratio features that define the devices that drive the semiconductor industry. Plasma etching and lithographic patterning are two of the most complex unit process types in the



(a) (b) (c)

Figure 1. What is "extreme scale" manufacturing and how does plasma processing contribute in this area? Cutting edge microelectronic devices are a combination of atomic scale layers and challenging geometric features such as high aspect ratio (HAR) structures, combined together to form devices. The fabrication of these layers and these structures requires very different plasma conditions that are increasingly having to work in synergy for advanced devices. This is a challenge for next generation plasma systems, shown by the examples in this image: (a) High-resolution transmission electron microscopy (HRTEM) image of the cross section of a HfO2 thin film. Reused with permission from Zhigang Xiao, Kim Kisslinger, Sam Chance, and Samuel Banks, Crystals 2020, 10, 136. Copyright (2020) under a Creative Commons License. (Ref [119]) (b) Cross section of a full 96 pair ONON stack with post-ALE after HfO2 deposition, with close-up images at the top, middle and bottom of the feature. Reprinted with permission from A. Fischer, A. Routzahn, R. J. Gasvoda, J. Sims and T. Lill, *J. Vac. Sci. Technol. A*, vol. 40, no. 2, 2022. Copyright (2022) American Vacuum Society. (Ref [112]) (c) TEM of HAR trenches showing top and bottom of trenches coated with TiO2 using thermal ALD and PEALD. Reprinted (adapted) with permission from P. Schindler, M. Logar, J. Provine, and F. B. Prinz, *Langmuir* 2015 31 (18), 5057-5062, DOI: 10.1021/acs.langmuir.5b00216. Copyright (2015) American Chemical Society. (Ref [120])

manufacturing flow for integrated circuits and are also the process technologies that have defined the pace of Moore's Law more than any other process technology in volume manufacturing. Plasma deposition and plasma surface modification also play key roles in semiconductor manufacturing as the introduction of new materials make proportionately larger contributions to the improved speed and efficiency of advanced devices.

The technical challenges facing plasma assisted process technology and the associated equipment used to fabricate nanoscale devices need to address the convergence of the continued scaling of Moore's Law, many novel materials, and the increasingly complex geometries of advanced devices and circuits. Further, there is a need to address the complexity and cost of these systems to make the future manufacturing processes for microelectronic devices more efficient, environmentally friendly, and economical. Advancing plasma reactor technology and the pace of reactor technology deployment are critical for a competitive semiconductor manufacturing sector in the United States. **There are no competing technologies to displace plasma processing in the fabrication of these electronic devices**. Therefore, it is a manufacturing imperative that advances in process capability, sustainability, and time to market through an integrated plasma science and engineering effort be realized in the next decade to maintain and solidify leadership in semiconductor manufacturing technology.

Scientific Challenges and Research Opportunities

Optimize plasma-generated fluxes for processing at extreme scales

At its core, the optimization of semiconductor manufacturing processes centers on the controlled delivery of chemically reactive species and energy to the material surface coupled with a high level of control over substrate temperatures. The first step in designing an effective plasma reactor for critical processes is to understand the exact combination of chemistry and energy that will enable this manufacturing process at extreme scales, then engineering a system that will reliably deliver these exacting conditions uniformly over a surface area approximately the size of a large dinner plate.

Our understanding of the interaction between plasma generated species must couple both the "plasma scale" and the "atomic scale." Currently these scales are treated relatively independent of each other and need to be better coupled. One example of where this challenge is substantial is in processes that leverage a plasma system's unique ability to drive surface processes with geometric anisotropy. The ability to form these high aspect ratio (HAR) features is a unique strength of plasma processing. However, process trends have strained hardware capabilities as feature aspect ratios have increased and device sizes have shrunk, while becoming increasingly important in cutting edge devices such as NAND memory and fin-FET transistor designs. Specifically, the need for higher ion energies has driven the voltage necessary to drive ions to the bottoms of these features to on the order of 10kV. These HAR processes are ion-flux dominant. This encourages implementation of complex power delivery modes that enable tailored ion energy distributions, pulsed source heating for time varying flux control, and remote plasma source generation of non-equilibrium reactive species fluxes. These process goals include extending HAR processes to greater depths as well as minimizing feature shape distortions such as tilting, twisting, and sidewall distortion that become more prevalent as device aspect ratios increase.

To achieve higher aspect ratio features for next generation devices, more efficient delivery of plasma energy to the bottoms of these remarkably deep and narrow features will be required. Overarching this challenge is a need for understanding how energetic species (ion, photon, or otherwise) interact with materials of interest. This includes controlling complex transport and surface chemical reactions within atomic scale features.

In contrast with etching HAR features, controlling processes at the atomic scale generally requires much lower energies at surfaces. For example, ions impacting surfaces at even a few eV can produce atomic scale point defects that can negatively impact these atomic monolayer processes; conversely, if appropriately designed, these ion fluxes can provide unique process benefits at the atomic scale. Atomic layer deposition and etch processes generally operate in a cyclic fashion. Understanding how cyclic processes and cyclical particle and energy fluxes impact material properties is needed. Manufacturing at extreme scales (e.g., at both high aspect ratio and atomic scale) will continue to require high process rates, across-substrate uniformity, and minimal edge exclusion.

Optimize plasma generation for cutting edge sustainable processes at extreme scales

The generalized needs for plasma assisted manufacturing of next generation electronic devices are (1) novel plasma generated chemistries and (2) energetic species control, both of which cannot reduce manufacturing productivity and are scalable to manufacturing levels. Novel plasma chemistries are obtained by modifying either the forming gas or the energy spectrum of dissociating electrons that form reactive byproducts through binary collisions. At the reactor level, finding new pathways to manipulate the electron energy spectrum can present novel dissociation pathways for new chemistries. This becomes increasingly important as commonly used processes gases that have significant global warming potential are phased out. This will require novel methods of replicating plasma chemistry compositions that match current conditions with new more environmentally benign feed gases.

Energetic species control centers on manipulating the electric potentials that naturally form in bound finite plasmas. This is typically manipulated by controlling the electrical impedance between components in the chamber and applying external static and/or time varying potentials to some of these components (the principal component being the substrate holder that the electronic devices being fabricated rest on). Time modulation of processes present new scaling relationships between species energy and processing metrics, where short periods of high energy flux are advantageous for some processes and suggest that some overlap may exist between the traditionally decoupled “high energy” vs. “low energy” process modalities. [3]

By contrast, in atomic scale manufacturing, the processes of film deposition and etch tend to be driven more by neutral species chemistry. Energetic species such as ions, electrons, and photons must be managed to provide a relatively ‘gentle’ surface reaction enhancement. Reduction of the sheath potential as well as the positive plasma potential that naturally forms between surfaces and the bulk plasma are needed to ensure charged species energies are below the displacement energy for surface atoms. This tends to require lower electron temperature to keep these bulk and periphery potentials minimal. Along with chemistry generation, exploration of plasma driven surface processes at extreme conditions such as cryogenic temperatures (i.e., typically sub -30C) have shown promise for decades. A better understanding of surface interactions with plasma species at these temperatures could open additional opportunities for advanced plasma assisted manufacturing. [4]

New plasma source technology will require improved sensor and control algorithms to maintain the tighter constraints for manufacturing devices at extreme scales. Sensors can be virtual or real, but any manufacturable solution requires integration into manufacturing platforms without increased cost or impact on process performance. Information must be processed sufficiently rapidly that real-time or near real-time control is achievable. Despite the increased complexity of process recipes, computational speed is approaching a level where simulated results and sensor inputs could provide a path for process emulation on the millisecond timescale. This might enable process re-optimization and “emulation on the fly.”

In the last two decades, plasma assisted processing has moved beyond its traditional PVD/CVD/etch roots and is now a contributing technology in lithography (as a novel light source as well as an integral patterning step through plasma assisted mask tapering and pitch multiplication) and implant (as an ion source and in plasma immersion ion implantation). The use of plasma sources for illumination during lithography presents a completely new process regime for plasma processing that has not been seen until the introduction of laser-plasma driven EUV light sources. This plasma application is very unique in that its requirements for success and typical plasma operating conditions are so disparate from those found in the traditional wafer level plasma processes that a greater level of unique learning, optimization, and control will be needed as this technology advances; of all the plasma enhanced processes critical to the semiconductor industry, this application is the most uncharted.

Eliminate of global warming byproducts in plasma processes

Plasma processes historically rely on gas feedstocks that are not necessarily environmentally friendly, and these may not be available in the future. Perfluorocarbons, hydrofluorocarbons, and other gases with greenhouse potentials many orders of magnitude greater than carbon dioxide are common feed gases. These will need to be replaced or mitigated if not through the tenets of environmental stewardship than likely through inevitable government policy restrictions. Helium is commonly used as a process gas and for wafer backside substrate cooling but is becoming increasingly expensive due to scarcity. Scarce resources such as helium will need to be replaced with alternatives, or methods for resource recovery and reuse will be needed.

It is expected that currently used plasma process gases with high greenhouse potentials will be phased out of manufacturing. [5] Fluoroether compounds have shown promising process enhancements with lower greenhouse potentials. [6] Developing new plasma sources, plasma chemistry and understanding plasma transport with these new families of gases that are more environmentally benign is a high priority for the industry. Plasma based reactor exhaust abatement is a well-established technology that is currently built into newer manufacturing facilities; however, the current plasma-based technologies have several limitations. Development of high efficiency environmentally benign plasma abatement solutions would also reduce GHG emissions from manufacturing facilities.

Improve sustainability of plasma processes

Plasma processes at extreme scales often require high levels of energy consumption. Per unit area of process substrate, the necessary electrical power has increased over threefold in the last two decades. As power requirements continue to increase, alternative technologies previously too energy-intensive for volume manufacturing will likely become viable. For example, plasma processing at cryogenic temperatures has historically been relatively energy-intensive compared to standard plasma technologies. But cryogenic process energy cost may soon be lower than traditional process technologies when applied to emerging process challenges.

Plasma power supplies' efficiencies have improved over the last decade, but additional efficiencies could be realized. For instance, understanding how power is transferred into the plasma and creates an impedance to which the power is delivered, ultimately matching power delivery to consumption, would improve power supply efficiencies. Similarly, power efficiencies of laser systems used to generate plasmas for next-generation EUV light sources have made similar gains and may be competitive for broader plasma heating as well as process diagnostics and monitoring.

Leverage co-design to advance plasma reactor development for manufacturing, reliability, and technology capability

The life cycle for semiconductor manufacturing technology, including plasma-assisted manufacturing, is largely 'siloed,' and technological advances suffer from barriers to co-design across the life cycle from concept to volume manufacturing product. The co-design of scalable reactors between research centers and the semiconductor manufacturing supply chain will accelerate the transfer of new source technologies to the manufacturing floor. Similarly, plasma and surface diagnostic development at the research level tends not to consider the challenges of integrating new technology into the manufacturing environment. Industry engagement at the research phase of these diagnostics could accelerate the practical introduction of new process monitoring technologies in manufacturing. Because of these limitations, effort should be placed not only on new diagnostic development but also on the increased utilization of available data on existing manufacturing-friendly, robust diagnostic solutions.

Closer collaboration between research teams and industry will speed the development of new reactor concepts in manufacturing. Further, co-design between plasma applications (PECVD, PVD, etch, etc.) presents significant opportunities for accelerated technology deployment.

Existing programs that promote synergy between universities, national labs, and industry can serve as a model for increased co-design. Within DOE-OFES, the INFUSE program is designed to accelerate new fusion technology by encouraging collaboration between companies, the DOE laboratory network, and US universities. In 2022, INFUSE supported 18 projects that connected 10 companies, 8 universities, and 3 DOE laboratories in collaborative research projects. [7] The NSF GOALI and I/UCRC programs promote academic/industry research collaboration. These programs are models for increasing collaborative research in plasma-assisted manufacturing. The DOE-supported network LaserNET-US and the MagNET-US network have reduced barriers to research facilities and opportunities for critical workforce development. The low-temperature plasma (LTP) cooperative research facilities at the Princeton Plasma Physics Laboratory and Sandia National Laboratory have similarly provided access to world-class diagnostics and simulation resources to the broader LTP community. These three research networks are potentially well aligned with the research needs of the plasma nanomanufacturing community. Further discussions of needed changes to institutional structures are provided in PRO 6.

PRO 2: Advance understanding, characterization, and control of plasma-surface interactions down to the atomic scale to enable materials and structures required for future microelectronics and semiconductor fabrication

A fundamental understanding of how plasma-generated energetic and reactive species interact with material surfaces, both at the wafer and chamber walls, is necessary to improve control of existing plasma processes and develop new ones. Plasma-surface interactions refer collectively to interactions at the plasma-material interface (i.e., the topmost surface of the material in contact with the plasma) and the near subsurface region.

The atomic scale processes in this near-surface region are diverse and complex. This diversity and complexity are brought about by the diversity of the species impinging on the surface and their cooperative synergies that may be either beneficial for processing or damaging. The research opportunities generally arise from the need to understand and control these plasma-surface interactions while leveraging the synergies between different species impinging on the surface.

Figure 2 is a schematic of different species produced in the plasma, impinging on the surface, and representative processes occurring on the surface of a material exposed to a plasma. This material can be a semiconductor, dielectric, metal, organic or inorganic, crystalline, or amorphous in microelectronics manufacturing. The diversity of materials used in microelectronics manufacturing, combined with the diversity of species that can be created in the plasma and impinge on the surface, results in an enormous number of possible plasma-material combinations.

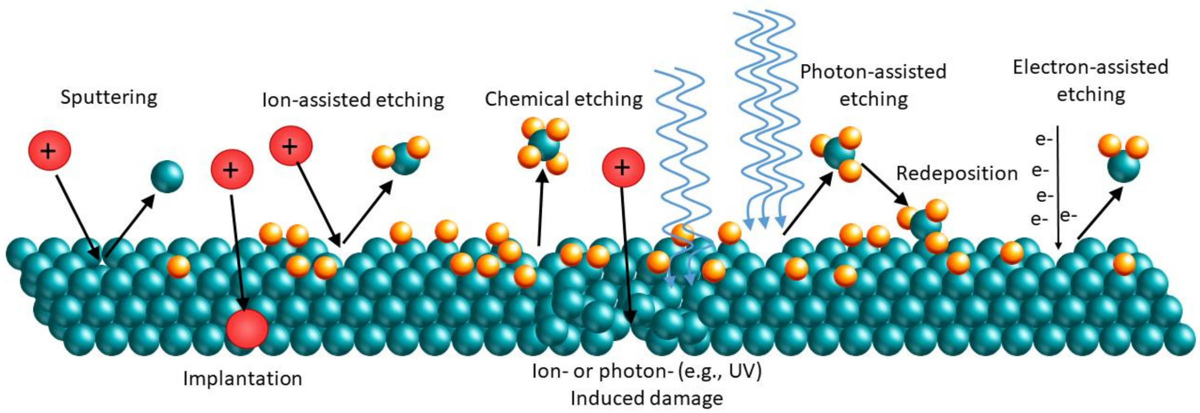


Figure 2. Schematic representation of the diversity of plasma-surface interactions and synergies.

Scientific Challenges and Research Opportunities

Understand and control the synergy among species that impinge surfaces

One of the challenges of understanding and controlling low-temperature plasma-surface interactions is the complexity and the variety of ways plasmas can interact with materials immersed in plasma (for example, Fig. 2). Plasmas are comprised of electrons, ions, and multicomponent mixtures of neutrals, radicals, and ions, and these all impinge on surfaces with energies varying from 0.026 eV (room temperature) to hundreds or even thousands of eV. Their fluxes are widely varied depending on how the plasma is generated. Consequently, ratios of the fluxes of these different species can be such that their effects on the surface are coupled. For instance, the synergistic effect of ions with neutrals and radicals on surfaces in the plasma etching and deposition of thin films has been well-known and exploited for ion-assisted etching or deposition. [8] Other synergistic effects include those between photons and neutrals and radicals [9] (photo-assisted etching or deposition) and electron beam-assisted etching [10]. In some cases, there could be a three-way coupling between the effects of various species impinging on the surfaces in low-temperature plasmas. The effect could synergistically enhance the etching rate or could be anti-synergistic. For instance, recently, anti-synergism between photo-assisted and ion-assisted etching was demonstrated. [11]

Designing and conducting well-defined experiments to reveal and quantify the coupling and synergy (or anti-synergy) among the different species impinging on the surface of a given material remains an important challenge. There is a continued need for surface diagnostics to interrogate the surfaces exposed to plasmas and to collect quantitative data for revealing the surface species, processes, and their rates either under conditions that mimic the plasma processing environments in plasma etching and deposition equipment or in situ in the actual equipment used in the manufacturing of chips.

Research is needed on how to independently control, vary, and optimize neutral, ion, electron, and photon fluxes and energies delivered to the surface. Moreover, this research is needed in the context of materials relevant to CMOS manufacturing (e.g., metal oxides, silicon oxides, nitrides, photoresists, carbon, and other mask materials) and emerging materials (e.g., 2-D materials) processing under various combination of fluxes and energies.

