Nanostructure Fabrication by Area Selective Deposition: A Brief Review

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Wider Impact

At the nanoscale, the conventional top-down approach to fabricate nanostructures has become increasingly challenging and complex. Area-selective deposition (ASD), which allows for the direct deposition of materials only on areas of interest, has emerged as a promising solution to overcome the critical challenges in current manufacturing processes. In this review, we describe how ASD can be achieved, discuss the factors that could affect the selectivity of an ASD process, and provide examples of various ASD techniques and applications. We also address current challenges in this field. The research area of ASD is of significant and growing interest due to the increasing need for precise process control in creating nanoscale feature patterns. There are rising applications of ASD in the semiconductor industry and other fields, including catalysts and optoelectronics. The future of ASD is highly promising, offering atomic-level accuracy in fabricating nanostructures and simplifying patterning processes. The insights provided in this review will help guide future research directions toward developing more reliable ASD processes, ultimately opening the door to more new applications in next-generation advanced technology.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

Nanostructure Fabrication by Area Selective Deposition: A Brief Review

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Abstract

In recent years, area-selective deposition (ASD) processes have attracted increasing interest in both academia and industry due to their bottom-up nature, which can simplify current fabrication processes with improved process accuracy. Hence, more research is being conducted to both expand the toolbox of ASD processes to fabricate nanostructured materials and to understand the underlying mechanisms that impact selectivity. This article provides an overview of current developments in ASD processes, beginning with an introduction to various approaches to achieve ASD and the factors that affect selectivity between growth and non-growth surfaces, using area-selective atomic layer deposition (AS-ALD) as the main model system. Following that, we discuss several other selective deposition processes, including area-selective chemical vapor deposition, area-selective sputter deposition, and area-selective molecular beam epitaxy. Finally, we provide some examples of current applications of ASD processes and discuss the primary challenges in this field.

I. Introduction

Nanostructured materials are widely employed in various applications, from electronic devices and catalysis to batteries and solar energy. To synthesize nanostructured materials, the approaches can be categorized into top-down and bottom-up techniques. In top-down methods, nanomaterials are fabricated by breaking down bulk materials into desired nanostructures. One important top-down approach in nanomanufacturing, especially in semiconductor processing, is photolithography. In this method, nanoscale features are created by patterning photo-sensitive organic materials via lithography technologies followed by etching away of unwanted materials.

Over the past decades, researchers have worked very hard to push the limit of top-down approaches by developing more advanced technologies, such as inventing new lithography tools with shorter wavelength, from deep ultraviolet (UV) (λ = 193 nm) to extreme UV (λ = 13.5 nm), and developing multiple patterning techniques to enhance the feature density. However, as the feature size becomes ever smaller, top-down approaches are facing more challenges. For example, the alignment between the top and the bottom layer becomes more critical, multiple patterning techniques increase the process complexity, and advanced EUV lithography tools consume a significant amount of energy and are very costly. Because of the above reasons, researchers are searching for alternative approaches for more reliable and precise process methods.

In contrast to top-down methods, bottom-up approaches assemble basic units into larger desired nanostructures. It has been considered a promising way to solve the challenges in current top-down methods due to its ability to create nanostructures with fewer defects and better precision. Because of these reasons, area selective deposition (ASD), which allows direct deposition of materials only on desired areas (often called the growth surface) and not on other areas (non-growth surface), has attracted great research interest due to its bottom-up nature.

In this review, we provide a brief summary of achievements and current understanding of area selective methods for vapor-phase thin film deposition. For more in-depth reviews, we refer the reader to other references.[1–3] We also recommend several worthwhile references that discuss specific ASD approaches,[4,5] selection and design for inhibitors and precursors in ASD,[6–8] and challenges and solutions in achieving high selectivity in ASD.[9] Here, we first introduce in Section II various methods to achieve ASD, including inhibitor blocking, surface functionalization, and inherent selectivity. We then address in Section III factors that influence the selectivity of ASD processes, such as the quality of inhibitors, the choice of ALD precursors, and ALD process parameters. The discussion in both sections uses area-selective atomic layer deposition (AS-ALD) as the main model system. Following that, we discuss in Section IV examples of other area selective chemical and physical vapor deposition technologies besides AS-ALD. In Section V, we delve into applications of the nanostructures fabricated by ASD, covering areas such as integrated circuits (ICs),[10] catalysts, [11–13] and optoelectronics.[14] Finally, the challenges in current ASD are addressed in Section VI.

II. Approaches to achieve area selective deposition

Several different approaches are used to achieve ASD, with three main concepts: deactivation, activation, and inherent selectivity. Here, we present the most common approaches, using AS-ALD as a representative system, and categorize them as follows: inhibitor blocking (deactivation), surface functionalization (can lead to deactivation or activation), and inherent selectivity. Note that in this review, we define surface functionalization as a category separate from the use of carbon-based inhibitor molecules, although technically, inhibitor blocking can also be considered a form of surface functionalization. ALD is chosen as the model deposition system because it relies heavily on the surface properties of the substrate, making it an ideal technique for developing selective deposition. The principle of ALD is based on self-limiting reactions between precursors and the growth surface. Hence, AS-ALD can be achieved by modifying the surface chemistry to either activate or block reactive sites for ALD. In addition, ALD is able to form uniform and conformal films on high-aspect ratio structures with atomic-level precision. These properties make it a desirable technique for developing ASD processes for nanomanufacturing.

