From the bottom-up: toward area-selective atomic layer deposition with high selectivity

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From the Bottom-Up: Toward Area-Selective Atomic Layer Deposition with High Selectivity†

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ABSTRACT: Bottom-up nanofabrication by area-selective atomic layer deposition (ALD) is currently gaining momentum in semiconductor processing, because of the increasing need for eliminating the edge placement errors of top-down processing. Moreover, area-selective ALD offers new opportunities in many other areas such as the synthesis of catalysts with atomic-level control. This Perspective provides an overview of the current developments in the field of area-selective ALD, discusses the challenge of achieving a high selectivity, and provides a vision for how area-selective ALD processes can be improved. A general cause for the loss of selectivity during deposition is that the character of surfaces on which no deposition should take place changes when it is exposed to the ALD chemistry. A solution is to implement correction steps during ALD involving for example surface functionalization or selective etching. This leads to the development of advanced ALD cycles by combining conventional two-step ALD cycles with correction steps in multistep cycle and/or supercycle recipes.

I. INTRODUCTION

It is a long-held dream in the field of nanotechnology to fabricate materials in a bottom-up fashion by using atoms as building blocks.1–3 This is in strong contrast to the current reality: the fabrication of nanoelectronics in the semiconductor industry relies almost completely on top-down processing, largely because of stringent requirements for reliability. However, the industry is currently facing prominent challenges that require the implementation of bottom-up schemes for some of the most demanding processing steps.4–6 The thin film deposition technique atomic layer deposition (ALD) can be characterized as bottom-up fabrication since it results in addition of atoms in a layer-by-layer fashion.7–8 In the past decade, ALD has become an essential element of semiconductor processing and is of growing importance,9–12 and therefore serves as an ideal vehicle for the implementation of industrial-compatible bottom-up approaches. However, ALD typically leads to uniform deposition on the entire surface, without any control of the lateral arrangement of the atoms. Area-selective ALD addresses the challenge of limiting the growth to specific areas by exploiting differences in local surface chemistry, which enables bottom-up processing of materials according to predefined patterns.13–15 Because of the atomic-level accuracy of ALD, this can be considered as a step toward the aforementioned dream of using atoms as building blocks for synthesizing materials from the bottom-up.

ALD is based on alternation of precursor and co-reactant exposures that lead to self-limiting surface reactions.11,12 Repetition of these exposures in ALD cycles allows for layer-by-layer deposition with precise thickness control, high uniformity on large wafers, and unparalleled conformality on nanostructured surfaces.14 ALD processes strongly rely on surface chemistry, which provides the opportunity to develop ALD processes for which the growth initiation depends on the substrate material.10 If such an ALD process results in immediate growth on the surface of one specific material, while there is a nucleation delay before the growth initiates on the surfaces of other materials that are present on the same sample, area-selective deposition occurs during the initial ALD cycles.

Previous work in the field of area-selective ALD focused for a large part on the patterning of ALD-grown films for nanoelectronics applications.10,13–24 By depositing the material only where it is needed, nanostructured materials can be synthesized without the need for additional subtractive processing steps such as etching or lift-off. Furthermore, area-selective ALD can provide new opportunities for catalysis,8,23–28 for example by enabling the controlled synthesis of core–shell nanoparticles.29–32 In recent years, area-selective ALD has attracted renewed attention in the semiconductor industry, mostly because of its potential application in self-aligned fabrication schemes,33 which is illustrated in Figure 1. With critical dimensions approaching the sub-5 nm level, the challenge of further downscaling nanoelectronics is not only in fabricating smaller features but also in the alignment of features in multilayer device stacks, which is becoming a major bottleneck.4 The maximum error in alignment, referred to as the edge placement error (EPE; see...
There are two main challenges in the field of area-selective ALD that require additional attention. Because ALD essentially results in isotropic deposition, lateral broadening relative to the predefined pattern occurs during area-selective ALD, which is often described as “mushroom” growth. Currently no solution for this challenge exists, although it has been suggested that plasma processes or combinations of ALD and anisotropic etching might provide a better control of the shape of the deposited material. A second major challenge is the defectivity on the non-growth area that results from insufficient selectivity. Such undesired growth can influence subsequent processing steps or compromise the device performance.