Focus on addition and subtraction of materials to and from the surface one layer at a time over large areas: plasma-enhanced atomic layer etching and deposition (PEALD and PEALD)

Atomic layer etching (ALE) and atomic layer deposition (ALD) emerged from the need to control thin film deposition and etching one atomic layer at a time. [12] Plasma-enhanced versions of ALE and ALD (PEALE and PEALD, respectively) bring additional flexibility and advantages, expanding the range of process variables and the variety of materials that can be deposited or etched. Figure 3 illustrates the PEALD of an Al_2O_3 film. In atomic layer deposition or etching, the addition or removal of a single atomic layer of a film is separated into two half cycles, both self-limited in the sense that the reaction stops after a single atomic layer has reacted. Understanding and controlling the synergies among the species created with plasma (ions, electrons, photons, radicals) can create tremendous opportunities in designing and developing PEALD and PEALE processes.

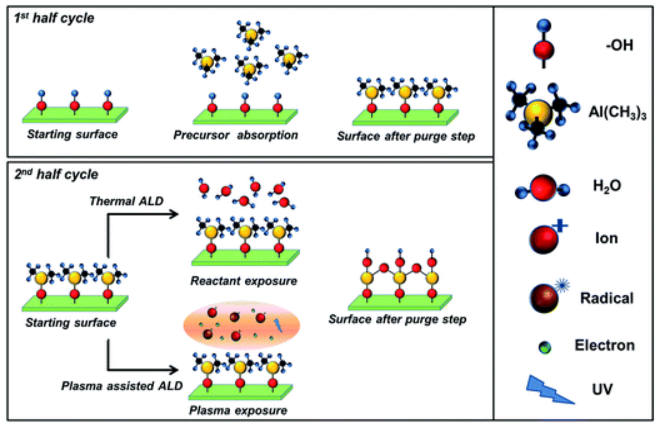


Figure 3. Illustration of the steps in the thermal and plasma assisted (enhanced) ALD for the deposition of Al_2O_3. Reproduced from V. Zardetto, B. L. Williams, A. Perrotta, F. D. Giacomo, M. A. Verheijen, R. Andriessen, W. M. M. Kessels and M. Creatore, *Sustainable Energy and Fuels*, vol. 1, no. 1, 2017, with permission from the Royal Society of Chemistry. https://doi.org/10.1039/C6SE00076B (Ref [116])

In the case of ALE, removing the material one layer at a time while maintaining a smooth surface at the Angstrom scale remains challenging. In most cases, something that resembles this idealized situation is achieved by pulsing the plasma power and/or gases and is referred to as quasi-PEALE. The research challenge in achieving true PEALE is controlling the LTP-produced fluxes and energies of reactive species incident onto the wafer surface with the reproducibility and precision that preserves the integrity of single atomic bonds. There is a need to develop PEALE processes that come as close to the self-limiting one atomic layer at a time etching as possible while maintaining high throughputs.

Focus on plasma-surface interactions in plasma etching and deposition for 3-D integrated circuits

Vertically integrated 3D circuits increase device density, enable faster signal transmission, and provide flexibility for novel architectures and integration of logic and memory. As noted in the previous

PRO, 3D circuits require plasma etching of extremely high aspect ratio (HAR) features. In addition, feature sidewall and bottom charging affect the fluxes and trajectories of ions. There is a need to understand chemistry and transport in complex HAR structures.

Controlling the interaction of LTP-produced reactive fluxes with the increasingly complex shapes of on-wafer features is essential. The control of 3-D complex structures is a major challenge for the manufacture of devices, and fundamental plasma-surface interactions relevant to surfaces and materials structured from a few nm to microns should receive more attention. In plasma process chambers, material from the wafer surface will generally be transported elsewhere in the chamber or vice versa. Such transport can also be across the scale of features. For example, wafers are coated with numerous materials (e.g., masks, many device layers, etc.), and a material removed from one feature on the wafer may end up in another feature elsewhere on the wafer. Especially for 3D devices and circuits, there is a need to understand and control how materials are transported within and between surfaces in contact with plasma.

Focus on interactions between plasma species and surfaces of emerging materials

There is an emerging need to study plasma-surface interactions relevant to the next generation of nanoelectronic devices and integrated circuits. This includes plasma synthesis, etching, and deposition of new materials and structures used in quantum computing and sensing, spintronics, and high-power and high-voltage electronics. Such materials may include but are not limited to carbon nanotubes, 2D materials such as graphene, h-BN, layered dichalcogenides (MoS_2, etc.), nitrogen-doped diamond, wide bandgap semiconductors such as gallium oxide for power electronics, ferromagnetic and antiferromagnetic materials, and ferroelectrics and multiferroics for low energy dissipation memory and logic and topological materials. In CMOS and emerging technologies, there is a need for materials with low thermal ceilings (~300C and below). We can expect new challenges specific to the new materials. For instance, new plasma gas mixtures will need to be found for plasma etching; new precursors may need to be synthesized for their plasma synthesis (e.g., PEALD or PECVD); interactions of these new chemicals and their fragments will need to be studied.

2-D materials are increasingly being explored, from candidates for single-photon emitters for quantum information processing networks to transistors for low-energy dissipation logic. Fabricating networks of such devices on a large scale will require a suite of plasma processes, including for synthesis, patterning, and doping. Plasma offers a particular advantage for processing on heat-sensitive substrates and within limited 'thermal budgets.' [13] There is a need to control the electronic and optical properties of 2D materials by controlling the stoichiometry of 2D compounds and introducing vacancies and local stoichiometry variations during their plasma deposition/synthesis or post-synthesis plasma treatments. Assembling devices and heterostructures for devices from 2-D materials will require their selective etching, layer by layer, over each other or masks.

Advance plasma synthesis and deposition of micro- and nanoelectronic device components

Synthesizing nanostructured device components such as nanotubes, nanowires, nanocrystals, and quantum dots either in the plasma [14] or on a substrate surface and then interconnecting them to form a device network is an alternative to the current CMOS paradigm. In principle, these components can be synthesized in the plasma and placed in precise locations or synthesized directly on the substrate surface. Nonthermal plasma is a viable synthesis technique for such components in high-purity and large quantities either in powder form or on surfaces, as demonstrated for a few materials such as silicon nanoparticles, carbon nanotubes, graphene, and 2-D materials such as MoS_2. The non-equilibrium environment in nonthermal plasmas has several advantages for synthesizing nanostructures as a powder, which can then be put in the form of colloidal dispersions to be placed on substrates. The advantages include energetic surface reactions that selectively heat these nanostructures to temperatures that can significantly exceed the gas temperature and in situ doping.

Nonthermal plasma can form metastable non-equilibrium phases of materials. They may form either due to the non-equilibrium environment the plasma provides or because the structures are stabilized because of their nanometer size, i.e., stabilizing the nanoscale structures that are not stable in bulk form. Embedding dopants into nanocrystals at high temperatures and quickly quenching them to produce hyper-doped materials may become possible. Nanometer-size materials often have unique properties not observed in bulk form. For instance, silicon quantum dots (nanocrystals with diameters less than 4 nm) emit light more efficiently than bulk silicon, potentially enabling optical circuits to be integrated with CMOS technologies.

However, understanding and controlling interactions of plasma species with nanoparticles in the gas phase remains challenging. Nanostructures nucleate and grow in the plasma, becoming charged and acting as part of the plasma, i.e., they become an additional charge-carrying plasma species. Thus, they present large surface areas to the plasma, strongly affecting the plasma speciation, charge distribution, and electric fields. Their properties are, in turn, determined by how their surfaces are affected by the plasma.

Understand and control plasma-produced defects on surfaces and sub-surfaces

Defects can be beneficial and desirable or detrimental to device performance. Intentional substitutional doping is routinely used to control materials' conductivity and electric fields at interfaces. However, plasma-generated particles that impact wafer surfaces reduce device yields. A dislocation-minimized diamond doped with nitrogen-vacancy (NV) (or other) defect centers is a candidate for quantum computing or sensing. Diamond films suitable for quantum devices are grown by plasma-enhanced chemical vapor deposition, and nitrogen vacancies can be introduced from nitrogen-containing plasmas. On the other hand, dislocations, which can destroy quantum coherence, must be eliminated, or their formation must be minimized. [15]

Plasmas are also used for patterning thin films associated with ion traps, superconducting transmons, silicon spin, and silicon photonic qubits, especially when integrating qubits with CMOS manufacturing steps. Therefore, understanding defects, surface roughness, surface residue, and contaminants that can compromise quantum coherence is vital. For instance, scalable photonic quantum information processing networks require single photon emitters, which may be formed by plasma etching or treatment of 2-D materials (e.g., h-BN). [15]

Improve understanding of plasma chamber wall interactions

In a plasma processing chamber, many surfaces other than the wafer contact the plasma. These include the chamber walls, electrodes, materials surrounding the wafers, windows, dielectric used for coupling electromagnetic inductive fields to the plasma, and tubes and piping for pumping or bringing gases to the chamber. In both experimental and high-volume manufacturing systems, there is a need for sensors that can be used in situ and in real-time to monitor chamber walls. The concentration and electric field discontinuities at wafer edges introduce nonuniform etching, thus reducing device yields. There is a need to understand the nature of these nonuniformities and develop ‘edge ring’ materials that allow the control of electric fields and species flux gradients to eliminate the nonuniform etching.

Expand plasma-surface diagnostics

Plasma-surface diagnostics must be as nonintrusive as possible to characterize the surface without disturbing the surface or the plasma. Metrology is needed to detect and quantify plasma-generated or healed defects, preferably in situ. Detecting plasma-induced damage in plasma etching and deposition, preferably in situ, remains an important challenge.

The existing arsenal of surface analysis tools generally relies on interrogating the surface with electrons, ions, and photons with well-defined energies under ultra-high vacuum. Only photons with energies lower than UV can travel through the plasma with minimal interactions, limiting the diagnostics to photon-in photon-out techniques. However, creative schemes, such as the spinning-wall technique [16, 17] have also been developed to employ UHV surface analytic tools, albeit to date for research reactors only.

There is a need to monitor feature shape evolution during plasma etching or deposition. Information such as the etched feature profiles or whether mask defects have developed are usually obtained post-etching using scanning electron microscopy. There is a need to obtain this information in situ and in real-time using optical or other methods. Post-etching SEM images may be used to train machine learning models to recognize optical signals from the surface and correlate them with feature profile shapes, mask defects, etc..

PRO 3: Develop fundamental data and centralized databases to enable comprehensive low-temperature plasma diagnostics and modeling

Reliable and readily available fundamental data are needed for plasma modeling, plasma-surface modeling, and plasma diagnostics. The term 'data' includes, but is not limited to, energy and angle dependence of electron-neutral cross sections; products and energies of electron impact molecular dissociation; electron and ion transport coefficient data; reaction rate coefficients for neutral and ion-molecule reactions; quenching coefficients for excited states; photon emission and absorption cross sections; energy and angle dependence of sputtering yields following energetic particle impact with surfaces; and coverage-dependent reaction probabilities of neutral species with surfaces.

A wide variety of gases and their mixtures are used in the semiconductor industry for plasma etching, deposition, cleaning, and modification of thin films. Data for collision cross-sections, rates, and reaction products have generally come from atomic, molecular, and optical physics (AMO) experiments and theoretical studies. Except for a few brief periods, [18] the focus of these AMO experiments has not generally been on gases of interest to the semiconductor industry. We, therefore, describe the major categories of the most needed fundamental data.

New gases and materials are regularly introduced for plasma processing in the semiconductor industry, and it would not be practical to experimentally generate fundamental data for every possible gas and material combination. It is, therefore, important to develop quantitatively accurate computational tools that can be used to generate the relevant data, coupled with experimental facilities to test prototype systems thoroughly. In addition, it is important to have experimental plasma facilities where a suite of diagnostics capabilities can be used to characterize some important classes of processing plasma systems thoroughly. This diagnostic data, along with fundamental data, can be used for modeling experiments and developing quantitatively accurate plasma models. Models should include validated mechanisms for plasma chemistry and associated plasma-surface interaction processes. Machine learning methodologies coupled with the experimental data can be used to develop and refine mechanisms efficiently. These data should be made available following the FAIR (findable, accessible, interoperable, and reusable) guiding principles.

Scientific Challenges and Research Opportunities

Expand data for electron impact processes

Energetic electrons play a major role in driving the chemistry in processing plasmas. To model these plasmas accurately, one of the major classes of fundamental data needed is the set of electron-impact collision cross-sections or reaction rates for the important ionization, excitation, attachment, dissociation, and elastic scattering processes. Measurement and computation of these cross-sections were addressed to some extent by the AMO research community in the past. This activity has dwindled markedly in recent years. Multiple scientific journals, including reviews, are available describing the status of electron impact cross-section data for some important gases. [18] Cross-sections for some electron-impact collision processes, such as ionization and dissociative ionization, are relatively easier to measure or compute, so these data are more abundant and can often be computed with sufficient accuracy for new gases.

Among electron-molecule collision processes, neutral dissociation is one of the least studied yet most important. Quantitatively accurate plasma models must predict both molecular fragmentation as well as the energy of the fragments. This latter effect is termed 'Franck-Condon' heating and can have a major effect on neutral gas temperature. Christophorou and Olthoff discuss techniques for measuring partial and total cross-sections for neutral dissociation. [18] There is a major need to refine these experimental techniques and apply them to molecules relevant to semiconductor plasma processing, including hydrofluorocarbons with high GWP.

Electron-impact dissociation cross-sections can be obtained, at least in principle, using theoretical and computational methods. Energetic electrons interact with molecules by perturbing the electron distribution in the molecule, creating electronically excited states. Much work has been done on this initial step, and methods based on the R-matrix approach are relatively mature. [19] These electronically excited molecules subsequently decay into various (neutral and ionic) fragments. Unfortunately, this second crucial step is much more complex to treat theoretically, as it involves treating the motion of the nuclei in addition to that of the electrons. Computational tools to predict product yields, distributions, and energies are generally lacking. Measuring dissociation cross-sections for all relevant molecules is impractical, but selected experimental measurements can be used to test computational models for a subset of the critical molecules. As noted above, there is general uncertainty about the energy and angular distribution of the reaction byproducts. The properties of collision byproducts are currently roughly estimated based on a limited set of measurements. [20]

Expand data for ion transport properties

Ion transport properties influence ion characteristics as well as overall plasma dynamics. Fundamental data for ion-neutral collision processes are critically important to developing quantitatively accurate plasma models. In the past, swarm experiments were used to measure ion mobility and related ion transport properties. There are many excellent reviews and catalogs of this data. [21] However, ion transport properties were generally measured in collisional plasmas under conditions of DC electric fields for generally non-reactive gases and parent molecules (and rarely for ions of dissociation products). When kinetic phenomena become important at low pressures, cross-sections for ion-neutral collisions are needed. It is also important to understand the energy and angular distribution of the collision byproducts. These data are only available for a few simple gases. [22] Available theoretical models often do not apply to complex molecules and radical ion species. Without ion-neutral collision cross-sections, developing accurate kinetic models for LTPs sustained in molecular gases becomes challenging.

Expand data for modeling gas phase and surface chemistry

Robust and predictive models for plasma processing systems require comprehensive data sets for gas phase and surface chemical and physical processes. These include reaction (e.g., recombination) coefficients of neutral species on surfaces; coefficients of secondary electron emission due to energetic ion, photon, and electron bombardment of surfaces; electron surface recombination coefficients; surface thermal accommodation coefficients; rate coefficients for reactions involving heavy species (neutral radicals and molecules, positive and negative ions); and rate coefficients for 3-body reactions. In some cases, these data can be obtained from *ab initio* molecular orbital theory, group additivity methods, and *ab initio* transition state calculations. Due to the wide variety of gases used, the variety of materials these species interact with, and the range of possible surface coverages, fundamental data will not be directly available for every situation. Estimation methods or semi-analytic expressions for these fundamental data would enable progress in modeling complex systems.

Published data are currently scattered in the literature, and there is often no critical assessment of the reliability of the available data. Some of these quantities, such as 'sticking coefficients,' are undefined as they encompass multiple underlying fundamental processes at surfaces (including adsorption, desorption, reaction, recombination, and deposition). Considering these uncertainties, plasma modelers often adjust key model parameters to match available experimental measurements.

Machine learning methods, coupled with measurements and computations, will likely be a fruitful approach for determining rate parameters and mechanisms for gas-phase and plasma-surface interactions. Research should be directed towards more accurate measurements of fundamental parameters and developing rapidly executing models for computing them.