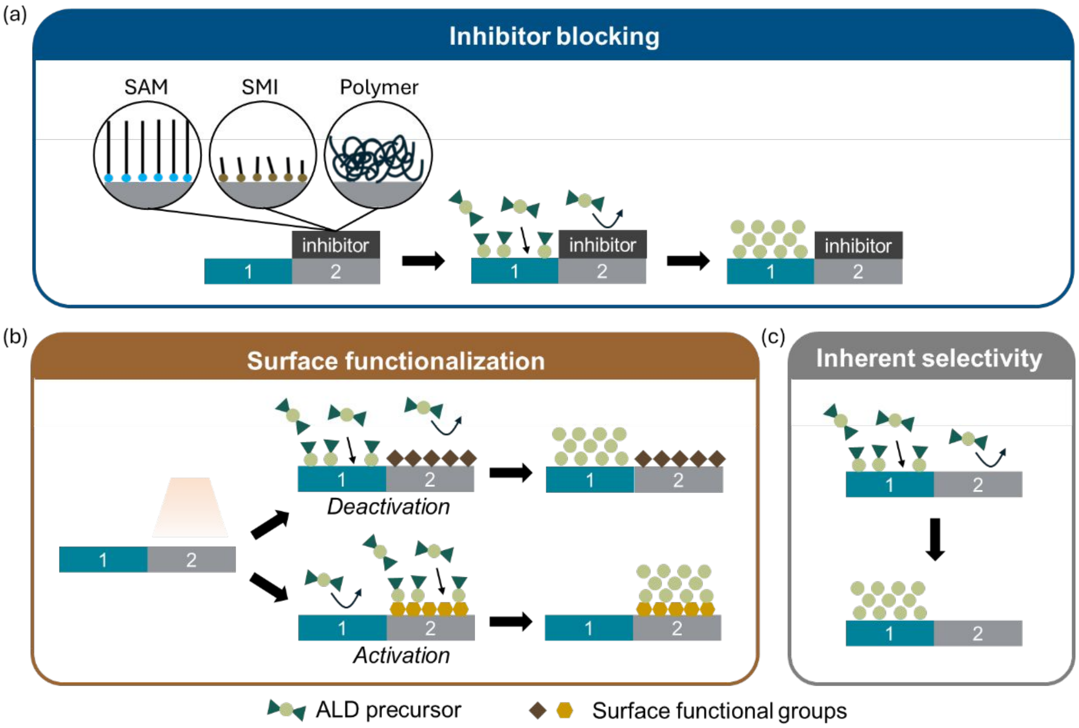

Figure 1. Schematic of different approaches to achieve selective deposition on one surface (surface 1) over the other (surface 2) or vice versa: (a) inhibitor blocking, with inhibitors such as self-assembled monolayers (SAMs), small molecule inhibitors (SMIs) and polymers, (b) surface functionalization, and (c) inherent selectivity.

Inhibitor blocking approaches

One of the most common ways to achieve ASD is by using inhibitors to protect the non-growth surface against deposition (Figure 1 (a)). Ideally, this approach involves a dually selective process. The first step requires the inhibitor adsorption to be selective on the non-growth surface. Then, film deposition must selectively occur only on the area not protected by the inhibitors. Typical inhibitors are self-assembled monolayers (SAMs), small molecule inhibitors (SMIs), polymers, or amorphous carbon. SAMs are organic molecules that can adsorb selectively onto specific surfaces and assemble into well-ordered structures; the resulting organic films deactivate the substrate making it resistant toward subsequent thin film growth. For example, organosilanes have been used on SiO_2 surfaces to block ALD, while alkanethiols and phosphonic acids SAMs have been shown to protect metal surfaces from the succeeding ALD process.[15–18] There have been many successful demonstrations of ASD using SAM inhibitors on a range of metal, semiconductor, and dielectric surfaces,[19–28] because the well-packed SAM tail groups can provide highly effective protection against deposition. On the other hand, SAM depositions often require solution processes and long deposition times,[29] which may limit their ultimate usefulness in industry-compatible processes.

Similar to SAMs, SMIs can adsorb on specific substrates to serve as a surface-deactivating agent to prevent thin film growth. For instance, the acetylacetone SMI has been used as an inhibitor to block ALD of SiO_2,[30]

Al_2O_3 [31] and WS_2.[32] Aniline SMI has been employed for AS-ALD of TiN on dielectrics over metals.[33] Furthermore, alkoxysilane SMIs have facilitated selective ALD of Al_2O_3,[34] and organosulfide SMIs have been used for AS-ALD in a multi-substrate system, permitting HfO_2 ALD on nitride surfaces while preventing ALD on metal and oxide surfaces.[35] Other examples of SMIs include aldehydes for inhibiting ALD on nitride over oxide,[36] and N-heterocyclic carbene inhibitors for AS-ALD on SiO_2 over metal.[37] Among various types of SMIs, precursor-based SMIs are particularly interesting due to their process compatibility and dual functionality as both inhibitors and ALD precursors. Aminosilane SMIs, such as bis(dimethylamino)dimethylsilane and (dimethylamino)trimethylsilane, have been used as Si precursors for SiO_2 ALD and have demonstrated effectiveness in passivating SiO_2 surfaces, enabling AS-ALD of Ru, Pt, Al_2O_3, TiO_2 and $Ge_2Sb_2Te_5$.[38–44] These aminosilane SMI molecules react with SiO_2 surface and form an inhibiting monolayer of $Si(CH_3)_2$ or $Si(CH_3)_3$. Other examples of precursor-based SMIs include the use of Ti and Ru precursors as inhibitors for ASD of TiO_2 and Ru films, respectively. The Ti precursor, trimethoxy(pentamethylcyclopentadienyl)titanium, and Ru precursor, bis(ethylcyclopentadienyl)ruthenium, do not react with a H_2O counter-reactant and thus can act as inhibitors on non-growth surfaces to prevent TiO_2 and Ru ALD when performing ALD with other Ti and Ru precursors and H_2O counter-reactant.[45,46]

The advantage of SMIs lies in their ease of delivery through vapor phase approaches because of their small molecular size and high vapor pressure. However, the main challenge of SMIs is their ability to efficiently prevent thin film growth on the non-growth surfaces due to their small molecular structure. SMIs may not form a well-packed and dense inhibitor layer, making it easier for ALD precursors to reach and react with reactive sites on non-growth surfaces. This could result in earlier ALD breakthrough at shorter cycle numbers compared to SAM-based ASD processes. Additionally, it may be easier for ALD precursors to interact with SMIs due to the poorer packing density of SMIs, leading to SMI loss, which is detrimental to ASD processes.

Despite these potential disadvantages, SMIs can be re-applied to the non-growth surface relatively easily, even after every single ALD cycle, to restore the damaged SMIs.[30,33] Hence, redosing of SMIs during an ASD process is usually preferred or required. In fact, the ease of redosing SMIs make them a good inhibitor choice for plasma-enhanced ALD or ozone-based ALD processes, as plasma and ozone can easily damage the inhibitors.[30,33] Therefore, they need to be restored during the deposition process to maintain good selectivity. However, during re-application, it is crucial to ensure that SMIs only adsorb onto the non-growth surfaces and not on the surfaces of the ALD-deposited materials, as this is essential for achieving continued deposition where desired.

Polymers are another commonly used inhibitor to achieve AS-ALD. For example, poly(methyl methacrylate) and poly(vinyl pyrrolidone) have been used to inhibit various ALD processes, including TiO_2, ZnO and Al_2O_3.[47,48] The advantage of using polymers as inhibitors for AS-ALD is that they can easily be deposited on the surface by spin coating, a simple and easy method to form organic thin films. However, most polymer deposition is not inherently selective.[49] Thus, for the purpose of acting as an inhibiting layer for AS-ALD processes, it is necessary to subsequently pattern the polymer on the substrate, which usually requires additional top-down methods such as photolithography or e-beam patterning.