The term selectivity captures two characteristics of an area-selective ALD process. First, it defines for an ALD process where the deposition occurs and where no deposition should take place, and these locations are often referred to as the growth and non-growth areas, respectively (see Figure 1). When considering self-aligned fabrication, the growth and non-growth areas represent the surfaces of different materials that are present in the device structure. This aspect of selectivity is sometimes described as the substrate- or material-selectivity. By categorizing materials based on their properties as metals, semiconductors, and dielectrics, the material-selectivity is typically described as, for example, metal-on-metal or dielectric-on-semiconductor deposition. Second, the selectivity describes the difference in how much material is deposited on the growth area relative to the non-growth area. In selective chemical vapor deposition (CVD), the generally accepted definition is

\[
\text{selectivity} = \frac{\theta_{GA} - \theta_{NGA}}{\theta_{GA} + \theta_{NGA}}
\]

where \(\theta_{GA}\) and \(\theta_{NGA}\) are the amounts of material present after deposition on the growth and non-growth areas, respectively.

In practice, area-selective ALD processes often exploit differences in nucleation behavior of an ALD process on different surfaces, as shown in Figure 2. The selectivity window can be defined as the number of cycles it takes before the ALD growth initiates on the non-growth area. The graph also illustrates that the selectivity is a function of the film thickness, which implies there are basically two ways of evaluating different area-selective ALD processes: (i) comparing selectivity values for a specific target thickness or (ii) comparing the thickness that can be reached when limiting the selectivity to a specific maximum value.

An important question that needs to be addressed is what the target selectivity should be for the applications. It can be expected that especially for applications in nanoelectronics high selectivity values are required, while applications in catalysis are likely less demanding. So far, with area-selective ALD only recently being considered in the semiconductor industry, no clear target has been defined. In addition, the metrology of determining the selectivity is a challenge in itself, typically consisting of taking many top-view electron microscopy images and counting visible defects on the non-growth area. Based on the literature on different area-selective ALD approaches, a selectivity value of 0.99 for a film of a few nanometers thick appears to be a difficult but in some cases an

Figure 1. (a) Conventional patterning. When conventional patterning consisting of film deposition, lithography, and etching is employed for the fabrication of sub-5 nm scale features, it is extremely challenging to align features on top of each other. The difference between the actual and intended position is referred to as the edge placement error (EPE). (b) Self-aligned fabrication. Area-selective ALD can enable self-aligned fabrication by allowing for deposition only on the surface of specific materials. The surface on which the growth occurs selectively is defined as the growth area, while the surface on which no growth should take place is defined as the non-growth area. In this way, fewer lithography and etching steps are needed and the alignment issue is eliminated.
achieved target. On the other hand, it has been stated that for semiconductor fabrication the number of defects on the non-growth area should be below 10^6 cm^−2.38 When considering only defects that are readily observable in electron microscopy (>∼0.5 nm), area-selective deposition of a 1 nm thick film with less than 10^6 defects cm^−2 on the non-growth area requires a selectivity as high as 0.99999999. This large gap between what is achievable using current technology and what might be needed for the applications reveals that alternative approaches need to be considered.

In this Perspective, it will be discussed that the conventional approach of combining surface preparation steps with standard AB-type (i.e., two-step) ALD cycles is often not sufficient for achieving area-selective ALD with a high selectivity. To improve the selectivity, it is necessary to implement correction steps in the ALD process, which includes various gas or plasma treatments for surface functionalization or selective etching. The implementation of these corrections steps leads to the development of advanced ALD cycles: ABC-, ABCD-type cycle and supercycle recipes. This work is organized as follows: First, in section II, a brief overview of conventional area-selective ALD approaches is provided. Section III discusses the challenge of obtaining area-selective ALD with a high selectivity. Subsequently, in section IV, the solution to this challenge is described, i.e., the implementation of corrections steps, for which several examples are reviewed. Finally, section V provides an outlook to future work in the field.

II. OVERVIEW OF CONVENTIONAL AREA-SELECTIVE ALD APPROACHES

One way of looking at the challenge of making ALD processes selective is to consider the main surface reactions that have to occur to result in deposition of material. If either precursor or co-reactant adsorption does not take place on a specific starting surface, this can be exploited for achieving area-selective ALD. Since the possibilities for selective precursor or co-reactant adsorption in standard two-step ALD processes are limited, an important alternative approach is to selectively functionalize the surface prior to the deposition. These three conventional approaches for area-selective ALD are schematically illustrated in Figure 3. In this section, a short overview of these approaches is provided, by presenting a few important examples. More information on how to obtain selectivity can also be found in earlier reports on selective epitaxial growth (SEG) and selective chemical vapor deposition (CVD).36,39-42

