

Emerging Molecular and Atomic Level Techniques for Nanoscale Applications

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As commercial applications across multiple disciplines enter the sub-nanometer scale regime, research and development (R&D) efforts to identify processing techniques that enable exceptional atomic level control of the composition, uniformity, and morphology of exceedingly thin film structures are intensifying.^{1,3} This overview provides an introduction and comparison of emerging processing technologies that represent the best contenders to satisfy future demands for ultrathin film applications.

Historically, the need for tighter control over film uniformity, conformality, and properties at decreasing thicknesses was met by a gradual evolution from physical vapor deposition (PVD), to chemical vapor deposition (CVD), and eventually atomic layer deposition (ALD) processes.^{4,6} As device design rules approach molecular radius and bond length dimensions, deposition processes with inherent control of atomic order become even more critical. To give a rather simplistic example of this criticality, a 2 nm-thick binary film (such as Al_2O_3 , Si_3N_4 , and GaAs) will consist of only a 10 to 20 atoms-thick layer, which must be deposited uniformly, continuously, and coherently. A number of terms and descriptors are used to depict these structures, including: ultra-thin films, atomic layers, molecular films, near-zero-thickness layers, and monolayers.

Overview of Ultra-Thin Film Processing Techniques

Of all manufacturing-worthy thin-film deposition processes, ALD has the greatest potential to satisfy these requirements. However, the intrinsic constraints of recurrent two atom reactivity and associated by-products have kindled tremendous interest in other self-limiting deposition processes such as molecular layer deposition (MLD), self-assembled monolayer (SAM), and click chemistry deposition (CCD) processes, either as alternatives to or in conjunction with ALD.⁶⁻¹²

PVD and CVD ▶ Despite various innovations that improve directional and conformal control, such as high ionization, long-throw chamber geometries, and capacitively-coupled substrate holders for wafer bias,¹³ PVD remains a line-of-sight technique in which species impinge on the substrate from the gas phase. Coupled with the challenge of achieving low growth rates consistent with tight control of film thickness, this characteristic has limited PVD's applicability to thicker films in less aggressive topographies.

In contrast, CVD offers the advantage of surface driven reactions, which can produce enhanced step coverage in minimum groundrule features.^{14,15} Gaseous reactants are usually transported intact to the substrate surface in thermal CVD growth mechanisms. In plasma-assisted CVD (PA-CVD) and plasma-enhanced

CVD (PE-CVD) mechanisms, on the other hand, plasma reactions are followed by transport of the resulting transient reactive species to the surface.^{16,17} The reactants are then adsorbed onto the substrate surface, followed by surface diffusion with potential desorption of some reactants, which is in turn followed by surface reaction with film nucleation and growth in island mode, layer-by-layer (step) mode, or a combination of the two. Finally, the resulting volatile reaction byproducts are emitted from the surface. In thermal CVD, higher substrate temperature allows longer surface diffusion lengths, leading to extended surface reaction times and resulting in improved step coverage and reduced contaminant incorporation. Pre-adsorption plasma reactions in PA-CVD or PE-CVD, on the other hand, can allow generation of more active reactant species, resulting in higher surface mobility and reaction rates at lower temperatures as well as shorter surface diffusion lengths, but yielding less contaminated films with poorer step coverage. However, CVD growth mechanisms typically require discrete islands or isolated layers to reach a certain thickness prior to connecting to achieve a coherent film, a feature that in some cases prohibits the growth of extremely thin films. Accomplishing low CVD deposition rates that enable ultrathin film thickness control is an additional challenge.

Alternatively, the sequential self-limiting surface reaction mechanisms in ALD enable control of film thickness and conformality with atomic accuracy, producing excellent step coverage in nanometer scale topographies.¹² As shown in Fig. 1, the most common ALD processes are based on dual surface reactions in which a first source