Surface functionalization

Another approach to achieve ASD is by surface functionalization to create different terminations on the surfaces to either deactivate or activate ALD processes, as shown in Figure 1 (b). Approaches to functionalize a surface to create deactivated sites include ion beam, plasma and chemical treatments. For example, AS-ALD on 3D Si nanostructures with topographic selectivity has been demonstrated using ion beam deposition of fluorocarbons (CF_x), a hydrophobic layer that can prevent ALD precursor adsorption.[50] Plasma treatments, such as H_2, CF_4 or Cl_2 plasma, have been employed to passivate amorphous carbon films, inhibiting subsequent ALD nucleation.[51–53] With H_2 plasma treatment, the chemisorbed oxygen species on amorphous carbon films, which serve as ALD nucleation sites, are reduced, leading to a delay in nucleation of ALD precursors. As for halogen-based plasmas, they help form a thin surface layer containing CCl_x and CF_x groups, which reduces the access of oxygen sites for ALD precursors.

There are also chemical treatments that functionalize the surface with passivating species. Lee et al. demonstrated AS-ALD of HfO_2 using a carbon-free surface functionalization method on SiO_2 over TiN.[54] In that work, the SiO_2 surface was passivated by terminal SiH_3 groups that were prepared via reaction of a di(isopropylamino)silane molecule, while adjacent TiN areas were unaffected by aminosilane exposure. Unlike previously discussed aminosilane SMIs, which leave a $Si(CH_3)_2$ or $Si(CH_3)_3$ layer on the non-growth surface after adsorption, this specific aminosilane molecule does not leave behind any carbon species. Since this ASD process does not involve a carbon-based inhibiting layer but instead relies on changing the termination to SiH_3, we categorize this approach as a method of achieving ASD through surface functionalization. Other examples of surface functionalization through chemical treatments include creating H-, Cl-, and Br-terminated surfaces to inhibit ALD on the non-growth surfaces.[55–58] For instance, H-terminated silicon surfaces can be produced using an HF solution, and Cl- and Br-terminated surface can be prepared by immersing H-terminated Si into Cl- or Br- containing solution under N_2 environment at elevated temperature.

In addition to deactivating ALD processes by surface treatments, functionalizing the surface to create active sites to achieve AS-ALD has been demonstrated. For instance, researchers have performed AS-ALD on functionalized graphene and graphite by laser or electron beam.[59,60] In this example, active groups such as hydroxyl and carbonyl groups were introduced to the desired areas of the surface of the carbon materials, enhancing the nucleation of ALD precursors at those regions exposed to the beam, while the non-exposed area on the carbon acted as the non-growth surface due to its intrinsic lack of active sites. Other approaches for creating active sites for AS-ALD on ALD-inert surfaces, such as H-terminated amorphous Si and CH_3-terminated low-*k* SiOC substrates, include plasma, electron beam-induced deposition, and UV irradiation.[61–63] These functionalization methods enable the formation of OH-terminated Si surfaces to facilitate subsequent adsorption of ALD precursors.

Surface functionalization offers the advantage of potentially avoiding carbon contamination, which can be an issue with inhibitor-based approaches. However, selectively functionalizing a substrate surface can be a challenge with this ASD approach. For directional ion beam functionalization, the substrate needs to have topographical features, otherwise all the surfaces would be exposed equally, resulting in no selectivity in ALD growth. In other cases, a direct writing technique such as by laser or electron beam is needed to selectively functionalize specific surfaces if no masks are used. In contrast, surface functionalization by chemical treatment may be particularly attractive, as it can impart new surface properties to different materials in a pattern without needing topographical features, direct writing technique or masks.

Inherent selectivity

By different surface properties

The distinctive properties naturally exhibited by some growth and non-growth surfaces can contribute to different ALD nucleation behaviors, resulting in inherent selectivity in ASD processes (Figure 1 (c)). In recent years, researchers have been diligently investigating surface properties to gain a deeper understanding of their potential impact on inherent selectivity. These surface properties include catalytic activity, diffusivity, electrical resistivity and electronegativity. For instance, the catalytic effect on some noble metal surfaces has been shown effective in achieving ASD. In one example, successful AS-ALD of metal oxides was demonstrated on Pt and Ir surfaces through the catalytic dissociation of oxygen molecules, while no ALD occurred on inert surfaces like SiO_2, Al_2O_3, and Au under the same conditions.[64] Research also shows that surface diffusivity can play a crucial role in ASD processes. ASD of Ru on metal nitride/SiO_2 patterns was demonstrated due to the migration of Ru adspecies from high-diffusivity (non-growth area) to low-diffusivity surfaces (growth area).[65] Moreover, the electric resistivity of the substrate surface can be leveraged to achieve ASD. For example, an Fe film selectively deposited on low-resistivity metal surfaces over high-resistivity SiO_2 surfaces when plasma electrons were used as the reducing agent for Fe deposition.[66] Selective deposition of Cu or Cu_2O, depending on the conductivity/type of majority point defects of a ZnO substrate, has also been demonstrated.[67] The electronegativity differences between the metal and oxygen in a metal oxide substrate can also affect the initial ALD nucleation rate, leading to some inherent selectivity.[68]

By ALD precursor selection

In addition to the examples above, other studies have shown that by selecting appropriate ALD precursors, nucleation may occur only on one surface over the other and lead to ASD. This approach takes advantage of the fact that how the ALD precursors interact with the substrate materials can dictate selectivity. For instance, selective SiO_2 ALD using aminodisilane as an ALD precursor has been demonstrated on SiO_2 substrates rather than on SiN substrates.[69,70] The unique chemoselectivity of aminosilanes allows these molecules to selectively adsorb on SiO_2 over nitrides or other metal oxides. Hence, the aminosilane can be used not only as an SMI or functionalization agent for subsequent ASD processes as described in examples provided in the previous sub-sections, but also as an inherent substrate-selective ALD precursor for selectively depositing SiO_2. The MoF_6 precursor, which reacts only with Si but not with SiO_2 and SiN, has been used to achieve AS-ALD of $MoSiO_x$.[71] Elemental Zn and S precursors also showed excellent inherent selectivity on Ti and TiO_2 surfaces over native SiO_2 and Al_2O_3 surfaces, leading to selective growth of ZnS.[72]

ASD achieved through inherent selectivity does not require additional process steps, such as inhibitor deposition or surface functionalization. Therefore, it has the potential to significantly simplify the ASD process. Additionally, because it solely relies on differences in surface properties without introducing foreign species, it is considered to have fewer impurities and does not require post-treatment steps to remove inhibitors or restore the functionalized surface to its original state. However, this method typically exhibits a limited selectivity window. The high reactivity of the precursors used in ALD usually results in a short nucleation delay on the non-growth surface. This property poses a disadvantage for industrially relevant applications, which require high selectivity for thicker films.