II.a. Selective Precursor Adsorption. Several area-selective ALD processes based on selective precursor adsorption exploit the large difference in chemical character between hydroxyl-terminated and hydrogen-terminated surfaces.43-47 This typically leads to area-selective ALD of metal oxides on OH-terminated Si and a nucleation delay on H-terminated Si,43-45 while the reverse selectivity of ALD on the H-terminated Si was demonstrated for Co ALD from t-Bu-AllylCo(CO)3 and dimethylhydrazine.46 Moreover, several studies have exploited differences in precursor adsorption on oxide versus metal surfaces.48,49

In a study by Longo et al., the selectivity of metal oxide ALD using TiCl4, TMA, and TDMAHf, precursors and H2O as the co-reactant at 150 °C on OH- versus H-terminated Si(001) was investigated.33 As illustrated in Figure 4, after 25 TiO2 ALD cycles, X-ray photoelectron spectroscopy (XPS) detected no TiO2 on the H-terminated surface revealing selectivity for growth on the OH-terminated surface. On the other hand, only a small difference was observed after 10 cycles of HfO2 ALD on these surfaces. Al2O3 ALD can be considered an intermediate case with a reduction of 38% of the Al2O3 signal after 10 cycles on the H-terminated Si compared to the oxidized surface. From density functional theory (DFT) calculations it was learned that the adsorption of all three precursors experience relatively high kinetic barriers (∼1.5 eV) on the H-terminated surface. However, the chemisorption reaction is most endothermic for the TiCl4 precursor, which explains the selectivity observed for the TiO2 ALD process.33 This study illustrates that exploiting differences in precursor
adsorption on various surfaces for achieving area-selective ALD is only feasible for certain precursors.

For most area-selective ALD approaches based on selective precursor adsorption, the substrate temperature greatly influences whether area-selective deposition can be obtained. For example, in a related study by McDonnel et al., the selectivity for TiO₂ ALD was found to be lower when the deposition was carried out at 30 °C instead of at 100 or 150 °C.⁴³

Area-selective ALD relying on selective precursor adsorption typically allows for selective deposition of films of only a few nanometers thick,⁴⁻⁵⁷ although there are exceptions.⁴⁴ The logical next step would be to design new ALD precursors that have the ability to selectively adsorb on specific materials. However, in practice, this will be extremely challenging considering that an ALD precursor already has to satisfy many requirements to function as a reliable ALD precursor, such as being sufficiently volatile and thermally stable while resulting in self-limiting adsorption.⁴⁰

II.b. Selective Co-reactant Adsorption. Area-selective ALD based on selective co-reactant adsorption has been explored less extensively as compared to the first category. Most of these studies focus on selective deposition on metals by exploiting the catalytic activity of the surface,⁴⁻⁵ⁱ⁻⁵⁴ often aimed at the synthesis of core/shell nanoparticles for catalysis applications.⁵⁸⁻⁶⁰ For example, area-selective ALD of Pt and Ru can be obtained when using thermal ALD processes in which O₂ gas is used as the co-reactant.⁵²,⁵³,⁵⁵ Noble metals have the ability to catalyze dissociative chemisorption of O₂ on the surface, leading to chemisorbed O that can participate in the combustion of the precursor ligands.⁵⁶ In the absence of a catalytic starting surface, molecular O₂ gas is not sufficiently reactive to eliminate the ligands of the precursor. This mechanism can therefore be employed for area-selective ALD of metal-on-metal in the presence of oxide as the non-growth area. Even if the precursor adsorbs on such an oxide surface, the ALD reactions do not proceed due to lack of reactive species during the co-reactant half-reaction. It has been shown that low substrate temperatures as well as low O₂ exposures are required to avoid nucleation on oxide substrates.⁵¹,⁵³,⁵⁵

Similar results have also been reported for area-selective ALD of Pd using H₂ gas as the co-reactant, which relies on catalytic dissociation of H₂ on metal surfaces.⁶⁻⁹ In our recent work, we extended this approach to area-selective ALD of oxide-on-metal with an oxide as the non-growth area.⁵⁵ As illustrated in Figure 5, area-selective ALD of Fe₂O₃ occurs selectively on Pt and not on SiO₂ because the tert-butylferrocene precursor only reacts where chemisorbed O is available.