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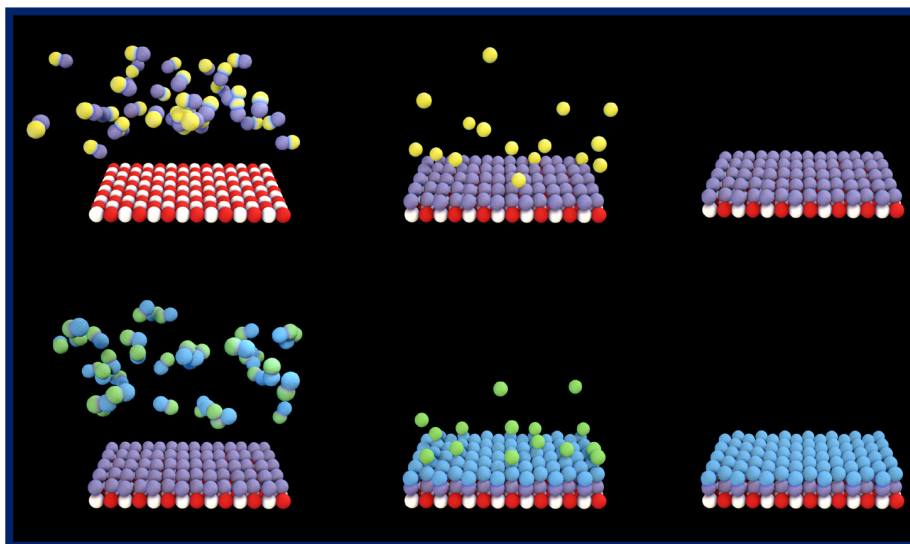


FIG. 1. Schematic diagram of the dual sequential reactions involved in the ALD growth of a single layer of a binary inorganic film: (a) a first source precursor is introduced into the reaction zone; (b) the precursor undergoes a surface self-limiting reaction with the substrate surface to deposit a single layer of a first element; (c) the remaining precursor species and reaction byproducts are completely removed from the reaction zone through a gas purge step; (d) a second source precursor is introduced into the reaction zone; (e) the second precursor undergoes a self-limiting surface reaction with the first element to form a binary material; and (f) the remaining precursor species and reaction byproducts are completely removed from the reaction zone through a gas purge step.

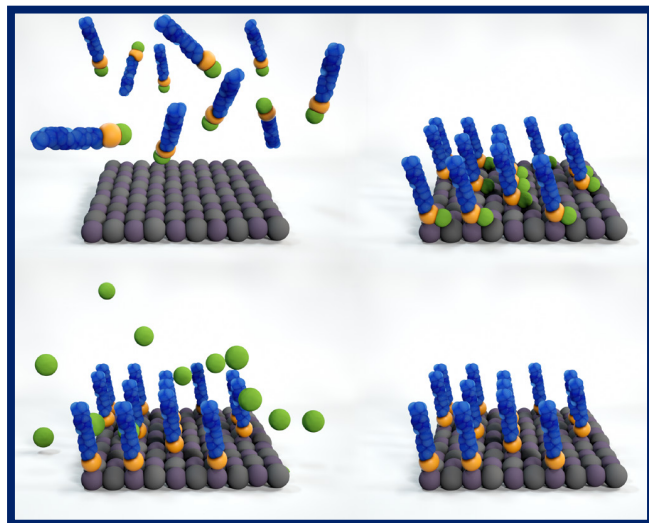


FIG. 2. Schematic depiction of the dual sequential reactions involved in the MLD growth of a single inorganic layer: (a) a source precursor is introduced into the reaction zone; (b) the precursor molecules are adsorbed to the substrate surface (c) the precursor molecules undergo a surface self-limiting reaction with the substrate surface leading to the formation and alignment of organic molecular fragments; and (d) the remaining precursor species and reaction byproducts are completely removed from the reaction zone through a gas purge step.

precursor-surface self-limiting reaction deposits a single layer of a first element, after which a second source-precursor self-limiting surface reaction causes a second element to react with the first to form a dual-component (binary) film. A key aspect of ALD is that the two source precursors never cross paths in the reaction zone, since there are intermediate purge steps between the two self-limiting reactions. The addition of plasma treatment in-between the two surface reactions has been shown to enhance surface adsorption by increasing the number of active surface sites and decreasing reaction activation energy, leading to lower processing temperatures.^{18,19}

ALD boasts a number of desirable features, including ALD-grown films being particle and pin-hole free; precise management of film thickness down to a few atoms; exceptional conformality and continuity in nanometer size device geometries and features; and the ability to deposit a wide and diverse portfolio of binary materials. Concurrently, the current shortcomings of ALD include excessive surface roughness; very low growth rates (and thus limited throughput); and being restricted to binary materials.