III. Factors impacting the selectivity

The success of ASD, i.e., achieving satisfactory selectivity, is influenced by various factors, including the inhibitor quality on non-growth surfaces, choice of ALD precursors, ALD process parameters, etc. Taking SAM inhibitors as an example, studies have shown that it is necessary to form a well-ordered SAM structure on non-growth surfaces to provide a hydrophobic layer in order to block ALD processes efficiently.[15] If the SAM inhibitor is not sufficiently well-packed, ALD precursors may diffuse through the inhibitor layer and react with reactive sites at the substrate.[29] ALD precursors could also physisorb onto defect sites on or within the inhibitor layer, with these physisorbed precursors serving as nucleation sites for the subsequent ASD process.[29,73,74] In both scenarios, a loss of selectivity occurs.

Features that impact the quality of inhibitors include the *inhibitor selection*—such as the chain length and molecular size and structure (e.g. aromatic group vs aliphatic chain)—and inhibitor deposition parameters, such as deposition time, temperature, and solvent used in a solution-based inhibitor deposition process. For SAM-based ASD processes, studies indicate that the formation of a well-packed SAM inhibitor structure requires the use of long alkyl chain SAM molecules with an extended deposition time (Figure 2 (a)).[15,29] A longer alkyl chain enhances van der Waals interactions, while a prolonged deposition time enhances the self-organization of adsorbed SAM molecules. Both promote the formation of a dense, well-packed monolayer structure. Regarding the impact of other inhibitor deposition parameters, temperature is found to be a complex factor. For example, studies have demonstrated that an organosilane SAM forms a disordered structure at elevated deposition temperature,[75,76] while ODPA SAMs exhibit improved packing at higher deposition temperatures.[23] As for solvent choice, studies indicate that opting for a non-polar solvent with weaker solvent-SAM and solvent-substrate interactions typically leads to better SAM formation.[22,23,77]

For SMI inhibitors, the molecular structure and size of SMIs has been shown to affect their blocking ability against ALD processes. A study by Yu et al. demonstrated that smaller SMIs form a denser packing layer on the non-growth surface, providing the best chemical passivation. Meanwhile, they showed that larger SMIs can also outperform medium-sized SMIs due to their bulky structure, which can sterically shield the ALD precursors.[78] The interaction between SMIs and the substrate surface should also be considered when developing an ASD process. A study has shown that an aniline SMI can form strong π-bonds with transition metal surfaces, potentially preventing aniline from being displaced from the surface by ALD precursors.[33] The number of reactive head groups on the SMI is also influential. A study by Yarbrough et al. showed that trifunctional methoxysilanes inhibit Al_2O_3 ALD better than monofunctional and bifunctional methoxysilanes. This was attributed to the ability of trifunctional silanes to block multiple active hydroxyl sites on a surface and to polymerize at the surface to produce a saturated passivation layer.[34]

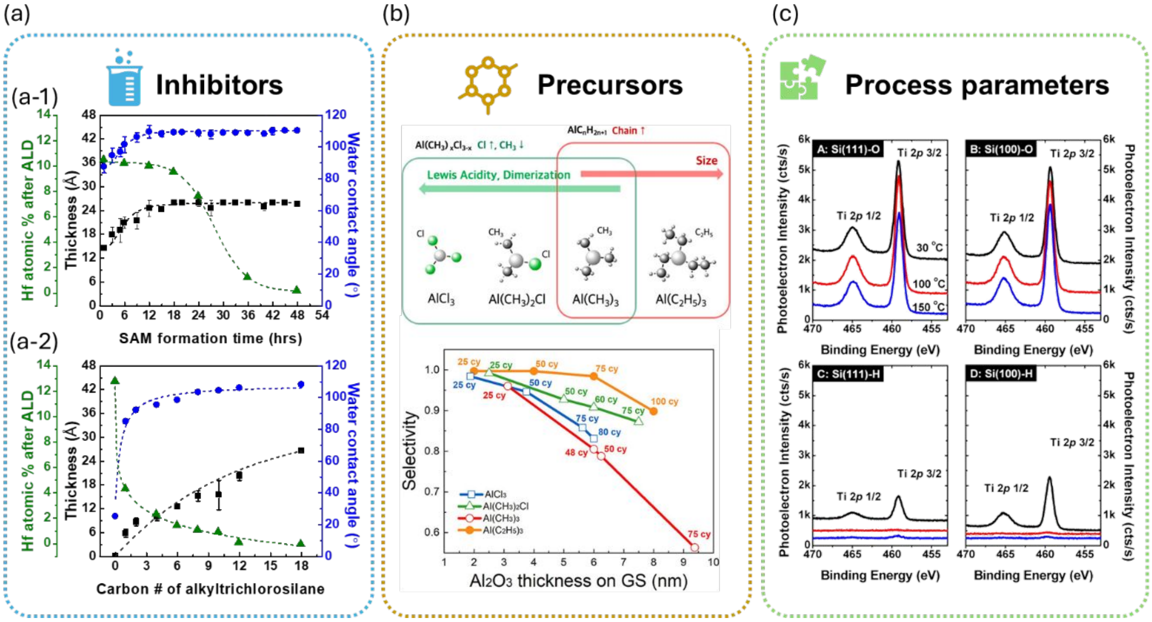

Figure 2. (a) Experimental blocking results for HfO_2 ALD as Hf% on non-growth surfaces protected by SAM inhibitors as a function of (a-1) SAM formation time (adapted with permission from ref 15. Copyright 2007 American Chemical Society.) and (a-2) chain length of the SAM inhibitor (adapted with permission from ref 29. Copyright 2005 American Chemical Society.), showing the impact of inhibitors on selectivity. The dashed curves serve as guides to the eye. (b) An example highlighting the importance of precursor selection in an ASD process. The experimental results demonstrate that the Lewis acidity and size of an ALD precursor can significantly affect selectivity in this study of Al_2O_3 AS-ALD. Reprinted with permission from ref [79]. Copyright 2021 American Chemical Society. (c) An example illustrating the effect of the ALD temperature on the selectivity in an ASD process, where OH-terminated Si is the growth surface and H-terminated Si is the non-growth surface. The three spectra in each panel correspond to 45 cycles of TiO_2 ALD at 30°C (black), 100°C (red), and 150°C (blue). Reprinted with permission from ref [80]. Copyright 2013 American Chemical Society.