Figure 4. X-ray photoelectron spectroscopy results measured after (left) 25 cycles of TiO₂ ALD from TiCl₄/H₂O, (middle) 10 cycles of Al₂O₃ ALD from TMA/H₂O, and (right) 10 cycles of HfO₂ ALD from TDMAHf/H₂O on OH- and H-terminated Si(001) substrates at 150 °C.⁵⁵ The graph illustrates that the selectivity of an ALD process depends strongly on the employed precursor. Reprinted with permission from ref 43. Copyright 2014 American Vacuum Society.

Figure 5. Area-selective ALD of Fe₂O₃ on Pt relying on selective co-reactant adsorption. (a) Dissociative chemisorption of O₂ on the Pt is illustrated. (b) tert-Butylferrocene (TBF) adsors in both areas but only leads to deposition where reactive chemisorbed O is available. (c) The result is that Fe₂O₃ is deposited selectively on the Pt. (d) X-ray photoelectron spectroscopy data show that Fe₂O₃ occurs on Pt and not on Al₂O₃, SiO₂, or Au. (e) Core/shell Fe₂O₃/Pt nanoparticles synthesized using (left) 25 or (right) 50 ALD cycles. Reprinted with permission from ref 32. Copyright 2018 American Chemical Society.

II.c. Selective Functionalization prior to ALD. The most extensively studied approach for area-selective ALD on prepatterned surfaces is to locally deactivate the ALD growth using self-assembled monolayers (SAMs).⁶⁷⁻⁻⁷⁰ The SAM is applied prior to the ALD process, typically by using wet chemistry. SAM monomers consists of a headgroup that facilitates the binding to the surface, an alkyl chain of a certain length that ensures the ordering in a monolayer, and a tail group that determines the character of the surface after functionalization.⁷¹ Many SAM monomers have the ability to selectively adsorb on specific materials. After functionalization, selectivity relies on either selective precursor or co-reactant adsorption, similar to what has been discussed in sections II.a and II.b. For example, when using SAMs with for instance CH₃ or CF₃ tail groups, the surface becomes unreactive toward most ALD chemistries due to the blocking of precursor adsorption.⁷¹ Seminal work by Chen and Bent demonstrated that the choice of the SAM determines where ALD takes place. For example, octadecyltrichlorosilane (ODTS) molecules adsorb selectively on OH-terminated SiO₂ regions on a substrate allowing for area-selective ALD of HfO₂ on H-terminated Si regions, while 1-octadecene molecules adsorb selectively on H-terminated Si allowing for ALD of Pt on SiO₂.⁷² Furthermore, it was established that the alkyl chain length determines the capability of the SAM to block the ALD growth because of improved ordering, with a length of 12
carbon atoms being required for effective blocking of HfO₂ ALD from HfCl₄ and H₂O.73

Besides SAMs, there are several other surface preparation treatments or gas/plasma dosage steps that can be employed prior to ALD for selective functionalization of the surface. For instance, in recent work by Zyulkov et al., a H₂ plasma treatment was employed to functionalize an amorphous carbon (a-C:H) non-growth area with CH₃ groups, allowing for area-selective ALD of ∼3 nm Ru on SiCN regions present on the same substrate.74 Kim et al. demonstrated that a fluorocarbon plasma can be used to selectively functionalize the horizontal surfaces of three-dimensional Fin arrays, in order to achieve area-selective ALD of Pt on the vertical surfaces.75 This type of area-selective deposition was described as topographically selective ALD.

III. THE CHALLENGE OF OBTAINING AREA-SELECTIVE ALD WITH A HIGH SELECTIVITY

As discussed in the Introduction, one of the main challenges for area-selective ALD is to obtain the high selectivity that is required for applications in nanoelectronics. In practice there are always defects and impurities present on the non-growth area on which the ALD growth can initiate. In this respect, it is relevant to mention that in order to avoid the introduction of foreign species on the surface during the ALD process, it is of crucial importance to work with precursor, co-reactant, and purge gases with a high purity level.36 On top of that, even if an area-selective ALD process could be designed such that either precursor adsorption or co-reactant adsorption reactions are perfectly selective in an area for a given combination of growth and non-growth areas, it also has to be considered that the character of the non-growth area can change during the deposition when it is exposed to the ALD chemistry (see Figure 6). In fact, modification of the non-growth area, for example due to the exposure to the ALD precursor or co-reactant, turns out to be one of the main reasons for loss of the selectivity of area-selective ALD. This will be illustrated in this section by describing a few examples.