Although there are no universally accepted descriptions of MLD, SAM, and CCD, they are techniques that, along with ALD, have the potential to enable formation of exceedingly thin film structures with atomic or molecular level control. Common features among these techniques include surface adsorption and the attachment of

sequences of atoms, typically organic molecular “fragments.”²⁰⁻²² Ordered arrangements of atoms or uniformly repeated configurations of atoms attach to the surface in a self-limiting manner at significantly lower process temperatures compared to traditional techniques.⁹ However, while MLD like ALD represents a process where single monolayers are deposited and then by iterative growth cycles can build thicker structures, SAM and CCD tend to be exclusively “single monolayer” type growth processes.

MLD ▶ The term MLD is predominantly used to describe a process identical to the sequential dual-surface reactions and self-limiting mechanisms that occur in ALD (shown in Fig. 2) except for the fact that while ALD focuses on ultrathin inorganic layers, MLD is employed for the formation of ultrathin organic molecular layers.^{2,23} Other reports define MLD as an equivalent technique to ALD for the deposition of organic molecular fragments that may contain inorganic constituents, but does not require the precise ALD atomic coverage, nor the self-limiting characteristics of the deposition process.²⁴

SAM ▶ Similarly, the most common portrayal of SAM deposition is a process wherein ordered organic molecular assemblies can adsorb and then spontaneously orient on a substrate surface from either the gaseous or liquid phase through intermolecular interactions.^{25,26} SAM deposition could be used as a surface modification template to custom design the formation and growth of the subsequent ultrathin film, which would then be grown by CVD or ALD.²⁷ One of the main benefits of SAM deposition is its ability to deposit a sole molecule or a single molecular length of essentially an individual monolayer. A SAM molecule typically consists of three sections: an anchor group which attaches to the underlying substrate surface, a molecular chain (e.g., an alkyl group), and a terminal group which may or may not have functionality, as indicated in Fig. 3.²⁸ The terminal group is important for area specific deposition. Non-functional terminal groups tend to suppress deposition processes while terminal groups with appropriate functionality initiate area selective deposition.

CCD ▶ The term “click chemistry” was first introduced in 2001 by Nobel Laureate Barry Sharpless. In the context of this report, CCD refers to chemical reactions that occur with sufficient thermodynamic driving force to enable deposition at or near room temperature with very little or no byproducts.^{29,30} CCD has the potential for a single reactant interaction with a substrate surface, producing total or near total atom-specific attachment of an ordered assembly of multiple atoms as a monolayer film. CCD could also comprise the reaction of multiple reagents, generating complete or near complete consumption and conversion to a single deposition. The latter would assume the form of an extremely thin or single monolayer on the substrate surface, as depicted schematically in Fig. 4.³¹

Comparison of Methods ▶ One of the attractive features of SAM and CCD is their demonstrated potential to catalyze, enable, or suppress area-specific or area-selective deposition.^{32,33} Specific chemistries (precursors) and surface structures can be made to interact so as to induce or prevent deposition on certain regions of the underlying surface, resulting in the growth of a “near-zero-thickness” layer only on the desirable areas of the substrate. This layer could then act as a seed template for subsequent area-selective ALD (AS-ALD)^{26,28} or CVD (AS-CVD).

In order to differentiate between MLD, SAM, and CCD, it is helpful to understand the relative roles of physisorption and chemisorption in the nucleation and growth process. In physisorption, precursors or molecules are adsorbed on the surface and constrained by weak forces, but remain intact. In chemisorption, adsorbed precursors or molecules do not remain intact, since they undergo a surface-induced reaction. The binding energy of a chemisorbed species is typically about 0.5 eV greater than that of a physisorbed species.

In MLD, an adsorbent is constrained on the surface by physisorption, after which the adsorbent undergoes a relatively rapid chemisorption reaction with a significant number of active surface sites.^{2,3} An adsorbent