In addition to the inhibitor quality, another factor that can greatly affect ASD selectivity is the *choice of ALD precursor*. For instance, reactivity, molecular size and extent of dimerization of ALD precursors can play important roles in ASD process. Studies have shown that precursors with weaker Lewis acidity, larger size, and a dimer structure under ALD temperatures are more easily blocked by inhibitors. (Figure 2 (b)).[79,81,82] For example, Oh et al. systematically investigated a series of Al precursors with different ligands—$Al(CH_3)_xCl_{3-x}$ and $Al(C_yH_{2y+1})_3$—and demonstrated that $Al(C_2H_5)_3$ achieved the best selectivity due to its weaker Lewis acidity and relatively large size.[79] In another study, Kim et al. compared trimethylaluminum and dimethylaluminum isopropoxide, showing that the dimerization of the DMAI precursor plays a key role in its high ASD selectivity.[81] In addition to pure steric shielding of ALD precursors by inhibitors, other studies have shown that selecting an ALD precursor that chemisorbs only on the same surface sites as the inhibitor can enhance blocking efficiency.[31] This competitive adsorption approach prevents undesired chemisorption of ALD precursors, particularly when the packing density of inhibitors is not sufficient to fully sterically block the precursors.

ALD process parameters can also impact the selectivity in an ASD process. Selectivity has been shown to improve by performing ALD under sub-saturation condition or decreasing the partial pressure of the ALD precursor to minimize the unwanted interactions between precursors and inhibitors.[41,83–85] Other approaches for improving selectivity include increasing precursor purging time to remove physisorbed precursors,[79] and increasing ALD temperature to allow more precursor desorption from the non-growth surfaces (Figure 2 (c)).[62,80]

IV. Beyond area-selective atomic layer deposition

While AS-ALD has attracted considerable research interest due to the powerful ability of ALD to deposit a uniform thin film with atomic-level precision, making it a very useful tool for nanofabrication, other ASD methods have also been investigated and are being further developed. In this section, we will introduce various selective vapor deposition methods in addition to AS-ALD and discuss the general approaches of each ASD method to obtain selectivity.

Area-selective chemical vapor deposition (CVD)

Similar to ALD, CVD also uses volatile and reactive gaseous precursors, which react and/or decompose on the substrate surface to deposit the thin film. It is a widely used tool in many industrial and academic fields to deposit various materials. The selective deposition concept of area-selective CVD is very similar to AS-ALD. It relies on differences in chemisorption of CVD precursors and subsequent nucleation on different surfaces. There have been several successful demonstrations of AS-CVD and actual implementations of the ASD process into industrial manufacturing process. Indeed, selective CVD methods were first developed a couple of decades before selective ALD was introduced.[86] Selective CVD of various metals by inherent selectivity, such as W, Co, and Ru, has been achieved and received much research interest for interconnect applications in semiconductor manufacturing processes.[86–88] Moreover, due to the inherent nucleation differences in various Si crystallographic planes, selective metalorganic CVD of GaAs on shallow-trench-isolation patterned Si substrates has been demonstrated for applications in electronic devices.[89]

In addition to inherent selectivity, AS-CVD can be accomplished by applying inhibitors to improve the selectivity. Several examples have been reported. For instance, ammonia as an SMI was used to demonstrate AS-CVD of MoC_xN_y, Fe, or Ru thin films on metal substrates but not on metal oxides.[90] An ultra-thin patterned polymer functional layer made by lithography was also used to selectively grow transition metal dichalcogenides, such as WSe_2 and MoS_2, by metalorganic CVD (MOCVD) as shown in Figure 3 (a).[91] Metalorganic precursors can also be used to inhibit CVD growth if the CVD reactor is operated at a temperature at which one precursor will nucleate and grow a film but not the other precursor. Using this approach, coflow of trimethylaluminum and $Hf(BH_4)_4$ precursors has been shown to enhance selectivity for HfB_2 deposition on metal over oxide surfaces, and selective Al deposition on metal over oxide was demonstrated when coflowing $Hf(BH_4)_4$ with $AlH_3{\cdot}NMe_3$ precursors.[92]

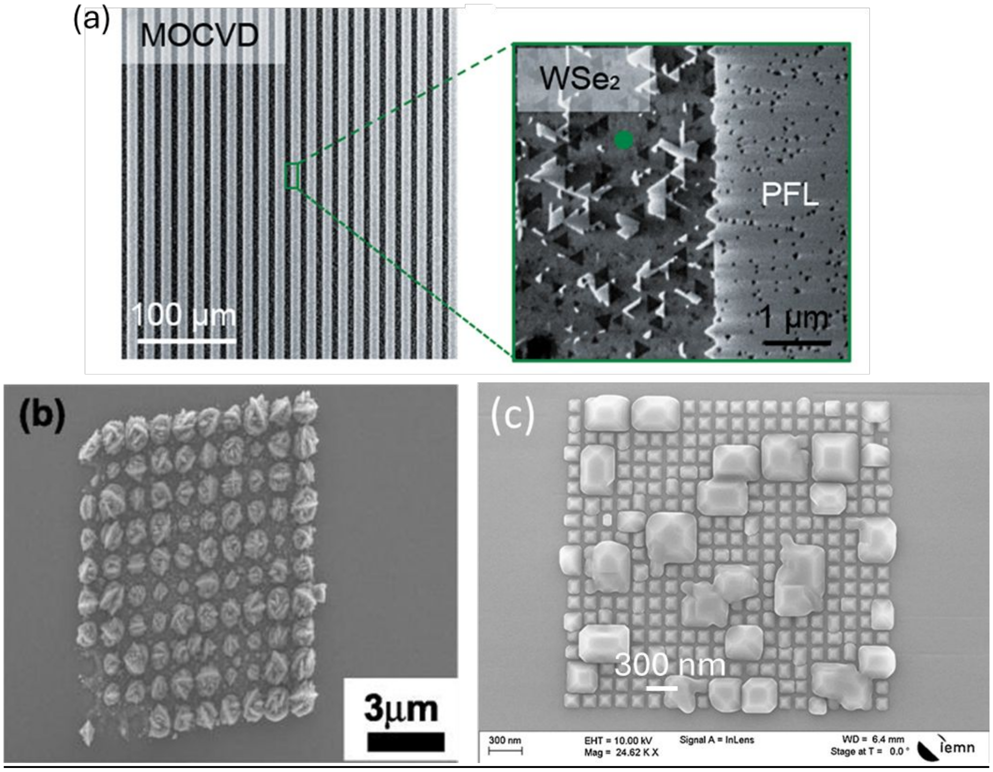

Figure 3: Scanning electron microscope images showing various ASD processes. (a) Area-selective MOCVD of WSe_2 using a polymer functional layer (PFL) as the inhibitor. © IOP Publishing Ltd. Reproduced with permission from ref [91]. All rights reserved. (b) Area-selective sputter deposition of Si films on Si over SiO_2 surfaces. Reprinted from ref [93], with the permission of AIP Publishing. (c) Area-selective MBE of InSb on InAs surfaces instead of on SiO_2 surfaces. Reprinted from ref [94]. Copyright (2019), with permission from Elsevier.