The selectivity of approaches based on the use of SAMs is for a large part limited by the thermal stability of the SAM. For example, thiol adsorbed to metal surfaces already start to desorb or degrade at a temperature of 100 °C.76 This leads to the formation of pinholes in the SAM where the ALD growth can initiate.69,77 Since most ALD processes have temperature windows in the range 100–400 °C, the low thermal stability of SAMs severely limits the applicability of SAMs for achieving area-selective ALD.

Besides the degradation of the SAM, it has recently been demonstrated that physisorption of the precursor on a SAM can greatly contribute to the loss of the selectivity. Seo et al. investigated the mechanism of Al₂O₃ ALD on octadecylphosphonic acid (ODPA) SAMs and concluded that TMA molecules physisorbed on the SAM act as nucleation sites for initiation of the ALD growth.78 This contribution could be reduced by decreasing the TMA pressure and by increasing the Ar pressure during the subsequent purge step, which allowed for area-selective ALD of Al₂O₃ films as thick as 60 nm.78 A general lesson from this study is that loss of selectivity is typically caused by side reactions that are not self-limiting. Consequently, as this study demonstrates, the selectivity can be dependent on the precursor or co-reactant pressure and/or exposure time.

Stevens et al. extended the approach of using a H₂ plasma for functionalization of a-C:H (see section II.c) to area-selective ALD of TiN, TiO₂, and HfO₂.79 A higher selectivity was obtained for TiN ALD from TiCl₄ and NH₃ as compared to TiO₂ and HfO₂ ALD using H₂O as the co-reactant. By performing additional experiments involving the dosing of H₂O during TiN ALD, it was established that the loss of selectivity can be attributed to the oxidation of the a-C:H non-growth area by H₂O.

Water physisorption has also been suggested to limit area-selective ALD of metal oxides with H-terminated Si as the non-growth area. The aforementioned low selectivity for area-selective ALD of TiO₂ at 30 °C in the study of McDonnel et al. was explained by referring to the long purge times that are required to remove physisorbed H₂O from surfaces at low temperatures.57

Although the limiting factor for achieving a high selectivity has not been investigated in most area-selective ALD studies, the examples presented above clearly demonstrate that loss of selectivity often involves the physisorption of species on the non-growth area and/or degradation of the surface functionalization. Taken together, this can be generalized as a change of the non-growth area as a result of the exposure to the ALD chemistry.

IV. SOLUTION: IMPLEMENTATION OF CORRECTION STEPS

In practice it is often unavoidable that the nature of the non-growth area gets altered during ALD. As discussed above, even a mild co-reactant such as H₂O is sufficiently reactive to modify H-terminated Si or a-C:H surfaces, while a low deposition temperature of 100 °C can already be too high for using certain SAMs. A solution to this challenge is to implement correction steps during the ALD process.

Inspiration for these corrections steps can be found in earlier literature on selective epitaxy and selective CVD.36,39–42 For example, in selective epitaxy of Si, HCl has been added to the Si source gas (e.g., SiH₄/H₂ or SiH₂Cl₂/H₂) to selectively etch Si atoms from the oxide non-growth area.39,80 Even alternation between deposition and etching steps has been explored,81 which more closely resembles approaches that can be used for area-selective ALD. Selective CVD of Cu on W can be achieved by selective functionalization of SiO₂ regions with chlorotrimethylsilane molecules.36,82 Similarly, in recent years, several area-selective ALD studies have followed the strategy of implementing correction steps for improving the selectivity and also for developing new area-selective ALD approaches. In this section, two main types of such corrections steps are
discussed: (i) repeating functionalization steps and (ii) selective etching to remove deposited material from the non-growth area. Furthermore, some unexplored possibilities for improvement of processes will be discussed.

**IV.a. Repeating Functionalization.** To correct for the desorption of SAM monomers, Hashemi and Bent investigated an approach involving sequential regeneration of the SAM by dosing SAM monomers, which is schematically depicted in Figure 7a.83 Instead of dipping the sample in solution to prepare the SAM, in this case dodecanethiol (DDT) SAMs were used that can be delivered to the surface in vapor-phase. These thiol molecules selectively adsorbed on Cu as the non-growth area, such that area-selective ALD of ZnO on SiO2 could be obtained. The partly degraded SAM was regenerated by dosing the DDT molecules after every 150 ZnO ALD cycles. In this way, ZnO films as thick as 81 nm could be deposited in an area-selective manner, which is three times thicker as compared to other approaches that rely on surface functionalization only prior to the deposition.83 In this case, the non-growth area is selectively functionalized. Copyright 2016 Wiley. Used with permission from ref 83. (b) Alternatively, inhibitor molecules can be dosed during every ALD cycle in an ABC-type ALD process.84 The inhibitor molecules adsorb selectively on the non-growth area during step A and subsequently block the precursor adsorption during step B. The co-reactant removes the precursor ligands and the inhibitor molecules during step C. Reprinted with permission from ref 84. Copyright 2017 American Chemical Society.