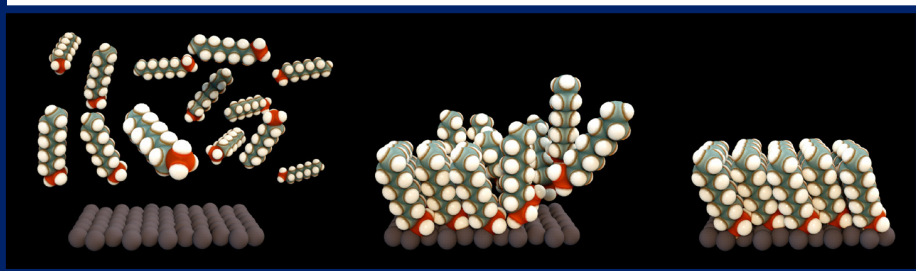


FIG. 3. Schematic illustration of the underlying adsorption and self-alignment mechanisms in a SAM process: (a) a source precursor is introduced into the reaction zone; (b) the precursor molecules are adsorbed to the substrate surface and are surface-constrained by physisorption; (c) weak forces (e.g., van der Waals, polar interaction) between the adsorbent molecules drive self-assembly and ultimate molecular orientation. The self-assembled adsorbent molecules monolayer thus become “anchored” to the substrate by relatively slow chemisorption.

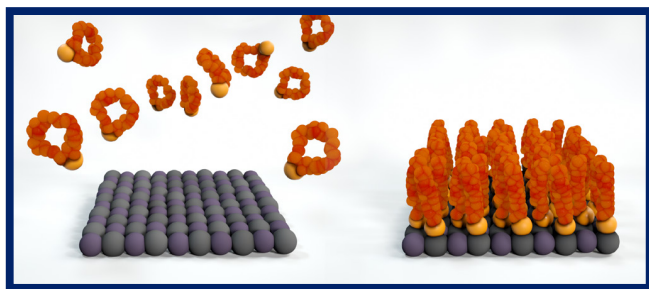


FIG. 4. Schematic depiction of the instantaneous chemisorption-driven molecular alignment in a CCD process: (a) a source precursor is introduced into the reaction zone; (b) the precursor molecules adsorb to the substrate and undergo chemisorption reaction at near 100% yield immediately upon contact with the surface. CCD can take place at near room temperature conditions without the formation of byproducts or byproducts that are readily removed.

is also surface-constrained by physisorption in SAM, but weak forces (e.g., van der Waals, polar interaction) between the adsorbent molecules drive self-assembly and orientation. The self-assembled adsorbent molecule monolayer thus becomes “anchored” to the substrate by relatively slow chemisorption. Unlike MLD, SAM relies on self-interactions to develop a stable atomic structure and only needs reactions with a minimal number of surface sites to anchor the structure.³⁴⁻³⁶

CCD can be considered a more straightforward, nearly instantaneous version of MLD, in the sense that physisorption plays virtually no role and the adsorbent undergoes chemisorption reaction at near 100% yield immediately upon contact with the surface. CCD can take place at near room temperature conditions without the formation of byproducts or byproducts that are readily removed.²⁷

Recent Key Developments in MLD, SAM, and CCD

These attractive features have ignited a flurry of R&D efforts in the applicability of MLD, SAM, and CCD to the formation of atomic-scale film structures. What follows is a capsular overview of recent developments in MLD, SAM, and CCD technologies, along with a synopsis of relevant properties of the resulting films. Additionally, Table I presents illustrative examples of the classes of precursors and source chemistries used in MLD, SAM, and CCD, while Table II summarizes potential applications as reported in the literature. The intent is not to provide a complete analysis of the relevant literature. Instead, the focus is on presenting highlights of pertinent R&D activities that show the most promise for incorporation in actual manufacturing methodologies, and to give the reader a sense of progress, achievements, and challenges.

MLD ▶ In terms of MLD, the report by Sharma et al.³⁷ represents one of the first demonstrations of a molecular layer growth technique to prepare non-fouling surfaces for biomedical microdevices. MLD-grown Poly(ethylene glycol) (PEG) ultrathin films were covalently bonded to Si from a liquid solution under in vivo type processing conditions. It was shown that the PEG-treated Si surfaces resisted protein and cell adhesion and exhibited enhanced biocompatibility, an important pre-requisite to the formation of Si-based microdevices for biomedical applications.

More recently, a noteworthy report by Belyansky et al.¹ examined the oxygen diffusion profiles, electrical properties (dielectric breakdown and leakage) and step coverage of 5- to 15 nm-thick MLD silicon nitride (SiN) for applications as dielectric thin film spacer in nanoscale devices. The authors reported the successful growth of high quality MLD SiN with excellent thickness control and good conformality using standard 300 mm wafer industrial type processing equipment. The films exhibited superior performance at lower deposition temperatures than their CVD counterparts. As such, the report represents one of the first thorough demonstrations of a manufacturing-worthy MLD process.