Advance available databases

A significant amount of fundamental data is available in the literature. However, it is generally too scattered and difficult for non-experts to judge which measurements or calculations are most trustworthy. The NIST chemistry webbook is one source with relevant data for neutral reactions. However, this database is not geared toward the special needs of the plasma community; data are typically limited to reaction rates for neutral species, and updates to the database are becoming less frequent. There are independent self-funded or volunteer-managed databases relevant to LTP modeling and diagnostics, perhaps the most successful being LXCat for electron impact cross sections and charged particle transport (https://us.lxcat.net/home/). [23] LXCat is a community-wide, web-based project involving researchers from more than 15 countries. Only a few datasets have reached the level of maturity such that they can be applied to a wide range of plasma conditions and reactors without additional verification and validation.

There are also commercial offerings for data relevant to LTP modeling, one example being the Quantemol DB database (https://quantemoldb.com/). [19] Quantemol-DB is an example of a commercial database, which includes reaction rate coefficients and cross-sections for various semiconductor industry-relevant gases and mechanisms summarized from the literature. Ideally, fundamental data should be hosted by a government agency (e.g., NIST) with oversight and review processes with strong participation from the research community. Periodic workshops would bring relevant people from different disciplines and communities (e.g., NIST, modelers, diagnostics experts, quantum chemistry and surface science experts, etc.) together to assess data needs and provide direction. The databases should ideally be publicly accessible with a well-defined application programming interface (API). These databases should be created following the FAIR (findable, accessible, interoperable, and reusable) guiding principles.

Assembling, verifying, and distributing data sets with common formats are activities that can be community-driven with participation from academia, national laboratories, and industry. That said, data critical to the national economy and security should be archived and distributed over the long term by Federal agencies. NIST and/or perhaps another government organization should play a role in data distribution and preservation by managing and maintaining these databases for plasma processing.

Full plasma chemistry mechanisms

Equally important as data for individual physical and chemical processes are full plasma chemistry mechanisms with experimental validation, ideally utilizing multiple sets of experiments and from different groups. Plasma modelers typically search the literature for available mechanisms and may find examples of plasma chemistry mechanisms for only simple gas mixtures. They must then decide how to extrapolate and extend the mechanism and data for the problem at hand. With enough adjustable parameters in these mechanisms, the modeler can often match available data. However, such models have limited ability to extrapolate beyond the conditions used for fitting the parameters. A systematic method is needed to develop, rigorously test, and publish reliable plasma chemistry mechanisms relevant to semiconductor plasma processing. Rigorous model testing and validation require substantial experimental data sets, acquired under well-controlled conditions and comprising absolute density measurements of the key (stable and radical) species, measured over a range of gas pressure and plasma densities. An even more stringent test is for a model prediction to match time-resolved measurements in modulated plasmas. Acquiring such detailed data sets is rare, even for diatomic gases, since they are costly and time-consuming. The GEC reference cell [24], developed in the late 1980s, was used for similar purposes with, in some cases, excellent results. A similar strategy is needed for current and future plasma processes.

Develop validated data for diagnostics and modeling of plasma-surface interactions

As discussed in PRO 2, understanding plasma interaction with materials, especially when the surfaces have nanoscale patterns, is critical to advancing the science of plasma processing in semiconductor device nanofabrication. Models for plasma-surface interactions range from fundamental quantum chemistry-based techniques and molecular dynamics models to Monte-Carlo-based empirical models for feature scale evolution. The molecular dynamics and Monte-Carlo-based feature scale models rely on fundamental data regarding basic processes at the surface, and the accuracy of these models is tied to the underlying data. The status of fundamental data for plasma-surface interactions is generally poor.

Plasma-surface interaction data exists for a few individual phenomena, such as ion sputter yield on selected surfaces. [25] There are only a few plasma processing applications (e.g., metal deposition using physical vapor deposition (PVD)) where such data can be used directly.

Beam experiments were used until the 1990s to examine basic phenomena at surfaces in isolated conditions, as illustrated in Fig. 4. The fundamental data generated in these experiments continues to guide technology development. As semiconductor manufacturing technology has evolved, there is a great need to develop new measurement techniques for plasma-surface interactions designed to provide fundamental data for state-of-the-art plasma conditions and materials. Emphasis should be on examining the etch, deposition, and film modification processes on planar films and within high-aspect-ratio structures.

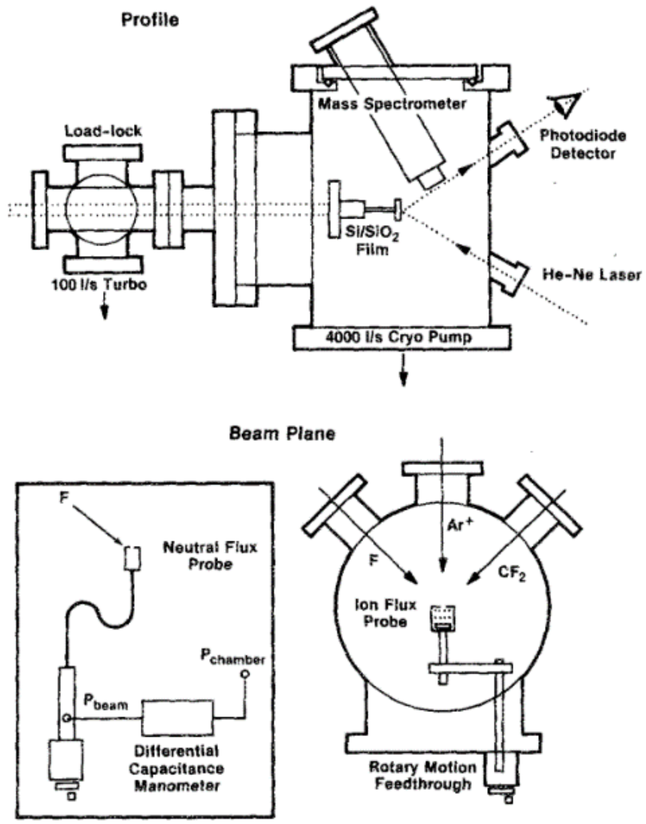


Figure 4. Experimental apparatus for beam experiments, simulating a plasma environment, while independently controlling the ion and neutral fluxes, their energies, and incident angle. Image from Ref [111]. Reprinted with permission from J. W. Butterbaugh, D. C. Gray, and H. H. Sawin, *J. Vac. Sci. Technol. B*, vol. 9, no. 3, 1991. Copyright (1991) American Vacuum Society.

Some of these data related to plasma-surface interaction can be obtained from molecular dynamics (MD) models, which rely on interatomic potentials to represent the fundamental interactions between plasma-based species and the surface. The potentials for MD simulations have been developed for only a few systems of interest for plasma processing [26] and the existing ones have primarily been used in qualitative studies of energetic ion interaction with plasmas. Given the range of new materials and conditions of interest in the industry, using machine learning methods to develop new interatomic potentials is a promising direction.

Summary of needs

The generation of new fundamental data for plasma applications in microelectronics applications is needed as new gases and materials emerge, and the processing requirements evolve. Needs are (a) the development of accurate models for gas phase plasma collisional phenomena and plasma surface interactions and (b) an associated experimental program to validate the models. The models can then be used to generate quantitatively accurate data for new gases and materials. Facilities and capabilities of the following type are the highest priority.

- Electron impact neutral dissociation cross-section measurements and theoretical models
- Energy and angle-resolved data for key ion and electron collision processes
- Quantum chemistry-based models for moderate energy ion-surface interaction processes, especially in the presence of reactive radicals

- Experimental facilities where comprehensive diagnostic measurements can be done to test and develop plasma chemistry mechanisms and plasma-surface interaction mechanisms

PRO 4: Enable experimentally validated, predictive, and integrated modeling of fundamental plasma physics, chemistry, and surface interactions to enable next-generation semiconductor plasma processing

Modeling and simulation (M&S) of plasma enabled fabrication of microelectronics devices require prediction of fluxes of reactive species (and their energy and angular distributions, or EADs) to the surface of the wafer and plasma facing surfaces; and employing those fluxes in feature scale models. The first goal of plasma reactor scale and feature scale models is to address fundamental processes of transport and reactivity in plasma and plasma-surface interactions through first principles computer simulation. The second goal is to provide a design capable M&S platform that can be used to optimize the design of specific plasma equipment and processes. In meeting both goals, a robust and complete database of fundamental cross sections, reaction probabilities and transport coefficients are required (as described in PRO 3).

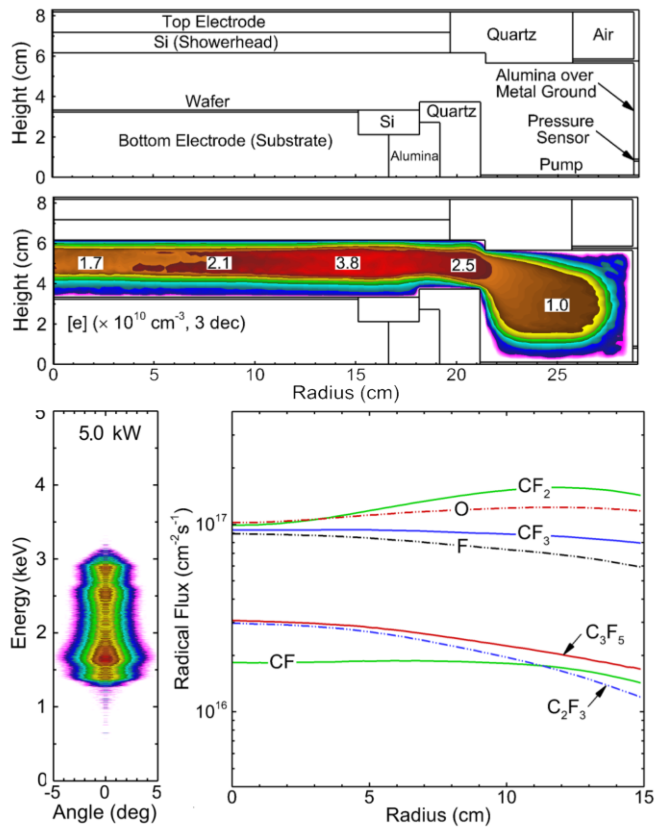


Figure 5. Illustration of plasma chemistry capable plasma model utilizing a hybrid plasma simulation of a 3-frequency capacitively coupled plasma sustained in $Ar/C_4F_8/O_2$ at 25 mTorr. The top image is a side view of the parallel plate plasma reactor, including all relevant materials. The middle top image plots contours of predicted cycle-averaged electron density profile in axial and radial dimensions. The bottom left image shows predicted ion energy and angular distributions at the processed surface. The bottom right image plots radical fluxes as a function of radial position on the wafer surface. [113] Reprinted with permission from S. Huang, C. Huard, S. Shim, S. K. Nam, I.-C. Song, S. Lu and M. J. Kushner, *J. Vac. Sci. Technol. A*, vol. 37, no. 3, 2019. Copyright (2019) American Vacuum Society.

One example of the type of model that is needed is shown in Figure 5. In this example, a hybrid plasma simulation is employed (combined fluid and kinetic techniques) for a 3-frequency (80MHz/10MHz/5MHz, 400W/2.5kW/5kW) capacitively coupled plasma sustained in $Ar/C_4F_8/O_2$ at 25 mTorr. The reaction mechanism includes 36 neutral species, 16 positive ions, 3 negative ions and electrons. Reactor and process design requires models capable of addressing complex chemistry in 2- and 3-dimensions, including material properties, multiple frequencies and sufficient breadth of plasma chemistry and kinetics to predict particle EADs to the wafer (and plasma facing materials). The models must be capable of addressing long enough time scales to achieve a steady state, which is several gas residence times and pulsed periods. The cycle average electron density, EAD for all ions and neutral fluxes to the wafer are shown.

The deployment and widespread adoption of validated, comprehensive, and robust models for reactor and feature scale processes and real-time control for plasma-enabled semiconductor fabrication will have an industry-changing impact. In today's mode of operation, M&S is typically in a support role, refining designs and providing insights to improve experience-based design. M&S typically does not start the 'clean-sheet' design process. This situation is very different than in aerospace and mechanical engineering, where the clean-sheet design typically begins with computer simulation.

The need for M&S to open new paths to plasma equipment and process design could not be greater than it is today. Consider narrowing the angular distribution of ions incident onto wafers for high aspect ratio (HAR) etching. The angle narrows with only the square root of the applied bias voltage. Bias powers are now as large as 20 kW. Further narrowing the ion angular distribution by a factor of two following current practice would require 80 kW biases. Perhaps other paths towards achieving this goal can be first vetted with M&S. The slowing of etch rates in HAR features due to ARDE (aspect ratio dependent etching) now demands longer than 30-minute etching processes. Doubling the aspect ratio without addressing ARDE and following current practice could lead to 90-minute-long etching durations. Instead, M&S-based reactor and in-feature engineering could address the fundamental causes of ARDE and dramatically decrease process times while reducing equipment costs.

For codes intended for industrial use, the form in which the software is provided is important to its impact. The complexity of the plasma tools and processes, a situation that is not static and continually evolving, continually challenges the capabilities of the available codes. Due to the inherently dynamic needs in a rapidly evolving industry, any software will require external support. That support comes from the code developers, an open-source community, or the support teams of the suppliers of commercial codes. The computing platforms on which the codes are executed and the execution speed are also important considerations. Computational tasks for designing equipment and processes have relatively long timescales. M&S platforms that require weeks of computation on tens of thousands of cores are likely not compatible with either of these scenarios. This 'need-for-speed' will become even more important as machine learning (ML) becomes more widely adopted, and thousands of cases must be executed to provide a training set. If high performance computing (HPC) is to be more effectively used in industry, it must be in a manner that protects intellectual property (IP) rights, probably leverages cloud computing, facilitates rapid turn-around (including problem setup), and is built around well-supported codes with close connections to the developers for the timely addition of capabilities.

Scientific Challenges and Research Opportunities

Achieve 'clean-sheet' design of plasma equipment and processes

To achieve the 'clean sheet' design of complex plasma tools, 3-dimensional models executed on unstructured meshes may be necessary in many cases, though process optimization can likely be performed with more rapidly executed 2-dimensional models. Over the large dynamic range of plasma tool operation currently in practice, the transport of both charged and neutral particles will span from local to non-local. Another form of non-local transport is radiation transport. As will be discussed in PRO 5, the consequences of visible, UV, and VUV radiation impinging onto surfaces (wafer and chamber walls) are poorly understood.

Models must also include complex plasma chemistries, including kinetics and transport of nano-particles. Most importantly, models must couple reactor scale phenomena with feature scale phenomena. It is presently unclear what degree of coupling is required between the reactor and feature scale to enable model based, 'clean-sheet' process development.

Process-relevant modeling capable of predicting reactive fluxes to plasma-facing surfaces (wafers and walls) must include complex plasma chemistry, addressing each species' continuity, momentum, and temperature (or their kinetic equivalents) in 2- and ideally 3-dimensions. Simulations must be able to achieve a (pulse periodic) steady state in a reasonable turn-around time. At the same time, fundamental plasma transport must be addressed to capture instabilities, non-local transport, and energy distributions. At present, achieving these requirements is beyond the state of the art. Plasma physics-focused and plasma chemistry-focused codes must move toward each other to incorporate additional capabilities to meet these needs.

Advance diagnostics, model verification, and validation

All models should go through some manner of V&V – verification and validation. Verification is the process of determining whether the equations in the model are being solved correctly. This can often be done using artificial (and sometimes non-physical) test problems. Validation is the process of determining if the model's physics (transport algorithms, reaction mechanisms) properly represent experiments. Validation requires experimental data – and that requires diagnostics.

A comprehensive suite of diagnostics and sensors will be required to characterize the plasma and plasma-facing surfaces for model validation, real-time control, and equipment development. Measurements are required of electrical quantities (voltage, current, power), charged and neutral particle densities and fluxes to surfaces, temperatures (energy distributions) of neutral and charged species, and state-of-the-surface (etch or deposition rate, composition). Ideally, these diagnostics and sensors will be non-intrusive (not disturbing the plasma or surface) and spatially- and time- resolved. One set of example diagnostics is shown in Fig. 6.