Area-selective sputter deposition

Sputter deposition is a physical vapor deposition method used extensively to deposit thin films.[95,96] In this process, material is ejected from a solid target due to the bombardment of the target by energetic ions. These ejected atoms then travel to the substrate and deposit onto it. Because of the bombardment nature of a sputter deposition process, achieving selective sputter deposition is more challenging for the following reasons. First, the bombardment of the substrate by energetic species makes using an organic inhibitor for ASD much less effective, as most organics will degrade or be damaged under such harsh conditions. Second, since sputter deposition is a physical vapor deposition method, it lacks the chemical specificity to different substrate surfaces that is a feature of CVD and ALD, making it more challenging to achieve ASD by selective chemisorption on one surface over the other. As a result, only a few literature reports describe successful ASD using the sputter deposition method.

One way to achieve selective sputter deposition is to leverage differences in the partial sputter yield of the thin film atoms on various substrates. During sputter deposition, ion bombardment can result in the re-sputtering of deposited material off of the substrate, leading to a decrease in the net film growth rate.

At a specific bias voltage, the net film growth rate on a substrate reaches zero. Hence, by operating the bias sputter deposition at a voltage where one substrate has zero net film growth rate while the other does not, ASD of sputter deposition can be achieved. Building on this principle, researchers have successfully demonstrated ASD of Al on SiO_2 over W surface via bias sputtering.[97,98]

Another approach to achieve area-selective sputter deposition is through the utilization of selective chemical sputtering. A research group at Osaka University demonstrated this process to selectively deposit Si films on Si over SiO_2 as shown in Figure 3 (b).[93] Their chemical sputtering technique involved utilizing H_2 plasma to chemically react with a solid Si target source, producing SiH_4 gas as a precursor for Si film deposition. Since the substrate was also exposed to the H_2 plasma, there was an incubation period before the Si film could initiate growth on the substrate surface. This incubation time varies based on the substrate types, offering a property that can be exploited to accomplish selective deposition.

Area-selective molecular beam epitaxy (MBE)

MBE is a technique used for the growth of high-purity epitaxial thin films. It involves evaporating target materials and depositing them onto a single-crystalline substrate surface at high temperatures under ultrahigh-vacuum conditions. The concept of area-selective MBE has attracted attention as a promising method for fabricating scalable III–V compound devices, with research ongoing since the 1990s, such as selective MBE of GaAs, GaN and InSb, as shown in Figure 3 (c).[94,99,100] Typically, selective MBE is accomplished via the inherent selectivity between distinct surfaces—specifically, an amorphous dielectric mask as the non-growth surface and a single crystal surface as the growth surface. This approach is preferred over using organic inhibitors, since most MBE processes require high temperatures (> 400°C), and organic inhibitors tend to be unstable under such high temperature conditions.

The success of selective MBE processes depends on several factors which are determined by the surface properties and MBE process conditions, including the difference in sticking coefficients on growth and non-growth surfaces, and the diffusion of adatoms from the non-growth surface to the growth surface. For example, a study indicates better selectivity in selective MBE of GaAs on patterned GaAs substrates with a SiN mask compared to using a SiO_2 mask, due to the higher re-evaporation rate of deposited GaAs from SiN than from SiO_2.[101] In addition, the choice of mask material can influence the selective growth mechanism, thereby affecting the patterns fabricated by selective MBE processes. A study observed distinct selective growth mechanisms of GaN MBE with different masks: surface diffusion of Ga adatoms on the Ti mask to the growth surface dominated in this system, while re-evaporation of Ga adatoms was the main contribution to selectivity with a SiO_2 mask. The former resulted in the formation of protuberances on the sidewalls of the selective growth patterns, while the latter produced flat GaN patterns.[102]

As for the MBE process parameters, temperature plays a crucial role in the selective growth process. If the growth temperature is too low, the deposited materials may not be able to desorb from the non-growth surface, and the diffusion length of the MBE material on the non-growth surface may not be long enough, causing MBE adatoms to remain on the non-growth surface. In contrast, if the temperature is too high, material desorption occurs on both growth and non-growth surface. Both cases result in poor selectivity.[103] Another process parameter that can significantly impact the selectivity is the material flux. It has been shown that the flux of MBE materials needs to be below a critical value in order to form a smooth epitaxial layer without any MBE nucleation on the masked area.[104] If the impinging MBE flux exceeds the desorption rate of the material from the mask at the process temperature, the material will grow on both surfaces and selectivity is lost. The N_2 flow rate can also affect the selectivity. A decrease in the N_2 flow rate results in an increase in the desorption and the diffusion length of MBE materials on the mask surface, thereby enhancing the selectivity of the MBE process.[105]

V. Applications for nanofabrication of materials by ASD

With ASD processes, diverse micro- and nanostructures can be fabricated for various applications. One particularly intriguing and well researched application is to make patterned thin films by ASD for semiconductor applications. Due to the bottom-up nature of ASD processes, it has been shown as a promising solution to address challenges in current manufacturing processes. In fact, selective deposition of Co on Cu for metal cap applications in back end of line (BEOL) interconnects has already been implemented in industry to prevent electromigration of Cu interconnect.[106,107] In addition, AS-ALD of dielectrics on dielectrics over metals (called "DoD") has been demonstrated to help form fully self-aligned vias in the BEOL to provide more tolerance to the processing errors (Figure 4).[10] Nanosheets of two-dimensional (2D) semiconductors have been fabricated by AS-ALD as channel materials for BEOL-compatible transistors.[108] Self-aligned metal-oxide-semiconductor (MOS) capacitors fabricated with AS-ALD of HfO_2 and Pt have been shown to exhibit similar electrical performance compared to those made by a nonselective process.[109] The AS-ALD of patterned HfO_2 thin films for applications in resistive random access memory devices has also been studied, revealing improvements in device reliability compared to the uniform ALD method.[110]

Beyond the fabrication of patterned thin films by ASD on planar substrates, ASD concepts can be employed to produce seamless films in high-aspect-ratio structures and to pattern three-dimensional (3D) nanoscale objects. For example, a study demonstrated AS-ALD of TiO_2 to seamlessly fill trenches in 3D nanostructures for optical device applications.[45] Mohabir et al. showed selective deposition of coaxial ZrO_2 thin films aligned with the dopant profile of the underlying Si nanowires.[111]