Another report by Bergsman et al.³⁸ described the development of a manufacturable MLD process for the formation of photoresist materials for nanoelectronics applications. This milestone was achieved by successfully embedding acid-labile groups (ALGs) into an MLD-formed polyurea photoresist chain grown on silicon (100) wafers. The MLD process employed a hot-wall flow reactor to yield extremely thin (~1.8 nm-thick) photoresist layers with high compositional uniformity.

SAM ▶ With respect to SAM, a comprehensive review by Love et al.³⁴ provided an excellent analysis of SAM fundamental mechanisms and underlying principles; preparation protocols, processes, and technologies; and applications in microcontact printing, photolithography, thin metal films, biochemistry, and biology, and nanostructures and metallic shells. Although the article predated most current SAM R&D efforts, it offered a thorough perspective on the effectiveness of SAM as template to investigate the role that molecular configurations and compositions play in the ultimate properties of macroscopic material systems. It also shed light on many of the potential technological applications of SAM techniques.

The work of Nuzzo et al.³⁶ represented one of the earliest embodiments of a SAM technique with the potential for incorporation into an industrial semiconductor process flow. The authors described a manufacturable process that employed the adsorption of sulfides from liquid solution onto gold substrates with zero valency. Gold was selected due to its known resistance towards oxidation and corrosion. The process yielded spontaneous arrangements of highly ordered polyfunctional organic molecules with a wide range of interfacial functional groups on the gold surface.

More recently, Sundaram et al.²⁶ reported on the application of SAM techniques to functionalize surfaces for the subsequent application of ALD processes to form an organic thin film transistor

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Table I. Selective examples of classes of precursors and source chemistries used in MLD, SAM, and CCD.

Chemistry	MLD Molecular Layer Deposition	SAM Self-Assembled Monolayers	CCD Click Chemistry Deposition	General Chemical Structure
Sulfur				
alkylthiols (mercaptans)		X	X	R—SH
Acids				
phosphonic acids	X	X		$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{P}-\text{OH} \\ \\ \text{OH} \end{array}$
carboxylic acids	X	X		$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{OH} \end{array}$
Silicon				
alkoxides	X	X		R—Si(OR') ₃
chlorides	X			R—SiCl ₃
amines	X			R—Si(NMe ₂) ₃
hydrides		X		R—SiH ₃
cyclic azasilanes			X	
Azides/Acetylene	X		X	R—N ₃ + ≡—R'

Table II. Summary of MLD, SAM, and CCD potential applications reported in the literature.

Potential Applications	MLD Molecular Layer Deposition	SAM Self-Assembled Monolayers	CCD Click Chemistry Deposition
Area-Selective Deposition			
enable deposition		$\chi^{21,26,27,34,37,40}$	χ^{30}
suppress deposition		$\chi^{8,32,34,37,41}$	χ^{30}
enable/suppress etching		χ^{39}	
Dielectrics/Polymers/Related Materials			
organic	$\chi^{22,31,38}$	$\chi^{7,8,34-36}$	χ^{29}
inorganic	$\chi^{1,11,24}$	$\chi^{9,11,25,42}$	
hybrid organic-inorganic	$\chi^{2,34,37,43}$	χ^{35}	χ^{31}
Other Organic Material Applications			
		$\chi^{34,35,37}$	
IC Metallization/Barrier Layer/Encapsulation Layer			
copper		$\chi^{28,32,44}$	
other		$\chi^{21,33,34,37}$	χ^{31}
Anti-stiction, Lubrication			
		χ^{45}	
NanoProbes for In Vivo Imaging			
	χ^{46}		
Photoluminescence			
	$\chi^{23,43}$	χ^{43}	
Lithium-Ion Battery Electrodes			
	χ^{47}		
Molecular/Organic Electronics			
		$\chi^{25,34,37,38,48-50}$	
Liquid Crystal Display			
		χ^{20}	χ^{51}
Nanoprobe Imaging			
			χ^{47}
Biomedical Devices			
		χ^{38}	

using a commercial ALD reactor. In their work, phosphonic acid SAMs were deposited on top of the aluminum oxide (AlO_x) layer using conventional casting from liquid solution. The introduction of the SAM ultrathin film was shown to produce a two order of magnitude enhancement in leakage current of the organic thin film transistor in comparison to its counterpart lacking the SAM film.