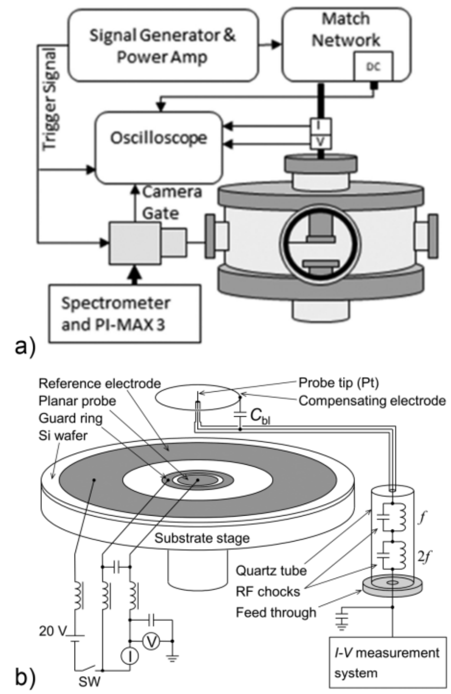


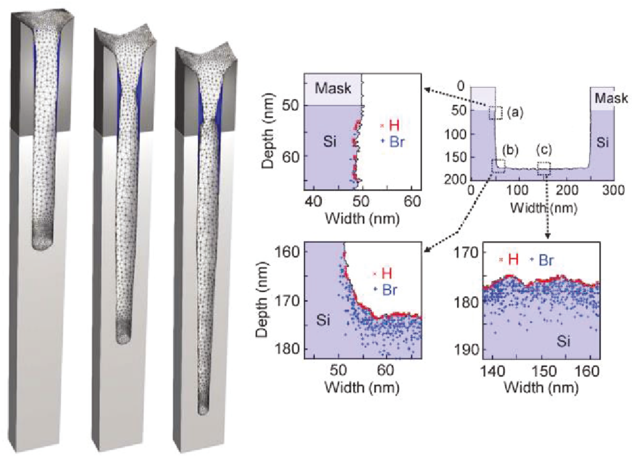
Figure 6. Illustration of plasma and surface diagnostics. Example diagnostics illustrated here: a) Phase resolved optical emission spectroscopy (PROES) and b) on-wafer probes that measure spatially and time dependent fluxes to the surface and conventional Langmuir probe. A challenge in deploying these diagnostics and sensors is gaining access to HVM relevant plasma chambers for fundamental studies and model validation and employing such sensors in actual HVM equipment. [Images adapted from a) [118] K. Hernandez, A. Press, M. J. Goeckner, and L. J. Overzet, *J. Vac. Sci. Technol. B* 1 March 2021; 39 (2): 024003, reprinted with permission, Copyright 2021, American Vacuum Society; b) [117] M. Hirayama ; A. Teramoto ; and S. Sugawa, *J. Vac. Sci. Technol. A* 1 May 2020; 38 (3): 032408, reprinted with permission, Copyright 2020, American Vacuum Society]

The range of diagnostics required to validate a model fully can be large. Ideally, measurements of the densities and temperatures of neutral and charged species throughout the reactor are required as a function of time. Values of electric field components and potential are also needed as a function of position and time and electrical diagnostics (current, voltage, forward/reflected power). The state of the surface, both on the wafer and on the reactor walls, must also be known as a function of time and position. The gas phase measurements will be provided by diagnostics, including optical emission spectroscopy, absorption spectroscopy, laser-induced fluorescence, E-FISH (electric field induced second harmonic), Raman spectroscopy, FTIR, mass spectroscopy, and electric probes (Langmuir, B-dot, capacitive) – and this is a non-exhaustive list. The surface measurements will be provided by diagnostics, including ex situ XPS, attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), scatterometry, photoluminescence, and interferometry.

Developing non-invasive plasma and surface diagnostics capable of fully characterizing the plasma and plasma-facing surfaces and providing data for model validation is now incompatible with high volume manufacturing (HVM)-capable plasma chambers that do not have the required access. We now have one set of diagnostics for plasma tool development and model validation and a second set of sensors for real-time control (RTC) on HVM-capable chambers. This inevitably leads to a disconnect in translating improvements in fundamental understanding and implementing sophisticated control schemes to the fab floor. Better diagnostics are required for real-time control, end-point detection, and actively managed processing. In the absence of greater access, non-intrusive diagnostics using the current access will need to be leveraged. These include higher fidelity optical emission or absorption and face-mounted, in-wall probes. Such face-mounted, in-wall electric probes are now available. The use of MEMS (micro-electromechanical systems) fabrication techniques for face-mounted probes (mass spectroscopy, ATR-FTIR) to sample the plasma or state of the surface are other possibilities.

Model validation and diagnostics development require a baseline of fundamental measurements and reference data that can be exchanged and collated. For the viability of the discipline, supporting intellectual diversity, and training of the next generation of researchers, these measurements should be made in laboratories across the domain, from the labs of individual investigators to central facilities. Standard plasma chambers would facilitate leveraging, comparing, and exchanging the resulting data. Following the success of the GEC Reference Cell, these standard plasma chambers would have geometries and power systems relevant to HVM while also having the needed access for diagnostics. A community-driven initiative, including a series of workshops, would best define the parameters of these chambers. Parameters include defining the chemistries and operating conditions to provide the baseline for code comparisons, validation, and diagnostics development.

Perfect feature scale and surface modeling



(a) (b)

Figure 7. Illustration of etch feature shape profile evolution modeling. Profile simulators use plasma-generated fluxes and reaction mechanisms for physical sputtering, chemically enhanced sputtering, deposition, implantation, passivation, and surface diffusion to predict feature evolution on the nanoscale. There are two dominant profile evolution simulation methods: level-set-methods (LSM, image (a)) and voxel based kinetic Monte Carlo methods (kMC, image (b)). [Images were adapted from (a) [115] and (b) [114]. (a) From Y. G. Yook, H. S. You, J. H. Park, W. S. Chang, D. C. Kwon, J. S. Yoon, K. H. Yoon, S. S. Shin, D. H. Yu and Y. H. Im, *J. Phys. D: Appl. Phys.* **55** 255202, reproduced by permission of IOP Publishing. (b) Reprinted with permission from M. Mori, S. Irie, Y. Osano, K. Eriguchi, K. Ono, *J. Vac. Sci. Technol. A* 1 July 2021; 39 (4): 043002 Copyright 2021, American Vacuum Society.

Profile simulation represents the evolution of surface features (e.g., vias, trenches, ALE, deposition, fins) due to the plasma-generated reactive fluxes (ions, radicals, electrons, photons) onto the lithographically patterned wafer. From an industrial perspective, this is the most relevant and final outcome of M&S. As one company most famously said – “we don't sell plasmas; we sell chips.” In order to perform accurate and predictive profile simulation, the reactor scale plasma processes must be understood and modeled. However, the final goal and outcome is profile simulation. Examples of such profile simulations are in Fig. 7.

Several modeling techniques are used in feature shape evolution – molecular dynamics (MD), kinetic Monte Carlo (kMC), and level-set methods (LSM). Each technique has its advantages and disadvantages. MD is the most fundamental approach and potentially the most accurate. MD requires inter-atomic potentials between all possible pairs of atoms and nearest neighbors while requiring very small timesteps (on the order of 1 fs). MD has successfully addressed small patches of materials (a few to 20 nm square by 10-20 nm deep). Addressing full HAR features (hundreds of nm to microns tall) or several finFET or GAA structures will be challenging.

Models based on LSM are the most rapid to execute and address the largest features. However, these methods are intrinsically surface-focused and are challenged at addressing complex chemistry, non-local processes, and implantation. kMC is an expedient hybrid technique that retains the ability to address complex structures on the appropriate spatial scales while including nearly all of the needed processes. kMC is significantly faster than MD and significantly slower than LSM. kMC does not have the atomistic detail associated with MD, so its reaction probabilities and mechanism must contain higher levels of approximation and tuning.

Surface chemistry models should become standard features of reactor scale models. As the plasma chemistry in models becomes more complex, the need for surface chemistry models also increases. Doing so then introduces multi-scale (time and space) integration issues, in addition to developing the proper surface reaction mechanisms.

Feature profile modeling is perhaps at a crossroads. All current models capable of addressing full and multiple features use some level of approximation for reaction probabilities and processes such as implantation. Models capable of addressing those issues from first principles are currently incapable of full (and multiple features) simulations. The first principles (but not process capable) models and the process capable (but not first principles) models need to work towards each other.

Exploit machine learning

There are at least three major roles for ML with respect to M&S: a) development of reaction mechanisms or reduced mechanisms, b) empirical models for real-time-control (RTC), and c) determining signatures for instabilities or unwanted plasma behavior. ML methods are best applied to repetitive or recurring conditions and are valid over a limited parameter space for which the training data has been collected (and the algorithms trained). In this regard, using ML-based control algorithms may be an ideal application. In any properly operating plasma tool, the deviation from ideal conditions will be small, the recipes are generally fixed, and the change in actuator settings required to correct observed deviations is small. A training data set (either computational or experimental) can exhaustively cover the parameter space and need not be frequently regenerated (and algorithms retrained). The use of ML for model reduction is also a needed field of research. One challenge of model reduction (ML or otherwise) is the breadth of application of the reduced model. The greater the reduction, the narrower the parameter space the reduced model will accurately apply. Model reduction will likely work well for real-time control (RTC), where the operating space is well-defined. If the intent is to perform parametric performance studies over a broader parameter space, the reduced models must apply to the entire parameter space.

Improve tool scale-up

A typical procedure for developing a new process is to use coupons (or chips) or to cover a wafer with a small window, exposing a small area of the wafer. These small, exposed areas of wafers (coupons, chips, or open windows) are used to reduce the cost of creating test structures for developing new processes and measuring outcomes. Once a process is developed using coupons, the process must be scaled to a full wafer. M&S could tremendously impact assessing differences between coupon-vs-full wafer processing and speed scaling.

Develop and exploit 'digital twins'

A goal in HVM plasma processing is for two nominally identical reactors running the same process to produce the same result. This is not always the case, so matching reactors' performance (or restoring performance after maintenance) is a continuing challenge. Is there a role for digital twins of plasma reactors akin to those that shadow jet engines? The digital twin would track the experiences and performance of a plasma tool, accounting for small changes in tolerances and materials while recommending remedies to restore the plasma tool's performance or predict when maintenance is needed.

PRO 5: Understand and control low-temperature plasma generation of radiation, radiation transport, and materials interactions in semiconductor processing systems

This PRO is directed towards the role of plasma-generated radiation and is divided into two key challenges: 5A, for the generation and control of extreme ultraviolet (EUV) radiation for lithography, and 5B, for the role of radiation in plasma-assisted thin film etching, deposition, and surface processing in general.

PRO 5A: EUV radiation for lithography applications

The optimal path to create EUV photons capable of printing patterns on the order of the 13.5 nm wavelength on a semiconductor chip – the scale used at the "7 nm node" and beyond – raises many questions, some of which are summarized below. Note that these general questions apply to any technology that can generate plasma capable of producing light in this energy range, but the laser-produced plasma option will be used to illustrate the physics and engineering challenges.

The continued quest and economic drive to extend Moore's Law largely depend on photolithography to define the features fabricated on semiconductor wafers. In photolithography, a radiation-sensitive coating, called photoresist, is applied to the wafer and is exposed to radiation through a mask that contains the pattern that will be transferred to the wafer. Fabricating smaller and smaller features requires shorter and shorter wavelengths to expose the photoresist to make finer and finer patterns. *All industrially important photolithography has been performed with plasma-produced photon sources*, first with plasma lamps (1970s-1980s), then plasma discharge excited excimer lasers (1990s-2010s), culminating in the ArF laser producing 193 nm photons, which were further compressed using liquid-immersion techniques. Sophisticated techniques are used to create features on the wafer that are small fractions of the exposing wavelength, down to about 10-20 nm. However, there is a limit to these techniques, and shorter wavelengths are eventually needed.

The current state of the art in photolithography photon sources is plasma generation of extreme ultraviolet (EUV) at 13.5 nm. [27, 28] EUV is capable of printing finer features in fewer exposures relative to the 193 nm photons produced by ArF excimer lasers (~3-4X reduction in exposure passes, with associated etch and deposition step reductions). The 13.5 nm EUV photons have energies of ~92 eV. There are no transparent materials at this wavelength, so all optics must be reflective. The mirrors used must be Bragg or grazing incidence reflectors. For Bragg reflectors at near-normal incidence, the wavelength is constrained by the selection of the multi-layer mirror materials and layer thicknesses and the feasibility and efficiency of plasma emitters at those wavelengths. 13.5 nm was chosen to use Si and Mo bilayers as mirror materials. Highly ionized Xe, Sn, and Li are known to generate photons in this range. [29, 30] Several methods were investigated for the production of EUV photons at the power levels needed for lithography, including laser-produced plasmas, discharge plasmas [31], and free-electron lasers [32]. Today, the only commercially available EUV photolithography system used in high-volume manufacturing uses a laser-produced plasma. A 10.6 µm laser focused onto an Sn droplet vaporizes and produces a highly

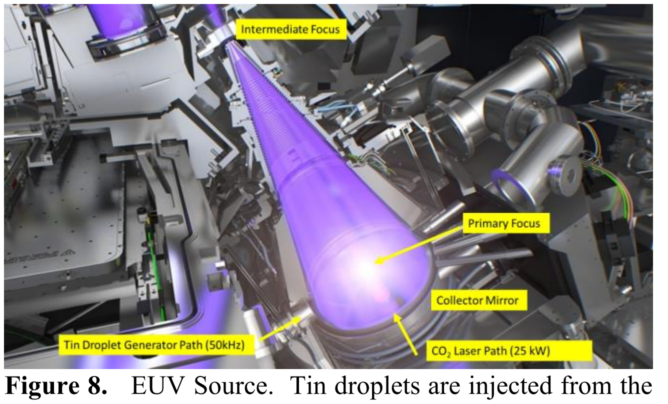


Figure 8. EUV Source. Tin droplets are injected from the left at 50 kHz. They are hit by a pulsed 25kW CO_2 laser at the primary focus, creating an intense plasma. Light is emitted at a wide variety of wavelengths in all directions. The collector mirror is a multi-layer Bragg reflector with a spacing such that only light in the 13.5 +/- 0.2 nm band is reflected. That light is focused to the intermediate focus which is the entrance to the scanner. (Picture courtesy of ASML.)

ionized Sn vapor with a plasma-produced emission at 13.5 nm. [33, 34, 35]

In current EUV sources, molten tin droplets with a diameter range of 20 to 30 microns are struck by a focused >20 kW CO_2 laser at a rate between 40 kHz and 100 kHz. [36] The laser light creates an intense plasma that ionizes the Sn to the +8 to +14 range, where it emits in the UTA (unresolved transition array) band. [37, 38] Hydrogen is used as a background gas at pressures of 100 – 200 Pa because it has a relatively high transmittance for EUV photons, creating a secondary weak background plasma in the region irradiated by photons and ions from the primary Sn plasma. [39] A schematic diagram of a commercial EUV plasma source is shown in Fig. 8.

This type of EUV source was introduced to high-volume manufacturing only at the end of 2019. [40] Therefore, the plasma science associated with this source is still in active development. Additional EUV plasma sources (so-called “table-top”) at a much lower average power scale are also a key area of development for metrology and material and optical characterization. [41, 42, 43, 44] Advances in these metrology techniques are also needed to resolve structures during and after lithography with sub-nm precision and in fundamental studies directed towards the improvement of masks, pellicles, mirrors, and resists.

Scientific Challenges and Research Opportunities

Efficiently generate EUV light for lithography and for table-top metrology

EUV light for lithography and for table-top metrology will likely continue to be produced by plasma-induced emission. Competing methods for producing the desired spectra and power levels for EUV radiation have not met expectations or are too expensive. Plasma-based methods will likely dominate well into the future. For EUV production by laser-produced plasmas, the optimal wavelength, target, geometry, and laser pulse shapes are not known. Advances in our fundamental understanding of laser-metal droplet-plasma interactions are needed to make assessments of spectra, efficiency, and final disposition of the debris in these systems. For discharge-produced plasmas, power-scalable geometries that do not destroy electrodes are not now available. For table-top sources, the specific demands of the application may require a customized approach.

Investigating alternate methods of plasma-produced EUV is encouraged, provided that the method's practical limitations and requirements are considered. These new configurations should have a possible path of development that exceeds the performance and reduces the cost of the current state of the art. These new methods should also be compatible with locating the entire apparatus in a semiconductor fabrication facility. For example, an accelerator-based technique for producing EUV that is 400 m long will not fit inside a fabrication facility at a reasonable cost.

Develop efficient, high repetition rate, high average power plasma excited lasers to meet future scaling goals

The current EUV production method for industrial lithography relies on a laser-produced plasma. Using the same basic configuration, future higher productivity systems with projected etendue and conversion efficiency limits imply the need for pulsed lasers having the following characteristics: ~20 kW - 50 kW range at between 50 kHz and 200 kHz with 10 ns to 100 ns pulses with optimal wavelengths between 1 μm and 10 μm, with improved wall-plug efficiencies relative to current systems (~5% electricity-to-photon). The systems currently used for EUV production are plasma-excited CO_2 lasers. Can these plasma-excited laser systems be scaled to have the necessary specifications? Are other plasma-excited lasers scalable to these specifications?

Identify and develop effective diagnostics and models for the multiple plasmas used in EUV production

There are three classes of plasma in the current process of industrial EUV production. 1) The primary EUV-producing Sn plasma, 2) secondary background plasmas sustained in hydrogen and wall-related gas species, and 3) plasma used to excite the laser. Improving EUV production for lithography will require new diagnostics and models to characterize and quantitatively predict the system performance of these plasmas over the system's lifetime. For example, plasma diagnostics will help guide the development of higher-efficiency EUV light production by identifying the intermediate species and transport phenomena which are at play. Additionally, the modeling of the plasma itself is a matter of considerable computational complexity, owing to both the highly dynamic nature of the radiation hydrodynamics and the complexity of the atomic processes participating in the EUV emission. [45] Advances in computational techniques targeting this regime can be expected to improve plasma engineering.