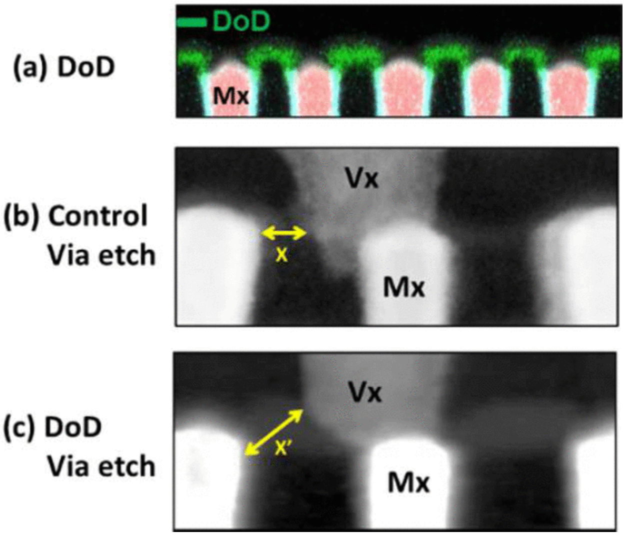

Figure 4. (a) Cross-sectional transmission electron microscopy (TEM) electron-dispersive spectroscopy spectral image of selective deposition of dielectric on dielectric (DoD). Cross-sectional TEM images of (b)

via etch without DoD, and (c) fully self-aligned vias with DoD. Reprinted with permission from ref 10. Copyright © 2021, IEEE.

Another emerging application area of ASD is in catalysis.[11–13] ASD can be used to selectively modify the surface of a catalyst to improve activity or selectivity by forming a continuous shell outside the catalyst core or a discontinuous film on specific sites on the catalyst. For example, AS-ALD of Pt was used to selectively form a core-shell structure on Pd nanoparticles which were first formed inside pinholes of a SAM-coated Si substrate for catalytic applications.[112] In another study, AS-ALD of CeO_x was selectively deposited on (111) facets instead of (100) facets of Pt nanoparticles, forming a nanofence structure as shown in Figure 5 that helped improve CO conversion activity and sintering resistance under oxidative atmospheric conditions.[113] AS-ALD of Al_2O_3 and FeO_x was also used to selectively block different coordination sites of a catalyst to tune the selectivity to benzaldehyde and toluene.[114] Another study showed AS-ALD of Pt only on the top/bottom surfaces of $TiSi_2$ "nanonets" with Pt {111} surfaces preferentially exposed. This preferentially exposed Pt surface showed high activity in oxygen reduction reaction.[115]

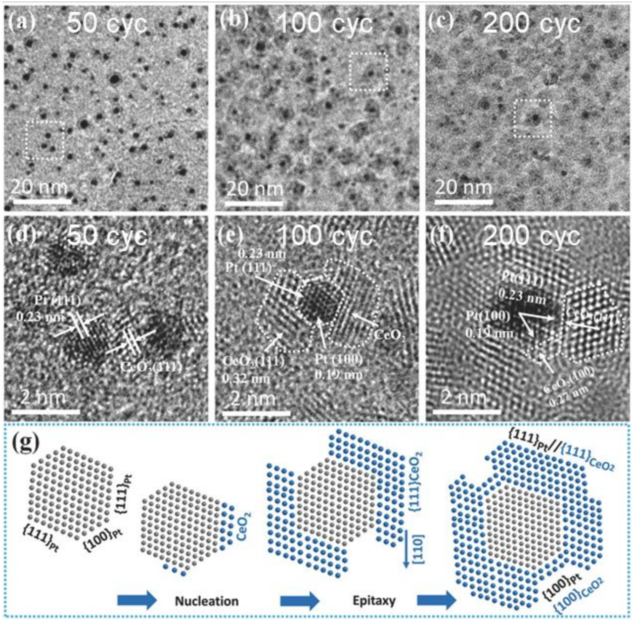

Figure 5. (a)–(c) TEM and (d)–(f) high-resolution TEM images of ALD CeO_x preferentially deposited on (111) facets of Pt nanoparticles. (g) The schematic illustrating the selective deposition process. Used with permission from ref [113]. © 2017 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

Another demonstrated use of ASD is in energy conversion applications. In one example, AS-ALD of Al_2O_3 was used to passivate the rear side of crystalline Si solar cells while leaving some open areas for the following contact metal deposition process.[14] With this selective deposition method, Cho et al. showed an improvement in the cell efficiency. Also, selective Pt ALD was used to form a current collector grid and patterned catalyst for solid oxide fuel cells, and the performance of the fuel cell was improved by a factor of 10.[116] While these examples are just a sampling, it is clear that ASD can be implemented to fabricate various nanomaterials for a wide range of applications.

VI. Challenges and outlook

Although there is considerable effort ongoing in ASD research and major achievements have already been reached, several challenges and questions still must be addressed to establish more reliable ASD processes and to broaden the ASD toolbox for various applications. Here we highlight several recurring challenges.

Achieving sufficient selectivity for targeted application

One main challenge of ASD processing is achieving sufficient selectivity on the complex material systems for practical applications. For example, in nanoelectronics applications, extremely high selectivity may be required to minimize defects on non-growth surfaces, since defects could lead to significant reduction in process yield. There have been several approaches introduced to improve selectivity. For example, redosing inhibitors to restore the damaged inhibitor layer has been shown to improve selectivity.[17,30] Another route to improve selectivity is to incorporate an etching step into an ASD process. While this etching step may decrease the net film deposition on the growth surface, it can help remove any undesired nuclei on the non-growth surface, thereby improving selectivity.[5,117]

Atomic scale precision at nanoscale features

In addition, it is important to keep in mind that even if excellent selectivity is achieved on growth vs. non-growth blanket substrates, limited selectivity may be obtained on patterned samples, especially those with nanoscale feature sizes. Such pattern effects have been attributed to the diffusion of adsorbed ALD precursors from growth to non-growth surfaces.[118] The selectivity of an ASD process can also be impacted by the 3D structure of a sample. A study demonstrated that the blocking ability of SAM inhibitors differs on planar vs. 3D nanostructured surfaces because more defect sites are formed in the inhibitor layer at regions of high curvature (Figure 6 (a)).[119]

Thus, a second challenge of the ASD process is how to achieve atomic scale precision on nanoscale features, especially at the interface between the growth and non-growth surfaces. Due to the isotropic deposition nature of ALD, patterned films fabricated by AS-ALD can laterally broaden over the non-growth area at the growth/non-growth interface, as shown in Figure 6 (b).[33,120] In addition to this ALD "mushrooming" growth, inhibitors can also mushroom out from the non-growth surface if a thicker inhibitor layer is used for ASD processes (Figure 6 (c)). This can result in undesired interfacial effects, such as a nonuniform ASD film on the growth region and prevention of ALD on the growth surface near the interface.[121] The diffusion of ALD precursors from the non-growth to the growth area can also result in undesired accumulation of ALD nuclei at the interface, leading to sharp spikes on the ASD film.[122]