![Figure 7. Repetition of surface functionalization as a correction step.](image)

Figure 7. Repetition of surface functionalization as a correction step. (a) By repeating surface functionalization after a certain number of ALD cycles, a SAM can be regenerated to correct for the desorption of SAM monomers over time. In this case, the non-growth area is selectively functionalized. Copyright 2016 Wiley. Used with permission from ref 83. (b) Alternatively, inhibitor molecules can be dosed during every ALD cycle in an ABC-type ALD process. The inhibitor molecules adsorb selectively on the non-growth area during step A and subsequently block the precursor adsorption during step B. The co-reactant removes the precursor ligands and the inhibitor molecules during step C. Reprinted with permission from ref 84. Copyright 2017 American Chemical Society.

molecules are relatively small molecules as compared to the monomers employed in SAM formation, such that they can be pulsed in vapor-phase during short dosage steps in the same chamber, resulting in an approach that is compatible with high throughput industrial process flows. The use of inhibitor molecules in ABC-type ALD cycles is inspired on work by Vangas-Gil et al., who employed such ALD cycles to deposit doped materials with enhanced doping efficiency.85 In that work, the inhibitor molecules reduce the number of adsorption sites for the dopant precursor molecule or, in other words, partly block the dopant precursor adsorption. As schematically shown in Figure 7b, to enable area-selective ALD, inhibitor molecules need to be used that selectively adsorb on the non-growth area in step A, and subsequently block the precursor adsorption completely in step B.84 The co-reactant exposure in step C should remove the inhibitor molecules together with the precursor ligands.

One of the merits of this approach is that it is compatible with the use of a plasma or ozone as the co-reactant, which is in contrast to conventional approaches based on the use of SAMs for deactivation. SAMs have been shown to quickly degrade when using for example NH3 plasma as the co-reactant.86 The use of ABC-type ALD cycles therefore potentially allows for area-selective ALD of a wider range of materials. The approach was demonstrated for area-selective ALD of SiO2, using acetylacetone (Hacac) as the inhibitor, BDEAS as the precursor, and O2 plasma as the co-reactant.84 This ABC-type process resulted in area-selective ALD of ~1 nm of SiO2 on for example GeO2 or WO3 growth areas, with Al2O3, HfO2, or TiO2 as the non-growth area, which represents a unique material-selectivity that differentiates between different oxide starting surfaces. It was found that the adsorbed Hacac molecules do not completely block precursor adsorption, suggesting there is room for improving the selectivity by employing alternative inhibitor molecules. Another merit of this approach is that the selectivity is provided by the inhibitor adsorption, instead of requiring the design of new precursor molecules that allow for selective precursor adsorption (as discussed in section II.a). The decoupling in two separate steps with different requirements offers more flexibility for developing new area-selective ALD processes.

**IV.b. Selective Etching.** Even when repeating surface functionalization, it remains challenging to achieve the high selectivity that is desired for reliable semiconductor processing. However, a promising solution is to combine optimized area-selective ALD approaches with selective etching to improve the selectivity further. Hashemi et al. explored the use of postdeposition etching as correction step aimed at removing deposited material on the non-growth area.87 Area-selective ALD of Al2O3 was performed on Si, while blocking the ALD on Cu using ODPA SAMs. Partly due to the use of reactive TMA as the precursor, only partial blocking of the ALD growth was demonstrated, resulting in area-selective deposition of Al2O3 on Si with a poor selectivity. After ALD, the sample was immersed in acetic acid which acts as a mild etchant for the native CuOx on the Cu surface. Selective etching of the thin CuOx layer also results in the removal of the SAM together with the Al2O3 deposited on top in a sort of lift-off step. In this way, the Al2O3 that was deposited on the non-growth area was removed, yielding a higher selectivity for the overall approach.
Instead of removing a sample from the ALD reactor to perform wet chemical etching, it is preferred to improve the selectivity by performing vapor-phase etching steps. As illustrated in Figure 8, an alternative approach is to switch back and forth between deposition and etching cycles in a supercycle recipe, which can result in area-selective ALD of a much thicker film. The starting point for this approach is to use an area-selective ALD processes that shows a difference in nucleation behavior on the growth and non-growth areas. After a certain number of ALD cycles, when the growth starts to initiate on the non-growth area, a selective etching step is performed to remove islands (or maybe individual atoms) of deposited material from the non-growth area. The etching process should be (material-)selective such that only the deposited material is etched, without significantly affecting the underlying substrate. This also implies that some deposited material is etched from the growth area, meaning that the etching process is not area-selective. However, as long as the amount of material deposited per supercycle is more than the amount that is etched per supercycle, the combined effect of the ALD cycles and etching steps is that area-selective ALD with improved selectivity is obtained.