Efficiently produce EUV photons

The EUV plasma-produced photons required for lithography are generated via a cascade of processes, each with some efficiency penalty, giving rise to a few watts of EUV on the wafer for a ~1 MW wall-plug power consumption per photolithography system. [46, 47] Two of the most important components of this small system efficiency are the electrical wall-plug efficiency of the laser light needed for the laser-produced plasma (typically on the order of a few percent up to ten percent) and the conversion efficiency of that laser energy into useful in-band EUV light emission (currently reported in a range between 2% and 5%, depending on the details of the target and wavelength). [48]

The CO_2 (gas mix CO_2:N_2:He) gas discharge lasers (10.6 μm) currently used to generate the laser pulses used for plasma EUV generation rely on a radio frequency (RF) generated plasma to generate the required vibrational state population inversion in the CO_2 molecule. [49] The wall-plug efficiency of the laser factors directly and significantly into the overall electrical efficiency of EUV lithography. The overall electrical-to-photon efficiency of the laser depends in part on maintaining the right balance of gas species in the plasma at the vibrational temperatures and densities to provide efficient gain for the laser pulse and a stable discharge. [50, 51, 52]The overall design of the laser flow, species collision rates, and the detailed interactions of the laser plasma with the walls can significantly impact the wall-plug efficiency. Innovations in laser plasma design and even in the choice of the laser itself could potentially deliver significant gains in efficiency and reduce the cost of ownership for chipmakers, leading to less expensive chips and higher production.

The conversion efficiency of the laser light into EUV radiation represents a second opportunity for overall efficiency improvement. For example, when focused laser light hits a molten Sn droplet, inverse Bremsstrahlung accelerates electrons, causing rapid ionization. The material becomes 'warm dense matter' with an optimal plasma density on the order 10^{19} m^{-3} and an electron temperature in the range of ~30eV, at which the plasma's spectral emission is well matched to the passband of near normal incidence Bragg mirrors. At lower intensities, laser pulses can also be used to manipulate a spherical droplet's shape, for example, creating a flattened nearly 1-D target that can subsequently be struck with a larger EUV-generating pulse. [53] While a more dense plasma may produce more EUV light, it will also re-absorb more within the core of the plasma, leading to an efficiency loss due to loss of the effective radiating volume. A lower-density plasma will provide fewer radiators in the available etendue (spread in area and angle) of the collection optics for the EUV scanner. The engineering optimization of this balance over the range of target sizes, morphologies, and densities over the time of laser pulse delivery constitutes the core design challenge in the efficient production of EUV light. There is significant room still for innovation and exploration in this area [54, 55, 56] that can lead to fundamental improvements to EUV production efficiency. The modeling of the plasma itself is a matter of considerable computational complexity, owing to both the highly dynamic nature of the radiation hydrodynamics and the complexity of the atomic processes participating in the EUV emission. [45] Advances in computational techniques targeting this regime can be expected to improve plasma engineering.

Current conversion efficiencies of the incident laser pulse energy to EUV photons are on the order of only 5%, and this can likely be increased, as not all parameters relevant to the efficiency have been demonstrated to be optimal. It is also important to fully understand what happens to the remaining 95% of laser energy. Many other wavelengths of photons are produced, particularly in the VUV range, which can be transmitted to the scanner, causing undesired effects, or contributing to undesired plasma chemistry in the gas or at surfaces. Further, fast electrons leave the plasma, accelerating ions in a 'Coulomb explosion' to many keV. These energetic hydrogen and tin ions would sputter adjacent surfaces, including the collector mirror if it were not for the background hydrogen gas. [57] As the loss of EUV radiation to the gas is also a contributor to the total energy efficiency of the system, the optimization of ion energetics and ion stopping near the plasma becomes another key consideration for overall efficiency. [58]

Control EUV photons and plasma species interactions with the background gas, optical, and plasma-facing surfaces

The photon flux generated in the primary laser-produced plasma in this pulsed process is large. Additionally, electrons, ions, and even the shock wave from the primary focus ionize the background gas and turn it into a plasma. This radiation and secondary plasma can interact with the background gas and the optical and plasma-facing surfaces, leading to complex and undesired effects in some cases. For example, the 92 eV photons impacting walls will emit photoelectrons up to 70 to 80 eV. The re-emitted photoelectrons from the wall will have a distribution of energies, which can generate plasma chemistry in the sheath region near the surface. This sudden electron flux from walls may invert the plasma sheath, reducing the transport of ions or other particles. Since there are multiple sources of energy input, there are generally multiple plasmas present. Their interaction and the resulting charge exchange processes can impact the transport of high energy ions from the plasma towards delicate optical surfaces and the transmission and spectrum of the light from the plasma to optical surfaces throughout the lithographic system (scanner).

Within the lithographic scanner (also maintained in a near vacuum hydrogen plasma environment), the plasma generated by radiation creates an aggressive environment that can reduce the overall optics lifetime in several ways, including roughening, blistering, chemical sputtering, and enhanced particle release. [59] In the area where a greater risk is from direct deposition of contamination (e.g., Sn) from the laser-produced plasma, the incidental or deliberate engineering of hydrogen radicals near the optics can deliver surface cleaning [60], aiding the overall optical transmission of the system over time. Demonstrating control over the plasma near the optics is a key consideration for engineering for EUV lithography. Improving optics lifetime can lower the cost of ownership and raise the overall system's productivity.

Several other plasma-facing surfaces are composed of a range of metallic materials. How energetic species from the plasma affect wall materials and debris products (like solid or liquid tin) is poorly understood. As current high-volume manufacturing targets lithography system availabilities (fractions of time operating) of >96%, the management of the plasma-radiation-wall physical chemistry is a key consideration for an industrial EUV source for lithography. Advances in the knowledge of cross-sections (both photon, electron, and collisional) and demonstration of control over the resulting plasma kinetics and transport processes near walls can aid the engineering of the plasma-facing surfaces in such systems and significantly improve the cost of ownership and availability for the overall system.

Manage Sn in the plasma ablated droplet

Specifically for the current EUV source architecture, the transport, and control of Sn species following plasma ablation of the Sn droplet is of primary importance for maintaining the cleanliness of the EUV collecting mirror closest to the plasma. Much of the Sn, which radiates to produce the EUV photons, remains in the system and will coat mirrors and walls. A significant fraction of the Sn exits through pump ducts. Depending on the local temperature, this Sn can be either in liquid or solid phase. A Sn film of even 1 nm on a mirror will severely degrade its reflectivity and, therefore, the throughput of the scanner. [61, 62] The hydrogen gas used to slow the energetic particles has another function. Hydrogen radicals are produced by photodissociation from the EUV and by the plasma produced by the droplet expansion. The H radicals etch Sn to form stannane (SnH_4), which is volatile but reactive with adjacent surfaces. [63, 64] The kinetics of the formation of SnH_4 and its resulting transport through the plasma environment are complicated by the well-known thermal instability of the molecule. [65, 66] The transport and chemistry of stannane with the materials and the background plasma are not well understood but can lead to unexpected phenomena. An example from the plasma fusion community is the formation of bubbles in liquid Sn under plasma loading, which can burst, resulting in the undesired transport of liquid Sn debris. [67] Advances in the understanding of how Sn in liquid, solid, and gaseous (e.g., stannane and related molecules) forms interact and transport in a plasma environment will aid the engineering of EUV systems in the foreseeable future, owing to the central importance of Sn as an EUV emitter in the right band for lithography.

PRO 5B: Radiation in plasma etching and deposition applications

All LTP processing recipes using plasmas have, by default, included radiation-induced effects. High-energy photons can cause chemical reactions in chemisorbed layers on these surfaces, potentially leading to the degradation of masking layers, insulating films, and critical regions of the silicon substrate. Large fluxes of UV and VUV photons can also lead to erosion of chamber materials. Photon irradiation, especially in the vacuum ultraviolet (VUV) region (<200 nm), is also thought to cause damage, though the mechanisms are less clear. Still less certain are the effects of VUV radiation on etching rates and feature profile shapes.

The types of LTPs used in semiconductor etching processing produce light throughout the vacuum ultraviolet (VUV) to visible regions, as well as in the infrared (IR), spanning energies from typically ~20 eV to 0.1 eV. VUV photon fluxes have been reported for Ar inductively coupled plasmas (ICPs). [68, 69, 70, 71, 72, 73, 74] Values of fluxes striking surfaces range from 1×10^{15} to 1×10^{17} photons/cm^2-s, depending on reactor and detector geometries, power densities, and experimental uncertainties. These fluxes span about the same range as those for positive ion bombardment of the substrate. Plasma-produced light, especially in the UV and VUV regions, can cause a number of effects during plasma-enhanced chemical vapor deposition or etching processes. Surfaces exposed to a plasma will absorb most, if not all, of the light escaping the plasma and striking that surface. Higher energy photons impinging on substrates can enhance etching [9, 75, 76, 77, 78, 79] and cause damage often sensed by the degradation of a particular device's electrical characteristics. [80, 81, 82, 83]

Schwentner and co-workers investigated photo-assisted etching Si in the presence of XeF_2 vapors and GaAs with Cl_2 using shorter wavelength light produced by a synchrotron. [84, 85] In both cases, the number of Si atoms etched per photon dramatically increased below about 130 nm and reached an incredible ~100 between 130 and 110 nm. Yields higher than unity were also reported for Cu etching in the presence of Cl_2 gas. [86] Since such short wavelength photons are produced in the plasma, it is perhaps unsurprising that similar, large photoetching yields of 90 to 240 Si/photon were recently found in plasma etching of p-Si(100) in a Cl_2/Ar ICP. [78]

Though less reported, photon-induced damage during plasma-enhanced chemical vapor deposition is also a continuing concern. VUV photons can create trapped charges or color centers, leading to a degradation in the device's electrical characteristics. This light can typically penetrate a few nanometers into films and can cause damage through thicker layers grown by a plasma-assisted process.

Scientific Challenges and Research Opportunities

Quantify plasma-generated VUV fluxes to surfaces

Determining the absolute intensity of VUV light in a plasma is often difficult. Observations through windows cut out the most important light at the higher energies. Consequently, measurements must be made with the sensing device in contact with the plasma gas. The most relevant measurement is at the wafer surface; side views through differentially pumped chambers will not provide accurate measurements. Therefore, in-situ sensors capable of providing wavelength-resolved, absolute measurements of light intensities at wavelengths between ~50 and 300 nm are required. [70]

Improve understanding of the generation and propagation of VUV light in processing plasmas

A more thorough understanding of the generation and propagation of VUV light in LTPs is required. Both experiments and theory are needed. VUV absorption spectra of radicals and especially etching product fragments are mostly unknown but are required to accurately assess the attenuation of light produced in the densest regions of the discharge as it traverses the plasma volume and reaches the substrate. With validated models, processes can be tailored to minimize VUV fluxes while maintaining required etching rates and other metrics. There are some potential benefits to pulsing the plasma power to reduce the ratio of VUV while not sacrificing as much of a drop in deposition or etching rates. This is partly because the high-energy electrons that produce VUV light lose energy rapidly after plasma power is switched off, while positive ions and low-energy electrons leave the plasma at a much slower rate. Such approaches have not been widely explored, either through experiments or simulations.

Validate mechanisms for VUV-induced etching and defect formation

Mechanisms of VUV photon-plasma-adsorbate-surface interactions are critically lacking and will be required to mitigate unwanted photo effects. Experiments both outside of the plasma and in the plasma are needed. Individual phenomena, such as photodesorption of neutrals and ions need to be studied outside of the plasma. The creation of defects, such as trapped charges in insulators, can also be clarified. Experiments with neutral beams of stable species and radicals, combined with wavelength variable photon beams, such as those supplied by a synchrotron, would provide conditions approaching those in plasma but with more control. Such experiments would provide the kind of insights that were obtained with ion and neutral beam experiments carried out in early investigations of plasma etching.

Most importantly, more experimental investigations in plasmas are needed. The interplay between photons, ions, neutrals, and electric fields provides ample possibilities for combined effects. Indeed, there have been reports of synergism of ions and photons on the dielectric constant of SiOCH as well as the roughening of photoresist. [87] Anti-synergistic effects have also been found. Ion bombardment, or the presence of adsorbed oxygen, has been found to slow the photo-assisted etching of Si in a chlorine plasma. [11]

Most studies of photon-induced etching of semiconductor materials have been carried out in a halogen gas atmosphere in the *absence of plasma*. [88, 89, 90, 91, 92, 93, 94] Though IR light has been reported to enhance anisotropic etching of copper in the presence of chlorine, [95] the majority of attention has been on the role of light in the visible to VUV regions. Semi-insulating and *p*-type Si (100) are etched if exposed to simultaneous Cl atom impingement (produced by photodissociation of Cl_2) and surface irradiation with UV or visible light. Etching is usually attributed to photo-generated carriers, though photodesorption has also been proposed as an explanation. In all of these studies, using light from lasers and lamps at wavelengths of ≥248 nm, the etching yields (Si atoms-per-incident photon) were much less than unity.

Since such short wavelength photons are produced in the plasma, it is perhaps unsurprising that similar, large photoetching yields of 90 to 240

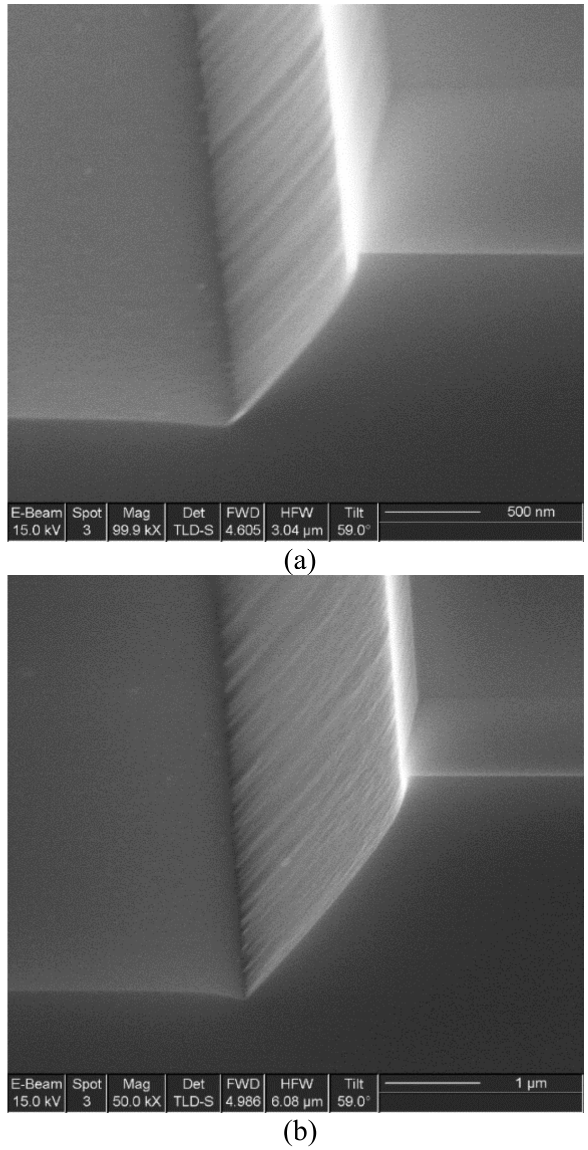
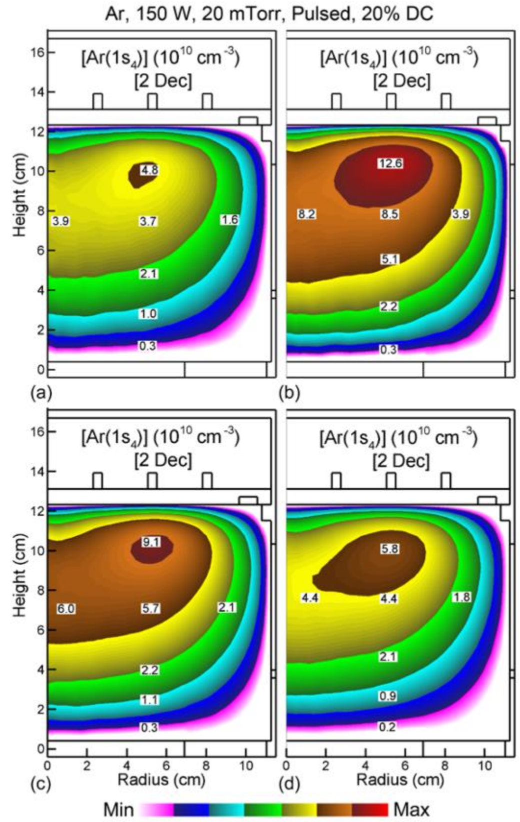
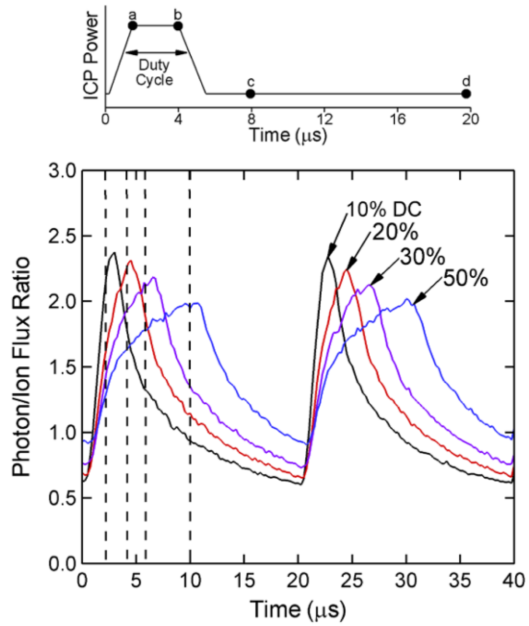


Figure 9: Cross-sectional scanning electron micrographs of SiO_2-masked p-Si(100) in an Ar/Cl_2 ICP with added VUV light provided by an Ar ICP. Etching periods: (a) 10 min, (b) 30 min. [78] Reprinted with permission from L. Du, D. J. Economou, V. M. Donnelly, *J. Vac. Sci. Technol. B* 1 March 2022; 40 (2): 022207. Copyright (2022) American Vacuum Society.