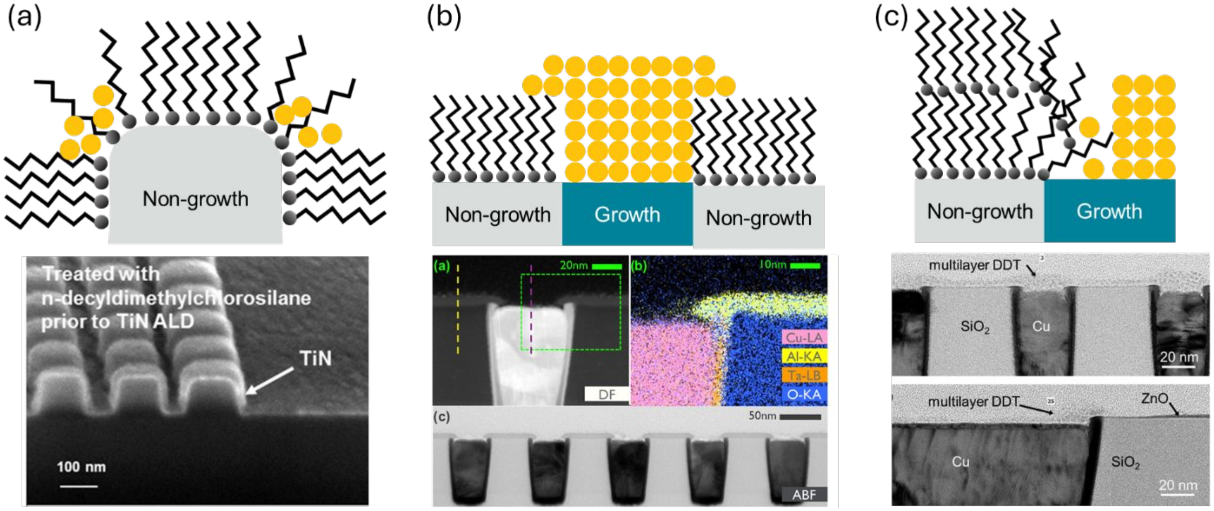

Figure 6. Examples of some of the challenges of ASD processes at the nanoscale, such as (a) poorer blocking ability of inhibitors at high curvature regions (reprinted with permission from ref [119]. Copyright 2016 American Chemical Society.), and mushrooming of (b) the ALD film (reprinted with permission from ref [120]. Copyright 2023 American Chemical Society.) and (c) inhibitors (reprinted with permission from ref [121]. Copyright 2020 American Chemical Society.), both of which could lead to defect formation at the interface between the growth and non-growth surfaces.

Better understanding of the surface chemistry

Another challenge in ASD is that most ASD processes strongly depend on surface chemistry and conditions, and are sensitive to, for instance, oxidation state of the substrate surface, etch processing performed on the substrates prior to ASD, chemical mechanical polishing, etc. The surface conditions play a critical role for inhibitor adsorption,[85,123] and impact the interaction between ALD precursors and surfaces of non-growth and growth substrates, which could affect selectivity significantly. It is especially important to understand which surface properties of a non-growth substrate impact the formation of a good quality inhibitor layer, and how precursor chemistry influences the blocking ability of inhibitors and ASD film growth on the growth region. Developing more general principles of the interdependence of surface chemistry with AS-ALD effectiveness should be a goal.

More effective inhibitors and precursors

Many studies have highlighted the importance of designing and selecting inhibitors and precursors, as discussed in the previous sections. To achieve high selectivity, it is crucial to develop a precursor that is reactive enough to form a high-quality film on the growth surface, but not so reactive that it interacts with or nucleates easily on inhibitors. Although a few studies have shown that a precursor with weaker Lewis acidity and larger size can help improve the selectivity, more systematic studies on precursor series, such as those with the same ligand but different metal centers or the same metal center with different ligands, will be very helpful to better understand the role of precursors in achieving good selectivity in ASD. Regarding inhibitor design, an effective inhibitor should exhibit rapid reactions on non-growth surfaces, and strong thermal and air stability to prevent degradation or decomposition before or during the ASD process. Additionally, it must possess a reactive functional group capable of selectively adsorbing onto one type of surface over another. After adsorption on the non-growth surface, the inhibitor should have an inert tail moiety, lack reactive sites, and form a well-packed layer to avoid facilitating interactions with the precursor. Other critical considerations when designing or selecting an effective inhibitor include its compatibility with vapor-phase delivery, which is desirable for most industrial ASD applications, and the ease of inhibitor removal after ASD to minimize contamination on non-growth surfaces. Finally, it is important to co-design the precursor and inhibitor when developing an ASD process, as different combinations of precursors and inhibitors can result in varying levels of selectivity. We also need more theoretical studies to improve our understanding of the mechanisms involved and to accelerate the precursor and inhibitor selection process.

Expanding the ASD toolbox

To broaden the application of ASD, more studies are required to expand the toolbox of ASD processes. For example, while most AS-ALD studies focus on the selective deposition of dielectric films (DoD) or metal films (MoD) on dielectric areas of dielectric/metal patterns, real-world applications involve a wide range of substrate combinations, including metal/metal, oxide/oxide, oxide/nitride, carbon/oxide, and even inorganic/organic combinations. Therefore, it is essential to investigate how to achieve selectivity on various substrate systems to expand the potential applications of ASD. Additionally, the ASD of transition metal dichalcogenide (TMD) layers has attracted increasing interest from both academia and industry, as these two-dimensional (2D) semiconductors hold significant promise for future nanodevice applications.[124] However, achieving both high selectivity and good crystallinity of TMDs on the growth surface remains a challenge.

Looking ahead

Looking forward, further research is essential to advance the development of ASD processes. To build more robust ASD systems with excellent selectivity, it is crucial to explore new chemistries for depositing thin films, such as novel ALD and CVD precursors, and new inhibitors that can withstand the harsh ASD process environments, typically characterized by highly reactive chemicals and elevated temperatures, while meeting the stringent requirements for high-volume production in industry. In summary, through the dedicated work of researchers, ASD processes will continue to show great promise for next-generation manufacturing to fabricate nanopatterned materials, and the application of ASD for high-volume production will become more feasible. At the same time, we anticipate that advances in ASD will open new opportunities for other applications such as catalysis, energy conversion, and optoelectronics.

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