This approach has been demonstrated by Vallat et al. for area-selective ALD of Ta2O5 from TBTDET and O2 plasma on TiN in the presence of SiO2 as non-growth area. A NF3 plasma was used, which was shown to etch Ta2O5 with a rate four times higher than etching SiO2. Instead of performing a supercycle of ALD and selective etching cycles, NF3 was added to the O2 plasma co-reactant during every eighth cycle. It was also shown that the NF3 plasma exposure does not only etch the Ta2O5 but also functionalizes the surfaces with Si–F or SiO–F bonds that can result in an additional nucleation delay on the SiO2.

IV.c. Other Possibilities for Correction Steps. There are many opportunities for adding simple gas or plasma exposures to an ALD cycle as a correction step in order to bring the non-growth area back to its initial state, although these kinds of approaches have not been explored extensively yet. For example, in the work of Kalanyan et al. aimed at area-selective ALD of W, H2 was added during the WF6 precursor dosage step, resulting in the formation of gas-phase HF. The formed HF molecules passivate Si–OH sites on the SiO2, non-growth area and thereby reduce the adsorption of the co-reactant silane on SiO2. Alternatively, a similar result can potentially be obtained when adding a HF, NF3, or SF6 plasma dosage step at the end of the cycle. When using a-C:H as the non-growth area, instead of performing a H2 plasma treatment to functionalize the non-growth area only prior to the deposition as in the study of Stevens et al., the oxidation of the a-C:H can likely be counteracted by periodically performing a H2 plasma step in a supercycle recipe.

Another example that was already discussed is the use of purge steps with a high Ar pressure to remove physisorbed species from the surface of a SAM in the work of Seo et al. When combining area-selective ALD and selective etching cycles in a supercycle for area-selective ALD with improved selectivity as discussed above, it should also be taken into account that the non-growth area can change during the etching step, similar to what is discussed for ALD in section III. This might lead to a loss of the difference in nucleation behavior on the growth and non-growth areas that is required for the approach to work. Such a change can potentially be counteracted by adding a gas/plasma treatment as a correction step to the selective etching cycle.

V. OUTLOOK

The design of new area-selective ALD approaches based on the implementation of correction steps requires the development of advanced ALD cycles, which is schematically illustrated in Figure 9. As discussed, surface functionalization can be repeated by including an inhibitor dosing step in ABC-type cycles (Figure 9b). Gas or plasma exposures can be added to the cycle to bring the non-growth area back to its initial state (Figure 9c). In some cases, it might be necessary to combine correction steps to achieve the desired selectivity, leading to the development of ABCD-type ALD cycles (Figure 9d,e). Although the implementation of these correction steps increases the cycle time, this can be acceptable if it leads to a substantial improvement of the selectivity, and as long as processing steps are used that are compatible with semiconductor fabrication schemes.

One of the additional challenges for area-selective ALD is that no universal strategy exists for making a specific ALD process selective. For example, a certain SAM might deactivate the surface toward an ALD chemistry, but another SAM might be needed when using a different precursor or co-reactant. As a result, it is for example very difficult to achieve area-selective ALD of mixed (i.e., ternary, quaternary, or doped) materials or nanolaminates, since the deposition of these materials requires the combination of two or more binary ALD processes. The need for process-specific solutions can however be seen as an alternative motivation for designing area-selective ALD processes based on vapor-phase dosing of inhibitors. Since a different inhibitor can be dosed depending on which precursor/co-reactant chemistry is employed, it is more straightforward to combine area-selective ALD processes.