(a)



(b)

Figure 10: Properties of a pulsed inductively coupled plasma (50 kHz) in 20 mTorr argon. (a) Density of Ar(1s$_4$) resonant state at 20% duty cycle. (b) Ratio of VUV photon flux to ion flux onto the bottom substrate for different duty cycle. The vertical lines are the end of the power pulse. [73] From P. Tian and M. J Kushner, *Plasma Sources Sci. Technol.,* vol. 24, no. 3, 2015, reproduced by permission of IOP Publishing.

Si/photon were recently found in plasma etching of p-Si(100) in a Cl_2/Ar ICP. [78] Photo-assisted etching of Si requires the presence of Cl atoms; no etching occurs with VUV light in the presence of Cl_2 gas. [78] Etched surfaces are smooth with insignificant undercutting of the mask (cf., Fig. 9). The sidewall is sloped at an angle of 125°, indicative of the (111) plane. Photoassisted etching of Si was also found in pure Cl_2 plasmas and HBr/Ar and Br_2/Ar plasmas. [79]

Control plasma-generated UV/VUV photons to enhance (or de-emphasize) photon-stimulated surface processes

The development of LTPs for semiconductor processing has been highly focused on controlling the fluxes of neutral radicals, electrons, and ions onto the wafer. There has been little emphasis on controlling the plasma-produced UV/VUV photon fluxes onto wafers (and other plasma-facing materials). Separately controlling, for example, ion fluxes and photon fluxes onto the wafer will be challenging. For example, increasing (or decreasing) power to increase (or decrease) ion fluxes will likely have the same effect on photon fluxes as the same electron impact processes that produce ions also produce UV/VUV photons. Increasing ion fluxes while reducing UV/VUV fluxes will be difficult. New reactor configurations, chemistries, and power delivery schemes may be needed to obtain independent control over radical, ion, and photon fluxes to the wafer (or other plasma-facing materials).

Using pulsed power is one possibility for separately controlling ion and VUV fluxes in LTPs. For short lifetime states, which is usually the case for UV/VUV emission, photon fluxes to the wafer are closely aligned with power deposition, even with radiation trapping. Since ions to the wafer have a finite transit time, there is some average ion flux to the wafer over a pulsed period. These disparities enable some control of the ratio of photon-to-ion fluxes to the wafer, which may control synergistic reactions. (cf., Fig. 10.)

VUV light can stimulate etching by several mechanisms. The most commonly studied and invoked process involves the formation of electron-hole pairs in non-metallic materials. Electrons and holes migrating to the surface can aid in the breaking of Si-Si bonds and/or cause desorption of products. For example, the conduction band minimum and valence band maximum energy levels of a p-type semiconductor can bend down at the surface in the absence of plasma due to Fermi level pinning at mid-gap by surface states. In the presence of a plasma, above-bandgap light (1.12 eV for silicon) creates electron-hole pairs within the photon penetration depth. For photon energies just above the bandgap energy, the minority carrier (i.e., electrons for p-type semiconductors) will "fall" to the surface. With higher energy VUV photons, the excess energy released into "hot" electrons and holes allows the majority carriers to overcome the potential barriers and reach the surface, slowing electron-hole recombination at defect sites, thereby increasing the effectiveness of charge carriers in enhancing surface chemistry. Higher energy carriers created by VUV light will also ionize, creating additional carriers. These effects might be further influenced by the thickness and composition of the etching surface layer containing electronegative species and perhaps negative ions.

Furthermore, the degree of band bending depends on dopant concentration and light intensity. It is also likely that the ion bombardment that causes etching also modifies the surface and influences the photo effects. Therefore, careful experiments to isolate the effects of dopant types and concentrations, photons, ions, electrons and adsorbates, carrier recombination rates, etc., combined with theory are needed to provide insights into this poorly understood aspect of plasma processing of semiconductors and enable the design of VUV emitting plasma sources to capitalize on (or deemphasize) these effects.

Identify alternative mechanisms for photo-assisted etching

VUV light can also stimulate etching by causing species desorption from the surface. Direct substrate bond breakage can also aid in opening up the lattice, aiding in etchant (e.g., Cl or F) penetration and enhanced etching. Such a mechanism has been proposed, but little supporting evidence exists for this process. Existing carrier-mediated and photo-stimulated desorption mechanisms cannot produce yields over unity. Yet it is reported that VUV light causes etching of semiconductors (Si in the presence of XeF_2 gas, Si in a chlorine plasma, and GaAs in the presence of Cl_2 gas) with yields of 100 per photon or more. Cu in the presence of Cl_2 gas has also been found to etch with a yield of 2-10 per photon. [86] Hence, no existing mechanism can explain the large yields. These processes will feedback to the plasma by introducing fluxes of reactive species from the desorption process. These synergistic processes are, in principle, controllable by managing the UV/VUV fluxes produced by the plasma.

Characterize VUV-induced creation of damage and defects

The energies of VUV photons exceed the bond strengths of semiconductors and insulating materials. Hence, in addition to the transient production of electrons and holes, VUV photons can also create long-lasting damage within the photon penetration depth, including bond fissure and trapped charges. This can occur during etching and plasma-enhanced chemical vapor deposition processes. The effects of UV and VUV light on insulating materials, including photoresist, SiO_2, and porous SiOCH, have been widely reported but are still relatively poorly understood. [81, 96, 97] For photoresists, the main effects involve roughening the sides of the lithographically defined features during plasma etching. For the low dielectric constant SiOCH films, a similar sidewall erosion occurs, causing a loss of CH_3 groups and an undesirable increase in the dielectric constant.

Quantify the effects of VUV light on processes at other plasma-facing surfaces and their feedback to the plasma

While photon-wafer interactions are the primary concern of device fabrication, it is also likely that photon interactions with the chamber walls affect plasma chemistry. As there is more area in contact with the plasma that is not wafer than is wafer, these interactions can have large consequences on plasma behavior. In addition to creating secondary electrons by photo-electron emission, since the energy of positive ions bombarding the walls is usually relatively low, energetic photons may be the dominant cause of deposited etch products desorbing and reentering the plasma. These products have lower ionization potentials than most plasma feed gases, so even a small increase in their concentration could significantly alter the plasma density and electron energy distribution.

PRO 6: Develop novel institutional structures to meet emerging challenges of the field

The CHIPS for America Act of 2022 specifically intends "to develop onshore domestic manufacturing of semiconductors critical to U.S. competitiveness and national security." [98] A summary of this Act also notes an alarming trend in US manufacturing: "Only 12% of chips are currently manufactured domestically, compared to 37% in the 1990s, and many foreign competitors, including China, are investing heavily to dominate the industry. The United States also lacks capabilities to produce the most advanced chips at volume." [98] The Act includes appropriations to (1) incentivize onshore manufacturing of semiconductor devices, circuits, and systems, (2) conduct research and development (R&D) into advanced semiconductor manufacturing, and (3) increase workforce development and training opportunities.

Advancements in plasma science and engineering are central to all three of these goals. Significant advancements in low-temperature plasma science and engineering (LTPSE) will require substantial investments in the research infrastructure in the US. In some important ways, the present institutional structures have served the country well and continue to do so. Even so, the LTPSE field should be further enabled and encouraged to propose novel institutional structures to meet the anticipated unprecedented challenges and opportunities even more effectively. One group has stated a key question well:

> "All of the published proposals we have seen so far advocate spending more on research, training the workforce for the future, and leveraging the infrastructure that the writers either already have in place or hope to build. *But a question we should ask is what kind of next-generation research and development (R&D) infrastructure will be needed to meet future challenges* in the face of the technological and economic obstacles that lie ahead?" (Emphasis added) [99]

The challenges faced by those doing research and development in LTPSE today have scientific, intellectual, and financial elements. Furthermore, the challenges for those engaged in educating the next generation of the LTPSE workforce are also unprecedented. Few scientists and engineers have the wide-ranging expertise to carry out groundbreaking research leading to advances at the atomic scale while also being able to transition their discoveries to high-volume manufacturing (HVM). The current compartmentalization of research performed in universities, national laboratories, and private industry does not accomplish this translational mission well enough today. Several major US corporations have noted this compartmentalization at conferences as part of encouraging enhanced collaboration and new, more effective, and sustainable business models. [99, 100, 101, 102, 103, 104] Adapting and creating new institutional infrastructures for LTPSE to meet these challenges should be a priority.

The nation faces a chronic shortage of engineers and scientists, which is particularly acute in the field of LTPSE. Few universities in the US have even a single course on plasmas for semiconductor manufacturing, and few community colleges and trade schools offer courses focused on plasma materials processing. This situation has resulted in a lack of domestic students pursuing educational opportunities that lead to employment in the semiconductor industry at all levels, from technician to researcher, a situation that should be corrected.

Challenges and Opportunities

Advancing LTPSE related to semiconductor manufacturing has become increasingly challenging for several reasons, including:

1. The lengths scales involved span ~9 orders of magnitude – from the sub-nanometer features on a chip to the meter-scale size of the plasma chambers used.
2. The knowledge base required throughout the industry is strongly multi-disciplinary and interdisciplinary.
3. Research and development have become extraordinarily expensive.
4. Finding optimal "recipes" (the workflow or steps for a plasma process) through trial and error or even

ordinary design of experiments has become too slow and cost-prohibitive as the number of possible recipes increases.

5. The pace of *Moore's Law* is unforgiving. The entire field is expected to double its capability every two years at the same or reduced cost and size. This requires a daunting influx of new ideas and understanding.
6. Moore's Law has progressed at commercial scales for the last 40 years. Those working in the field throughout this progression are now retiring.
7. Device dimensions are reaching atomic scale, making "simple" scaling by shrinking device dimensions no longer feasible. As a direct result, the industry is moving to new materials. [105, 99, 100, 101, 102] Many materials are incompatible with existing technologies.
8. There is insufficient diversity within the LTPSE field, which, unfortunately, also makes the field less attractive to significant sections of the potential workforce.
9. Too few universities and community colleges can teach relevant subject matter.
10. Many of the needed teaching materials for LTPSE and semiconductor manufacturing are either dated or have yet to be developed.
11. Semiconductor manufacturing has become "largely invisible (to most students and the public)" [104], and LTPSE has become even more invisible today.

US universities have attracted some of the most innovative individuals worldwide who have entered the semiconductor workforce. Many of the US semiconductor industry leaders came to the US as graduate students. With the lack of domestic students entering the field, the current semiconductor workforce is highly dependent on this international source of talent. Strategies are needed to increase the pipeline of domestic students entering the plasma-focused semiconductor workforce at all levels while attracting international talent.

Due to the CHIPS Act, the Semiconductor Industry Association (SIA) has produced a projection on the needed workforce for the semiconductor manufacturing industry. [106] Scientists and engineers conversant in LTPSE are critically important to both the R&D and operations roles, which will comprise more than half the projected 300,000 employees by the 6th year. By comparison, the US annually produces at most a few thousand scientists and engineers conversant in LTPSE today, many of them being non-domestic students educated at US universities. We are educating at least an order of magnitude too few people in LTPSE in the US compared to what the semiconductor industry needs just for this projected growth (not even considering replacing a retiring workforce).

Proposals are currently being put forward to address these challenges. (See, for example, [99], [101] regarding research infrastructure and [104] regarding education infrastructure. See also the CPP Strategic Plan [107] and [108].) Both the CHIPS Act and the related FABS Act [109] note that semiconductor manufacturing requires an extraordinarily well-trained workforce. With plasmas playing such an integral role in semiconductor manufacturing, it is crucial for a substantial fraction of its workforce to be conversant in how to use plasmas in semiconductor manufacturing.

Workers are needed at all levels of education. High school graduates, technicians with a two-year Associates Degree, BS-level scientists and engineers, and those with a Masters or PhD degree are all critically needed. Educating these future leaders is challenging because available teaching materials in LTPSE at all levels are generally outdated. This is especially true of educational materials about plasmas for semiconductor manufacturing. This may be for several reasons, but one likely reason is that LTPSE is highly multidisciplinary. Second, LTPSE research funding in the US has diminished significantly in the last decade, causing universities to focus on hiring new faculty in other areas. There have also been far too few efforts to connect research institutions with semiconductor manufacturers and post-secondary institutions (and even K-12 institutions) to produce level-appropriate educational materials that benefit US industry.

Important qualities of proposed solutions

The unprecedented challenges faced by the LTPSE community clearly indicate that enhanced and novel institutional infrastructures will be a crucially important part of the solution. This needed infrastructure can include expanding current programs, but such incremental changes are unlikely to produce the needed advances. Novel institutional infrastructures should be a top priority to address today's challenges. The LTPSE community has identified several pressing needs in infrastructure and workforce development:

1. Improved capabilities to collaborate in research across university, national laboratory, and industry boundaries, both in emerging research areas and in existing fields.
2. Increased public and student awareness of LTPSE within semiconductor manufacturing. [104, 107, 108]
3. Increased pipeline of students ready to work in the semiconductor industry [105, 101, 104, 107, 108, 110]
4. Incentives to create new teaching materials, teaching collaborations/infrastructures/business models, and teaching technologies.
5. A stable increase in funding for LTPSE research to encourage universities to hire in this field.

These needs and challenges indicate that novel infrastructures for the LTPSE community should:

1. Enhance access to resources for conducting relevant and groundbreaking research.
2. Encourage diversity and inclusion throughout the LTPSE community, including incentives to reach diversity goals.
3. Enhance collaboration among the LTPSE constituencies, including, but not limited to, industrial researchers, academic researchers, and educators.
4. Support translational research at all levels.
5. Create programs that encourage supporting and hiring more faculty at universities, colleges, and trade schools who research and/or teach LTPSE related to semiconductor manufacturing. Encourage cross-over of industrial personnel into educational roles at all levels.
6. Engage with high school teachers to develop modules that introduce students to LTPSE.
7. Develop scalable programs to teach LTPSE at all levels and distribute those programs broadly.
8. Enlist and support the efforts of professional societies and organizations related to plasma-based semiconductor manufacturing.

One example of a proposed infrastructure modification to address this challenge has been put forward in a report by SEMI-ASA. [104] That report encourages cross-personnel appointments between industry, academia, and national labs to enhance collaboration, cross-fertilization, and education. Another example could be focused Professional Masters programs. Education at the BS level and below is also essential to support microelectronics manufacturing. Here, the impediment is not usually the cost but rather the ability of the school to create and teach the relevant curriculum. Partnerships with LTPSE-capable educational institutions, which would develop the curricular tools, are one model that has enabled such programs to flourish. Another is creating and maintaining educational clearing houses devoted to a particular subject.

Summary goals

Within the next five years, the following goals should be achieved:

1. DOE should lead the effort to both find and implement novel infrastructures for conducting groundbreaking research in low-temperature plasma science and engineering (LTPSE).
2. The number of programs at educational institutions that teach LTPSE directed at semiconductor manufacturing must increase substantially with a commensurate increase in students entering the field. This implies that the number of faculty devoted to such tasks will also need a significant increase.
3. Every engineering and physical science department at US universities should aim to have at least a

course or seminar in LTPSE related to semiconductor manufacturing.

4. Instructional materials in LTPSE related to semiconductor manufacturing appropriate for community colleges or advanced high schools should be made widely available. Training resources on how to teach those materials must also be easily accessible.