Pertaining to the application of a SAM process to enable or suppress area-specific or area-selective deposition, Kaufman-Osborn et al.⁸ reported the application of a two-step SAM process in a manufacturing-worthy processing system to catalyze the growth of densely packed, pinhole-free molecules. In a first phase, the substrate surface was treated with a hydroxyl moiety from the gas or liquid phase. The treatment led to the reduction or elimination of the reactive ligands that cause steric hindrance on the insulating (e.g., silicon dioxide, SiO_2) but not conducting (e.g., copper, Cu) regions of the substrate surface. In a second phase, a molecular deposition step was carried out using MLD precursors of the class of silylamines. The authors reported the formation of densely-packed and aligned molecular structures on the SiO_2 but not Cu areas of the substrate.

Alternatively, Wang et al.³⁹ described a SAM-like method for preferential etching of SiN in comparison to Si and SiO_2 . The method involved treating the patterned substrate with SAM precursors prior to the etching step to preferentially passivate the SiO_2 sections. The SAM precursor consisted of two segments: a head moiety (HM) and a tail moiety (TM), with the HM being designed to form a bond with OH group on the exposed SiO_2 but not the Si

or the SiN sections of the patterned substrate, and the tail moiety stretching out from the substrate. By employing SAM molecules of the type n-octadecyltrimethoxysilane, n-propyltrimethoxysilane, or n-octyltrimethoxysilane, with the HM portion being the methoxysilane, the researchers were able to selectively etch the SiN versus the Si and SiO_2 areas of the substrate. It should be noted that the deposition described is not precisely SAM, but is in fact a single layer MLD, since chemical reaction on the surface precedes the orientation process associated with self-assembly.

CCD For CCD, the work by Caipa Campos et al.⁵¹ employed thiol-ene CCD under ambient environment and room temperature to enable attachment of alkene-terminated molecules on oxide-free Si (111) surfaces. The Si surface was then characterized by static water contact angle, attenuated total reflection infrared spectroscopy (ATR-IR), and x-ray photoelectron spectroscopy (XPS). These analyses confirmed the presence of a covalently-bonded organic monolayer on the Si surface. The treated Si (111) surfaces were subsequently exposed to light at 365 nm wavelength in the presence of various thiols, along with 2,2-dimethoxy-2-phenylacetophenone (DMPA) which was employed as a photoinitiator. Light exposure resulted in the formation of a hydrophilic monolayer, which demonstrates the successful occurrence of light-induced micro-patterning. As such, the work holds the promise for a new approach to the fabrication of biofunctional electronics.

Similarly, Wang et al.³⁰ reported on the successful combination of CCD with microcontact printing (μCP) to engrave azide (azido-oligo(ethylene glycol) (OEG)-NH₂) inks on alkyne-terminated self-assembled monolayers (SAM) on hydrogen-terminated Si (100) and Si-on-sapphire (SOS) surfaces. The process used a flat featureless polydimethylsiloxane (PDMS) stamp, as well as a PDMS stamp with specific features. Subsequent characterization of the sample treated with the flat featureless PDMS indicated that the application of μCP to perform CCD was efficient and non-destructive. Additionally, light-addressable potentiometric sensor (LAPS) analysis of the sample engraved with the PDMS with specific features yielded a similar pattern to that of the PDMS stamp.

Summary

Based on the published work discussed above, it is clear that the nature and type of the chemical bonding and molecular configurations of the source chemistries, and the underlying mechanisms of substrate-precursor interactions will play a prominent role in driving the development of deposition processes for molecular layers with precise control of atomic order. MLD, SAM, and CCD are currently the top contenders to deliver such atomic level accuracy, primarily as enablers to the subsequent application of blanket and area-selective CVD or ALD techniques in the short-term. However, these growth technologies require new non-intrusive and non-destructive high-resolution physical and chemical imaging and analysis techniques to derive the structural, compositional, and interfacial data necessary to fully characterize the resulting molecular structures. Additionally, further R&D efforts are required to validate the reliability and reproducibility of such processes before they can be incorporated into real manufacturing protocols, such as prevailing industrial process flows of the semiconductor industry.

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