Considering that for most area-selective ALD approaches it is extremely challenging to achieve a high selectivity, in practice area-selective ALD will often need to be combined with a selective etching process as a correction step to increase the overall selectivity to the desired level. For the
implementation of selective etching, it is preferred to use an atomic layer etching (ALE) process such that the hallmarks of ALD (i.e., atomic-level control and high uniformity/conformality) are preserved. When using an ALE process, the self-limiting nature of the ALE reactions ensures that the same amount of material is etched uniformly on the growth area. Note that the etching reactions on the non-growth area do not need to be self-limiting, since the material needs to be removed completely.

In case a three-dimensional device structure is considered, an isotropic ALE process should be used for improving the selectivity of area-selective ALD. This approach can therefore greatly benefit from the field of ALE, where the characterization of processes for isotropic ALE is a relatively new development. The most straightforward approach to combine area-selective ALD and ALE is to develop supercycle recipes, as illustrated in Figure 9f. Since also undesirable etching of material on the growth area occurs, preferably ALE processes should be developed that result in a higher etch rate for individual atoms or islands on the non-growth area as compared to the etching of a continuous layer on the growth area. In other words, in an ideal case scenario, only etching of material on the non-growth area should occur. In this case it can even be considered to implement an etch correction step after every cycle (in an ABC- or ABCD-type ALD cycle) as a new approach for achieving area-selective ALD.

The change of the character of the non-growth area during deposition due to the exposure to the ALD chemistry is identified in this work as one of the main causes for how the selectivity of an area-selective ALD process is lost. In addition to the development of correction steps, there is especially a need for a better understanding of the interaction of ALD precursors and co-reactants with relevant surfaces. Fundamental studies using in situ techniques are required to obtain insight into the initial ALD growth on various surfaces. Furthermore, in situ studies of the reaction mechanisms of the corrections steps can provide the information that is needed for further improving area-selective ALD approaches.

With the development of more reliable and industry-compatible methods for area-selective ALD, the application in high volume production appears to be approaching. Besides the imminent applications in the fabrication of nanoelectronics, area-selective ALD provides novel opportunities for many other fields, most prominently in catalysis. The area-selective ALD approaches aimed at material-selectivity that are currently being developed can eventually also be employed for bottom-up fabrication of model catalysts. In addition to the synthesis of core/shell nanoparticles, it has been demonstrated that ALD growth can in some cases be selective to specific facets of a nanoparticle (referred to as facet-selective ALD), which provides new avenues for the synthesis of catalysts tailored at the nanoscale. These applications are only the first demonstrations of the unique opportunities area-selective ALD provides for bottom-up nanofabrication with atomic-level precision.

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**Notes**
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2013, respectively. His Ph.D. thesis work focused on atomic layer deposition (ALD) of platinum and comprised pioneering work on the use of area-selective ALD in nanopatterning. Adrie carried out his postdoctoral research at the department of Chemical Engineering at Stanford University in 2014–2016, for which he obtained a personal NWO Rubicon grant in 2014. At Stanford he studied the reaction mechanisms of ALD of ternary materials using in situ techniques, aimed at the synthesis of electrocatalysts. In 2016 he returned to TUE for a tenure track position in the Department of Applied Physics. His current research encompasses thin film deposition and etching for applications in nanoelectronics, with a focus on selective processing for bottom-up fabrication. Adrie is a founding member of the Early Career Investigator network within COST Action HERALD and chaired the 2nd Area Selective Deposition workshop (ASD2017) in Eindhoven in 2017.

Marc Merkx is a Ph.D. student at TUE, where he recently received his M.Sc. degree in Applied Physics. His Ph.D. project focuses on the development of new approaches for area-selective ALD of oxides and nitrides, for example based on the use of inhibitors in advanced ALD cycles. In 2016 he worked on the characterization of vanadium oxide films during an internship at the Laboratoire des Technologies de la Microélectronique in Grenoble, France.

Erwin Kessels is a full professor at TUE, where he is also the director of the NanoLab@TU/e clean room facilities. Erwin received his M.Sc. and Ph.D. degrees (with highest honors) in Applied Physics from TUE in 1996 and 2000, respectively. His research interests cover the Applied Physics from TU/e in 1996 and 2000, respectively. His current research encompasses thin film deposition and etching for applications in nanoelectronics, with a focus on selective processing for bottom-up fabrication. Erwin is also the driving force behind the AtomicLimits.com blog and the founder of the ALD Academy.

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