Passage of the CHIPS for America Act of 2022 and related legislation is an unprecedented opportunity to make a major and lasting change to US-based semiconductor manufacturing. Since low-temperature plasmas are critically important in semiconductor manufacturing, and plasma tools help determine the quality, quantity, and speed of chip production, renewed efforts should be directed into this field. These programs are an opportunity for institutional and infrastructural change, which can help grow the US semiconductor manufacturing industry. Doing so will enable vibrant and cross-disciplinary research in LTPSE, new business models for sharing research costs and benefits, increase the speed of commercialization of new knowledge and technologies, and dramatically increase our ability to educate in this area.

3. Summary

Low-temperature plasmas (LTPs) have been and continue to be a critical enabler for advanced microelectronics fabrication. With the diversity and complexity of microelectronic devices continuing to increase, the role of LTPs in enabling the fabrication of these devices will become even more critical. This critical role impacts nearly every aspect of microelectronics fabrication – from lithography, etching, deposition, surface modification, and packaging to sustainability. In order for plasma processing to fulfill this role, advances are needed in our fundamental understanding of plasma transport, chemistry, and materials interactions, from reactor scale to feature scale and even atomic scale. Improved methods are needed to translate that understanding to technology development in a co-design environment, and new collaborative relationships are needed between academia, industry, and national laboratories, including new models for workforce development. In this paper, we present and discuss the priority research opportunities (PROs) developed by the attendees of the Department of Energy Office of Science Fusion Energy Sciences Basic Research Needs (BRN) workshop Plasma Science for Microelectronics Nanofabrication, held August 2022. In the spirit of BRN reports, the PROs and their explanations are presented as research challenges and proposed directions for future research investments, not solutions to those challenges. We hope the international LTP community and supporting agencies will use these challenges and proposed directions in formulating their future research agendas to provide those solutions.

Acknowledgments

The authors would like to thank all of the *Plasma Science for Microelectronics Nanofabrication* workshop participants, whose inputs formed the basis for this report. [2]

The authors would like to thank the Department of Energy Office of Science Fusion Energy Sciences, and in particular Nirmol Podder and John Mandrekas, for sponsoring the *Plasma Science for Microelectronics Nanofabrication* workshop.

The work of M. J. Kushner was supported by the National Science Foundation (PHY-2009219), the Department of Energy Office of Fusion Energy Sciences (PHY-2009219) and Samsung Electronics.

The work of David B. Graves was supported in part by the US Department of Energy OFES (Contract No. DE-AC02-09CH11466) and Samsung Electronics.

Vincent Donnelly acknowledges financial supported by the National Science Foundation (PHY-1500518) and the Department of Energy, Office of Fusion Energy Science (DE –SC0001939).

E.S.A. gratefully acknowledges support from Alstadt Lord Mark Chair.

J.P.C. acknowledges support from William F. Seyer Chair at UCLA.

Conflicts of Interest

The authors have no conflicts to disclose.

Data Availability

Data sharing is not applicable to this article, as no new data were created or analyzed.

References

[1] C. A. Murray, S. Guha, D. Reed, G. Herrera, K. K. van Dam, S. S. Salahuddin, J. Ang, T. M. Conte, D. Jena, R. J. Kaplar, H. A. Atwater, R. L. Stevens, D. Boroyevich, W. J. Chappell, T.-J. K. Liu, J. R. Rattner, M. S. Witherell, K. K. Afridi, S. S. Ang, J. Bock, S. Chowdhury, S. Datta, K. S. Evans, J. D. Flicker, M. A. Hollis, N. M. Johnson, K. A. Jones, P. M. Kogge, S. Krishnamoorthy, M. J. Marinella, T. C. Monson, S. Narumanchi, P. R. Ohodnicki, R. Ramesh, M. L. Schuette, J. Shalf, S. Shahedipour-Sandvik, J. A. Simmons, V. S. Taylor, T. N. Theis, E. R. Colby, R. E. Pino, A. Schwartz, K. Runkles, J. E. Harmon, M. Nelson and V. Skonicki, "Basic Research Needs for Microelectronics: Report of the Office of Science Workshop on Basic Research Needs for Microelectronics, October 23 – 25, 2018," 2018.

[2] D. B. Graves, C. B. Labelle and M. J. Kushner, "Plasma Science for Microelectronics Nanofabrication," Dept. of Energy Office of Science Fusion Energy Sciences, 2023.

[3] K. J. Kanarik, S. Tan, W. Yang, I. L. Berry, Y. Pan and R. A. Gottscho, "Universal scaling relationship for atomic layer etching," *Journal of Vacuum Science & Technology A,* vol. 39, no. 1, 2021.

[4] G. Antoun, T. Tillocher, P. Lefaucheux, J. Faguet, K. Maekawa and R. Dussart, "Mechanism understanding in cryo atomic layer etching of SiO2 based upon C4F8 physisorption," *Scientific Reports,* vol. 11, no. 1, 2021.

[5] *Public Law 116 - 260 - Consolidated Appropriations Act,* U.S. House, 116th Congress, 2021.

[6] T. Cha, Y. Kim, S. Lee, Y. Cho and H. Chae, "Low-global warming potential fluoroether compounds for plasma etching of SiO 2 and Si 3 N 4 layers," *Journal of Vacuum Science & Technology A,* vol. 37, no. 5, 2019.

[7] "Infuse ORNL - First round 2022 awards announced by DOE," [Online]. Available: https://infuse.ornl.gov/news/first-round-2022-awards-announced-by-doe/.

[8] J. W. Coburn and H. F. Winters, "Ion- and electron-assisted gas-surface chemistry - An important effect in plasma etching," *Journal of Applied Physics,* vol. 50, no. 5, 1979.

[9] S. Sridhar, L. Liu, E. W. Hirsch, V. M. Donnelly and D. J. Economou, "Insights into the mechanism of in-plasma photo-assisted etching using optical emission spectroscopy," *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films,* vol. 34, no. 6, 2016.

[10] G. S. Oehrlein, R. J. Phaneuf and D. B. Graves, "Plasma-polymer interactions: A review of progress in understanding polymer resist mask durability during plasma etching for nanoscale fabrication," *Journal of Vacuum Science & Technology B, Nanotechnology and Microelectronics: Materials, Processing, Measurement, and Phenomena,* vol. 29, no. 1, 2011.

[11] E. W. Hirsch, L. Du, D. J. Economou and V. M. Donnelly, "Evidence for anti-synergism between ion-assisted etching and in-plasma photoassisted etching of silicon in a high-density chlorine plasma," *Journal of Vacuum Science & Technology A,* vol. 38, no. 2, 2020.

[12] K. J. Kanarik, T. Lill, E. A. Hudson, S. Sriraman, S. Tan, J. Marks, V. Vahedi and R. A. Gottscho, "Overview of atomic layer etching in the semiconductor industry," *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films,* vol. 33, no. 2, 2015.

[13] K. Yi, D. Liu, X. Chen, J. Yang, D. Wei, Y. Liu and D. Wei, "Plasma-Enhanced Chemical Vapor Deposition of Two-Dimensional Materials for Applications," *Accounts of Chemical Research,* vol. 54, no. 4, 2021.

[14] U. R. Kortshagen, R. M. Sankaran, R. N. Pereira, S. L. Girshick, J. J. Wu and E. S. Aydil, *Nonthermal plasma synthesis of nanocrystals: Fundamental principles, materials, and applications,* vol. 116, 2016.

[15] C. E. Nebel, *Nitrogen-vacancy doped CVD diamond for quantum applications: A review,* vol. 103, 2020.

[16] P. F. Kurunczi, J. Guha and V. M. Donnelly, "Plasma-surface reactions at a spinning wall," *Physical Review Letters,* vol. 96, no. 1, 2006.

[17] V. M. Donnelly, J. Guha and L. Stafford, "Critical review: Plasma-surface reactions and the spinning wall method," *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films,* vol. 29, no. 1, 2011.

[18] L. G. Christophorou and J. K. Olthoff, Fundamental Electron Interactions with Plasma Processing Gases, 2004.

[19] "Quantemol," [Online]. Available: https://www.quantemol.com/.

[20] C. B. Opal, W. K. Peterson and E. C. Beaty, "Measurements of secondary-electron spectra produced by electron impact ionization of a number of simple gases," *The Journal of Chemical Physics,* vol. 55, no. 8, 1971.

[21] H. W. Ellis, R. Y. Pai, E. W. McDaniel, E. A. Mason and L. A. Viehland, "Transport properties of gaseous ions over a wide energy range," *Atomic Data and Nuclear Data Tables,* vol. 17, no. 3, 1976.

[22] A. V. Phelps, "The application of scattering cross sections to ion flux models in discharge sheaths," *Journal of Applied Physics,* vol. 76, no. 2, 1994.

[23] "nl.lxcat.net," [Online]. Available: https://nl.lxcat.net/home.

[24] J. K. Olthoff and K. E. Greenberg, "The Gaseous Electronics Conference RF Reference Cell - An Introduction," *Journal of Research of the National Institute of Standards and Technology,* vol. 100, no. 4, 1995.

[25] Y. Yamamura and H. Tawara, "Energy dependence of ion-induced sputtering yields from monatomic solids at normal incidence," *Atomic Data and Nuclear Data Tables,* vol. 62, no. 2, 1996.

[26] J. Tanaka, C. F. Abrams and D. B. Graves, "New C–F interatomic potential for molecular dynamics simulation of fluorocarbon film formation," *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films,* vol. 18, no. 3, 2000.

[27] V. Bakshi, EUV Lithography, SPIE, 2018.

[28] D. C. Brandt, M. Purvis, I. Fomenkov, D. Brown, A. Schafgans, P. Mayer and R. Rafac, "Advances toward high power EUV sources for EUVL scanners for HVM in the next decade and beyond," *Proc. SPIE 11609, Extreme Ultraviolet (EUV) Lithography XII,* 22 February 2021.

[29] R. L. Kauffman, D. W. Phillion and R. C. Spitzer, "X-ray production 13 nm from laser-produced plasmas for projection x-ray lithography applications," *Applied Optics,* pp. 6897-6900, 1993.

[30] S. A. George, W. T. Silfvast, K. Takenoshita, R. T. Bernath, C.-S. Koay, G. Shimkaveg and M. C. Richardson, "Comparative extreme ultraviolet emission measurements for lithium and tin laser plasmas," *Optics Letters,* pp. 997-999, 2007.

[31] K. Bergmann, S. V. Danylyuk and L. Juschkin, "Optimization of a gas discharge plasma source for extreme ultraviolet interference lithography at a wavelength of 11 nm," *J. Appl. Phys.,* p. 073309, 2009.

[32] E. R. Hosler, O. R. W. II and W. A. Barletta, "Free-electron laser emission architecture impact on extreme ultraviolet lithography," *J. Micro/Nanolith. MEMS MOEMS,* 2017.

[33] J. White, P. Dunne, P. Hayden, F. O'Reilly and G. O'Sullivan, "Optimizing 13.5 nm laser-produced tin plasma emission as a function of laser wavelength," *Appl. Phys. Lett.,* p. 181502, 2007.

[34] F. Torretti, J. Sheil, R. Schupp, M. M. Basko, M. Bayraktar, R. A. Meijer, S. Witte, W. Ubachs, R. Hoekstra, O. O. Versolato, A. J. Neukirch and J. Colgan, "Prominent radiative contributions from

multiply-excited states in laser-produced tin plasma for nanolithography," *Nature Communications,* pp. 1-8, 2020.

[35] E. Verhoeven, R. Schuurhuis, M. Mastenbroek, P. Jonkers, F. Bornebroek, A. Minnaert, H. V. Dijck, P. Yaghoobi, G. Fisser, P. Tayebati, K. Hummler and R. V. Es, "0.33 NA EUV systems for High Volume Manufacturing," in *Proc. SPIE 11609, Extreme Ultraviolet (EUV) Lithography XII*, 2021.

[36] I. Fomenkov, D. Brandt, A. Ershov, A. Schafgans, Y. Tao, G. Vaschenko, S. Rokitski, M. Kats, M. Vargas, M. Purvis, R. Rafac, B. L. Fontaine, S. D. Dea, A. LaForge, J. Stewart, S. Chang, M. Graham, D. Riggs, T. Taylor, M. Abraham and D. Brown, "Light sources for high-volume manufacturing EUV lithography: Technology, performance, and power scaling," *Advanced Optical Technologies,* vol. 6, no. 3-4, 2017.

[37] K. Nishihara, A. Sunahara, A. Sasaki and others, "Plasma physics and radiation hydrodynamics in developing an extreme ultraviolet light source for lithography," *Phys. Plasmas,* p. 056708, 2008.

[38] O. O. Versolato, "Physics of laser-driven tin plasma sources of EUV radiation for nanolithography," *Plasma Sources Sci. Technol.,* pp. 1-16, 2019.

[39] J. Beckers, T. v. d. Ven, R. v. d. Horst, D. Astakhov and V. Banine, "EUV-Induced Plasma: A Peculiar Phenomenon of a Modern Lithographic Technology," *Appl. Sci.,* p. 2927, 2019.

[40] M. Purvis, I. V. Fomenkov, A. A. Schafgans, P. Mayer, K. Hummler, M. H. Leenders, Y. Tao, S. I. Rokitski, J. Stewart, A. I. Ershov, R. J. Rafac, S. D. Dea, G. O. Vaschenko, D. C. Brandt and D. J. B, "Laser-produced plasma incoherent EUV light sources for high-volume manufacturing semiconductor lithography," *Proc. SPIE 11111, X-Ray Lasers and Coherent X-Ray Sources: Development and Applications XIII,* 9 September 2019.

[41] W. Eschen, L. Loetgering, V. Schuster, R. Klas, A. Kirsche, L. Berthold, M. Steinert, T. Pertsch, H. Gross, M. Krause, J. Limpert and J. Rothhardt, "Material-specific high-resolution table-top extreme ultraviolet microscopy," *Light: Science & Applications,* 2022.

[42] M. D. Seaberg, B. Zhang, D. F. Gardner, E. R. Shanblatt, M. M. Murnane, H. C. Kapteyn and D. E. Adams, "Tabletop Nanometer Extreme Ultraviolet Imaging in an Extended Reflection Mode using Coherent Fresnel Ptychography," *Optica,* 2014.

[43] D. F. Gardner, M. Tanksalvala, E. R. Shanblatt, X. Zhang, B. R. Galloway, C. L. Porter, R. K. Jr, C. Bevis, D. E. Adams, H. C. Kapteyn, M. M. Murnane and G. F. Mancini, "Subwavelength coherent imaging of periodic samples using a 13.5 nm tabletop high-harmonic light source," *Nature Photonics,* pp. 259-263, 2017.

[44] F. Barkusky, A. Bayer, S. Döring, P. Grossmann and K. Mann, "Damage threshold measurements on EUV optics using focused radiation from a table-top laser produced plasma source," *Optics Express,* pp. 4346-4355, 2010.

[45] A. Sasaki, A. Sunahara, K. Nishihara, T. Nishikawa, K. Fujima, T. Kagawa, F. Koike and H. Tanuma, "Atomic modeling of the plasma EUV sources," *High Energy Density Physics,* pp. 250-255, 2007.

[46] A. Thoss, "EUV lithography revisited," 29 August 2019. [Online]. Available: https://www.laserfocusworld.com/blogs/article/14039015/how-does-the-laser-technology-in-euv-lithography-work.

[47] B. Hou and S. Stapczynski, "Chipmaking's Next Big Thing Guzzles as Much Power as Entire Countries," *Bloomberg US Edition,* 25 August 2022.

[48] R. Schupp, F. Torretti, R. Meijer, M. Bayraktar, J. Scheers, D. Kurilovich, A. Bayerle, K. Eikema, S. Witte, W. Ubachs, R. Hoekstra and O. Versolato, "Efficient Generation of Extreme Ultraviolet Light From Nd:YAG-Driven Microdroplet-Tin Plasma," *PHYSICAL REVIEW APPLIED,* p. 014010, 2019.

[49] K. M. Nowak, T. Ohta, T. Suganuma, J. Fujimoto, H. Mizoguchi, A. Sumitani and A. Endo, "CO2 laser drives extreme ultraviolet nano-lithography — second life of mature laser technology," *Opto-Electronics Review,* pp. 345-354, 2013.

[50] A. Garscadden, M. Kushner and G. Eden, "Plasma Physics Issues in Gas Discharge Laser Development," *IEEE Transations on Plasma Science,* pp. 1013-1031, 1991.

[51] W. J. Witteman, The CO2 Laser, Springer, 1987.

[52] J. A. Macken, "CO2 laser performance with a distributed gold catalyst," *IEEE Journal of Quantum Electronics,* pp. 1695-1703, 1989.

[53] A. A. Schafgans, D. J. Brown, I. V. Fomenkov, R. Sandstrom, A. Ershov, G. Vaschenko, R. Rafac, M. Purvis, S. Rokitski, Y. Tao, D. J. Riggs, W. J. Dunstan, M. Graham and others, "Performance optimization of MOPA pre-pulse LPP light source," *Proceedings of the SPIE,* 2015.

[54] R. Schupp, L. Behnke, Z. Bouza, Z. Mazzotta, Y. Mostafa, A. Lassise, L. Poirier, J. Sheil, M. Bayraktar, W. Ubachs, R. Hoekstra and O. O. Versolato, "Characterization of angularly resolved EUV emission from 2-μm-wavelength laser-driven Sn plasmas using preformed liquid disk targets," *Journal of Physics D: Applied Physics,* p. 365103, 2021.

[55] L. Yin, H. Wang, B. A. Reagan, C. Baumgarten, Z. Lyu, R. Soufli, E. Gullikson, V. N. Shlyaptsev and J. J. Rocca, "Using Temporally Synthesized Laser Pulses to Enhance the Conversion Efficiency of Sn Plasmas for EUV Lithography," *IEEE Photonics Journal,* 2021.

[56] M. v. d. Kerkhof, F. Liu, M. Meeuwissen, X. Zhang, M. Bayraktar, R. d. Kruif and N. Davydovaa, "High-power EUV lithography: spectral purity and imaging performance," *J. Micro/Nanolith. MEMS MOEMS,* p. 033801, 2020.

[57] S. Harilal, B. O'shay, Y. Tao and M. Tillack, "“Ion debris mitigation from tin plasma using ambient gas, magnetic field and combined effects," *Appl. Phys. B: LAsers Opt.,* pp. 547-553, 2007.

[58] D. B. Abramenko, M. V. Spiridonov, P. V. Krainov, V. M. Krivtsun, D. I. Astakhov, V. V. Medvedev, M. van Kampen, D. Smeets and K. N. Koshelev, "Measurements of hydrogen gas stopping efficiency for tin ions from laser-produced plasma," *Applied Physics Letters,* p. 164102, 2018.

[59] M. v. d. Kerkhof, A. M. Yakunin, V. Kvon, A. Nikipelov, D. Astakhov, P. Krainov and V. Banine, "EUV-induced hydrogen plasma and particle release," *Radiation Effects and Defects in Solids,* pp. 486-512, 2022.

[60] D. T. Elg, G. A. Panici, S. Liu, G. Girolami, S. N. Srivastava and D. N. Ruzic, "Removal of Tin from Extreme Ultraviolet Collector Optics by In-Situ Hydrogen Plasma Etching," *Plasma Chemistry and Plasma Processing,* pp. 223-245, 2018.

[61] C. Onwudinanti, G. Brocks and V. Koelman, "Tin deposition on ruthenium and its influence on blistering in multi-layer mirrors," *Royal Society of Chemistry,* p. 13878, 2021.

[62] C. Onwudinanti, I. Tranca, T. Morgan and S. Tao, "Tin, The Enabler—Hydrogen Diffusion into Ruthenium," *Nanomaterials,* p. 129, 2019.

[63] D. Ugur, A. Storm, R. Verberk, J. Brouwer and W. Sloof, "Generation and decomposition of volatile tin hydrides monitored by in situ quartz crystal microbalances," *Chemical Physics Letters,* pp. 122-125, 2012.

[64] D. Qerimi, A. C. Herschberg, G. Panici, P. Hays, T. Pohlman and D. N. Ruzic, "Tin removal by an annular surface wave plasma antenna in an extreme ultraviolet lithography source," *Journal of Applied Physics,* vol. 132, p. 113302, 2022.

[65] S. F. A. Kettle, "The kinetics of the decomposition of stannane on a tin surface," *Journal of the Chemical Society,* 1961.

[66] R. Garza, N. Bartlett, J. Crouse, A. Herschberg, R. Mohan Sankaran, M. Amzad Hossain and D. N. Ruzic, "Stannane in extreme ultraviolet lithography and vacuum technology: Synthesis and characterization," *Journal of Vacuum Science & Technology A,* vol. 41, p. 063209, October 2023.

[67] W. Ou, F. Brochard and T. W. Morgan, "Bubble formation in liquid Sn under different plasma loading conditions leading to droplet ejection," *Nuclear Fusion,* p. 066030, 2021.

[68] J. R. Woodworth, M. E. Riley, V. A. Amatucci, T. W. Hamilton and B. P. Aragon, "Absolute intensities of the vacuum ultraviolet spectra in oxide etch plasma processing discharges," *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films,* vol. 19, no. 1, pp. 45-55, 2001.

[69] M. J. Titus, D. Nest and D. B. Graves, "Absolute vacuum ultraviolet flux in inductively coupled plasmas and chemical modifications of 193 nm photoresist," *Applied Physics Letters,* vol. 94, no. 17, 2009.

[70] B. Jinnai, S. Fukuda, H. Ohtake and S. Samukawa, "Prediction of UV spectra and UV-radiation damage in actual plasma etching processes using on-wafer monitoring technique," *Journal of Applied Physics,* vol. 107, no. 4, 2010.

[71] J. B. Boffard, C. C. Lin, C. Culver, S. Wang, A. E. Wendt, S. Radovanov and H. Persing, "Comparison of surface vacuum ultraviolet emissions with resonance level number densities. I. Argon plasmas," *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films,* vol. 32, no. 2, 2014.

[72] E. J. Iglesias, F. Mitschker, M. Fiebrandt, N. Bibinov and P. Awakowicz, "In situ measurement of VUV/UV radiation from low-pressure microwave-produced plasma in Ar/O2 gas mixtures," *Measurement Science and Technology,* vol. 28, no. 8, 2017.

[73] P. Tian and M. J. Kushner, "Controlling VUV photon fluxes in low-pressure inductively coupled plasmas," *Plasma Sources Science and Technology,* vol. 24, no. 3, 2015.

[74] L. Du, P. Ruchhoeft, D. J. Economou and V. M. Donnelly, "Absolute measurement of vacuum ultraviolet photon flux in an inductively coupled plasma using a Au thin film," *Journal of Vacuum Science & Technology B,* vol. 40, no. 2, p. 022206, March 2022.

[75] K. Choi and C. Han, "Low Temperature Copper Etching Using an Inductively Coupled Plasma with Ultraviolet Light Irradiation," *Journal of The Electrochemical Society,* vol. 145, no. 3, 1998.

[76] H. Shin, W. Zhu, V. M. Donnelly and D. J. Economou, "Surprising importance of photo-assisted etching of silicon in chlorine-containing plasmas," *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films,* vol. 30, no. 2, 2012.

[77] L. Du, E. W. Hirsch, D. J. Economou and V. M. Donnelly, "Effects of O 2 addition on in-plasma photo-assisted etching of Si with chlorine," *Journal of Vacuum Science & Technology A,* vol. 38, no. 5, 2020.

[78] L. Du, D. J. Economou and V. M. Donnelly, "In-plasma photo-assisted etching of Si with chlorine aided by an external vacuum ultraviolet source," *Journal of Vacuum Science & Technology B,* vol. 40, no. 2, 2022.

[79] W. Zhu, S. Sridhar, L. Liu, E. Hernandez, V. M. Donnelly and D. J. Economou, "Photo-assisted etching of silicon in chlorine- and bromine-containing plasmas," *Journal of Applied Physics,* vol. 115, no. 20, 2014.

[80] M. Okigawa, Y. Ishikawa and S. Samukawa, "Reduction of ultraviolet-radiation damage in SiO[sub 2] using pulse-time-modulated plasma and its application to charge coupled 44 device image sensor processes," *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures,* vol. 21, no. 6, 2003.

[81] J. Lee and D. B. Graves, "The effect of VUV radiation from Ar/O2 plasmas on low-k SiOCH films," *Journal of Physics D: Applied Physics,* vol. 44, no. 32, 2011.

[82] M. Fukasawa, H. Matsugai, T. Honda, Y. Miyawaki, Y. Kondo, K. Takeda, H. Kondo, K. Ishikawa, M. Sekine, K. Nagahata, F. Uesawa, M. Hori and T. Tatsumi, "Wavelength dependence of photon-induced interface defects in hydrogenated silicon nitride/Si structure during plasma etching processes," *Japanese Journal of Applied Physics,* vol. 52, no. 5 PART 3, 2013.

[83] K. Eriguchi, "Defect generation in electronic devices under plasma exposure: Plasma-induced damage," *Japanese Journal of Applied Physics,* vol. 56, no. 6, 2017.

[84] V. Ney and N. Schwentner, "Reactions of halogens with surfaces stimulated by VUV light," *Journal of Physics Condensed Matter,* vol. 18, no. 30, 2006.

[85] U. Streller, B. Li, A. Krabbe, H. P. Krause, I. Twesten and N. Schwentner, "Photochemical etching with tunable VUV radiation," *Journal of Electron Spectroscopy and Related Phenomena,* vol. 80, 1996.

[86] H. Raaf and N. Schwentner, "Efficiencies above unity in light-induced reaction of Cu with Cl 2 : Excitation, amplification, and diffusion processes," *Applied Surface Science,* vol. 174, no. 1, 2001.

[87] D. Nest, D. B. Graves, S. Engelmann, R. L. Bruce, F. Weilnboeck, G. S. Oehrlein, C. Andes and E. A. Hudson, "Synergistic effects of vacuum ultraviolet radiation, ion bombardment, and heating in 193 nm photoresist roughening and degradation," *Applied Physics Letters,* vol. 92, no. 15, 2008.

[88] H. Okano, Y. Horiike and M. Sekine, "Photo-excited etching of poly-crystalline and single-crystalline silicon in cl2 atmosphere," *Japanese Journal of Applied Physics,* vol. 24, no. 1 R, 1985.

[89] R. Kullmer and D. Bäuerle, "Laser-induced chemical etching of silicon in chlorine atmosphere - I. Pulsed irradiation," *Applied Physics A Solids and Surfaces,* vol. 43, no. 3, 1987.

[90] R. B. Jackman, H. Ebert and J. S. Foord, "Reaction mechanisms for the photon-enhanced etching of semiconductors: An investigation of the UV-stimulated interaction of chlorine with Si(100)," *Surface Science,* vol. 176, no. 1-2, 1986.

[91] W. Sesselmann, "Reaction of silicon with chlorine and ultraviolet laser induced chemical etching mechanisms," *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures,* vol. 7, no. 5, 1989.

[92] F. A. Houle, "Photochemical etching of silicon: The influence of photogenerated charge carriers," *Physical Review B,* vol. 39, no. 14, 1989.

[93] P. Mogyorosi, K. Piglmayer, R. Kullmer and D. Bauerle, "Laser-induced chemical etching of silicon in chlorine atmosphere - II. Continuous irradiation," *Applied Physics A Solids and Surfaces,* vol. 45, no. 4, pp. 293-299, April 1988.

[94] S. Samukawa, B. Jinnai, F. Oda and Y. Morimoto, "Surface reaction enhancement by UV irradiation during Si etching process with chlorine atom beam," *Japanese Journal of Applied Physics, Part 2: Letters,* vol. 46, no. 1-3, 2007.

[95] Y. Ohshita and N. Hosoi, "Lower temperature plasma etching of Cu using IR light irradiation," *Thin Solid Films,* vol. 262, no. 1-2, 1995.

[96] M. R. Baklanov, J. F. D. Marneffe, D. Shamiryan, A. M. Urbanowicz, H. Shi, T. V. Rakhimova, H. Huang and P. S. Ho, "Plasma processing of low-k dielectrics," *Journal of Applied Physics,* vol. 113, no. 4, 2013.

[97] J. K. Jang, H. W. Tak, Y. J. Shin, D. S. Kim and G. Y. Yeom, "Plasma Induced Damage Reduction of Ultra Low-k Dielectric by Using Source Pulsed Plasma Etching for Next BEOL Interconnect Manufacturing," *IEEE Transactions on Semiconductor Manufacturing,* vol. 33, no. 2, 2020.

[98] "A Summary of the CHIPS and SCIENCE Act," [Online]. Available: https://www.vanhollen.senate.gov/imo/media/doc/CHIPS%20and%20Science%20Act%20of%202022%20Summary.pdf.

[99] R. A. Gottscho, E. V. Levine, T.-J. K. Liu, P. C. McIntyre, S. Mitra, B. Murmann, J. M. Rabaey, S. Salahuddin, W. C. Shih and H.-S. P. Wong, "Innovating at Speed and at Scale: A Next Generation Infrastructure for Accelerating Semiconductor Technologies," *arXiv:2204.02216 [cs.OH],* 2022.

[100] "SIA Comments to NIST - 83 Fed. Reg 32842 (July 2018)," [Online]. Available: https://www.semiconductors.org/wp-content/uploads/2018/11/NIST-workforce-RFI-august-2018.pdf .

[101] C. Murray, *Semiconductor Technology Panel,* Stanford University, 2020.

[102] O. Nalamasu, "Materials to Systems in Semiconductor Manufacturing and Beyond," *Semiconductor Digest,* p. 20, Dec 2021.

[103] "Tim Archer - Lam Research Senate Testimony," [Online]. Available: https://www.commerce.senate.gov/2022/3/developing-next-generation-technology-for-innovation.

[104] SEMI and ASA, "Fueling American Innovation & Growth: A National Network for Microelectronics Education and Workforce Development," SEMI & ASA, 2022.

[105] "Gottscho - Forbes Interview," [Online]. Available: https://www.forbes.com/sites/willyshih/2021/08/12/semiconductor-manufacturing-making-impossibly-small-features/?sh=f7deb8a2ca50.

[106] "SIA-Impact May 2021," [Online]. Available: https://www.semiconductors.org/wp-content/uploads/2021/05/SIA-Impact_May2021-FINAL-May-19-2021_2.pdf.

[107] S. Baalrud, N. Ferraro, L. Garrison, N. Howard, C. Kuranz, J. Sarff, E. Scime and W. Solomon, "A Community Plan for Fusion Energy and Discovery Plasma Sciences," American Physical Society, 2019-2020.

[108] *Appendix to the CPP Strategic Plan on recommendations B-1 to C-2,* 2019-2020.

[109] "S.2107 - FABS Act," [Online]. Available: https://www.congress.gov/bill/117th-congress/senate-bill/2107.

[110] "Foreign Born STEM Workers United States," [Online]. Available: https://www.americanimmigrationcouncil.org/research/foreign-born-stem-workers-united-states.

[111] J. W. Butterbaugh, "Plasma–surface interactions in fluorocarbon etching of silicon dioxide," *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures,* vol. 9, no. 3, 1991.

[112] A. Fischer, A. Routzahn, R. J. Gasvoda, J. Sims and T. Lill, "Control of etch profiles in high aspect ratio holes via precise reactant dosing in thermal atomic layer etching," *Journal of Vacuum Science & Technology A,* vol. 40, no. 2, 2022.

[113] S. Huang, C. Huard, S. Shim, S. K. Nam, I.-C. Song, S. Lu and M. J. Kushner, "Plasma etching of high aspect ratio features in SiO 2 using Ar/C 4 F 8 /O 2 mixtures: A computational investigation," *Journal of Vacuum Science & Technology A,* vol. 37, no. 3, 2019.

[114] M. Mori, S. Irie, Y. Osano, K. Eriguchi and K. Ono, "Model analysis of the feature profile evolution during Si etching in HBr-containing plasmas," *Journal of Vacuum Science & Technology A,* vol. 39, no. 4, 2021.

[115] Y. G. Yook, H. S. You, J. H. Park, W. S. Chang, D. C. Kwon, J. S. Yoon, K. H. Yoon, S. S. Shin, D. H. Yu and Y. H. Im, "Fast and realistic 3D feature profile simulation platform for plasma etching process," *Journal of Physics D: Applied Physics,* vol. 55, no. 25, 2022.

[116] V. Zardetto, B. L. Williams, A. Perrotta, F. D. Giacomo, M. A. Verheijen, R. Andriessen, W. M. M. Kessels and M. Creatore, "Atomic layer deposition for perovskite solar cells: Research status, opportunities and challenges," *Sustainable Energy and Fuels,* vol. 1, no. 1, 2017.

[117] M. Hirayama, A. Teramoto and S. Sugawa, "Control of ion-flux and ion-energy in direct inductively coupled plasma reactor for interfacial-mixing plasma-enhanced atomic layer deposition," *J. Vac. Sci. Technol. A,* vol. 38, p. 032408, April 2020.

[118] K. Hernandez, A. Press, M. J. Goeckner and L. J. Overzet, "Optical emission intensity overshoot and electron heating mechanisms during the re-ignition of pulsed capacitively coupled Ar plasmas," *J. Vac. Sci. Technol. B,* vol. 39, no. 2, p. 024003, March 2021.

[119] Z. Xiao, K. Kisslinger, S. Chance and S. Banks, "Comparison of Hafnium Dioxide and Zirconium Dioxide Grown by Plasma-Enhanced Atomic Layer Deposition for the Application of Electronic Materials," *Crystals,* vol. 10, 2020.

[120] P. Schindler, M. Logar, J. Provine and F. B. Prinz, "Enhanced Step Coverage of TiO2 Deposited on High Aspect Ratio Surfaces by Plasma-Enhanced Atomic Layer Deposition," *Langmuir,* vol. 31, pp. 5057-5062, 2015.