Area-selective atomic layer deposition of Al_2O_3 on SiN_x with SiO_2 as the nongrowth surface

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Area-selective atomic layer deposition (ALD) of dielectrics on chemically similar growth and nongrowth surfaces is very challenging. SiO_2 and SiN_x are the most extensively used dielectric materials in semiconductor manufacturing. Inhibitors used to functionalize SiO_2 and SiN_x are similar, and include aminosilanes, chlorosilanes, and alkoxysilanes. Among these, aminosilanes are the most reactive and are more suitable for vapor phase functionalization. Aminosilanes are also commonly used as Si precursors for ALD of both SiO_2 and SiN_x. However, for a given aminosilane precursor, the growth temperature for SiO_2 is generally lower than that for SiN_x, likely due to the lower activation energy barrier for the reaction of aminosilanes with surface SiOH groups compared to surface $SiNH_x$ ($x = 1, 2$) groups. Therefore, we can expect that there will be a greater attachment of aminosilanes to SiO_2 than SiN_x, which may allow for area-selective ALD on SiN_x versus SiO_2. The SiO_2 and SiN_x surfaces were exposed to bis(dimethylamino)dimethylsilane followed by (N,N-dimethylamino)trimethylsilane through the vapor phase at 150 °C. At the same substrate temperature, Al_2O_3 films were grown by ALD using dimethylaluminum isoproxide and H_2O. *In situ* surface infrared spectroscopy shows that aminosilane inhibitors react with almost all the surface −SiOH groups on SiO_2, but reaction with surface $-NH_x$ groups on the SiN_x surface is incomplete, thereby leaving potential growth sites for ALD of Al_2O_3. *In situ* ellipsometry results shows that a ~2.7 nm Al_2O_3 film can be selectively deposited on SiN_x versus SiO_2 (see Figure 1). Upon exposure of the plasma-deposited SiN_x to the atmosphere, a higher attachment of aminosilanes and longer nucleation delay during the ALD of Al_2O_3 were observed, indicating the need to remove the native surface oxynitride prior to functionalization. This study shows that while fully passivating the nongrowth surface is necessary for achieving growth inhibition, ALD can initiate on a partially passivated growth surface.

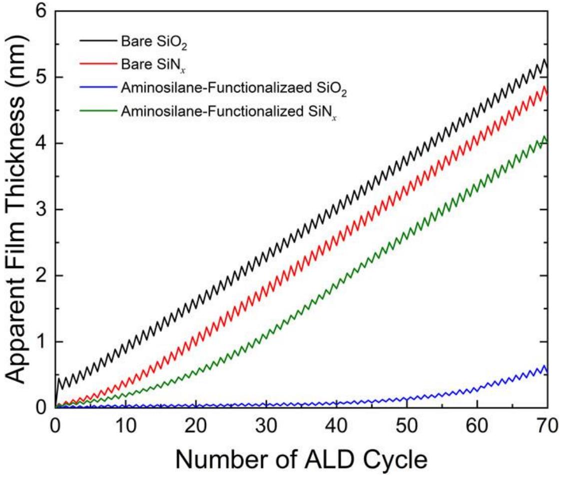

Figure 1: Apparent film thickness of Al_2O_3 measured by *in situ* four-wavelength ellipsometry on bare and aminosilane-functionalized SiO_2 and SiN_x surfaces.

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Using Chemical Selectivity to Control Atomic Placement in ALD

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The rapid growth of technologies such as machine learning and autonomous vehicles is fueling a need for more powerful electronic chips, and the semiconductor industry is working to meet this need with ever-more complex nanoscale device structures. With the growing demands on nanostructure fabrication, selective deposition is gaining attention as an important process to achieve pattern features at the sub-10 nm length scale. Selective deposition is also being explored for applications within fields as diverse as catalysis and optoelectronics. In this presentation, I will describe how control over the substrate surface properties via chemical selectivity can lead to area selective atomic layer deposition (ALD). ALD, which relies on self-saturating, layer-by-layer, gas-surface reactions to deposit conformal thin film materials, is a good choice for selective deposition because its chemical specificity provides a means to achieve selectivity on a spatially patterned substrate. In particular, inhibitory layers such as self-assembled monolayers SAMs or small molecules can selectively alter the native surface reactivity, in turn allowing control over ALD nucleation. I will describe several examples where this process provides excellent selectivity for deposited films on different materials, including dielectrics and metals. The important role of ALD precursor design on the selectivity will also be discussed using Al_2O_3 AS-ALD as a model. These and other strategies are needed to achieve atomic-scale precision on nanoscale patterns.

Atomic-scale Simulation Frameworks for ASD

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Area selective deposition (ASD) techniques hold a high potential for atomically fine-tuned manufacturing of nanoelectronic devices. In addition to the benefits of going to the extreme fabrication limit in a controlled bottom-up approach, ASD also finds applications in new device architectures for optical and chemical/catalytic devices. Despite the promising scientific results, ASD still needs to manifest itself in big-scale industrial applications. To achieve this, a better understanding of the physical-chemistry interactions at the molecular level is needed to characterize molecule-surface interactions, selectivity, passivation, material/surface dependencies, and stability of generated surfaces. To that end, atomistic simulations present themselves as a highly valuable tool that can be used to deepen the understanding and support the development of such technologies by providing unprecedented insight into the microscopic properties.

In this talk, we show how the Synopsys QuantumATK software for atomistic simulations can assist to quantify area selective processes and extend the atomistic/physical/chemical understanding of selective deposition. We exemplify the potential of simulations through case studies of (i) self-assembled monolayer (SAM) formation on Cu surfaces and (ii) selective deposition of alumina precursors using SAMs on Cu.

We will present quasi-random and symmetric SAM formation simulation data at different coverages to extract the saturation coverage (Fig. 1). We will further compare two alumina precursors adsorbed on Cu, and alkanethiolate SAM-passivated Cu, and analyze differences in selectivity and temperature stability (Fig. 2). Chemical analysis is used to explain the observed differences from molecule-metal interactions and the local charge distribution, illustrating how density functional theory (DFT) modeling can provide insight into molecule and material-specific ASD processes.

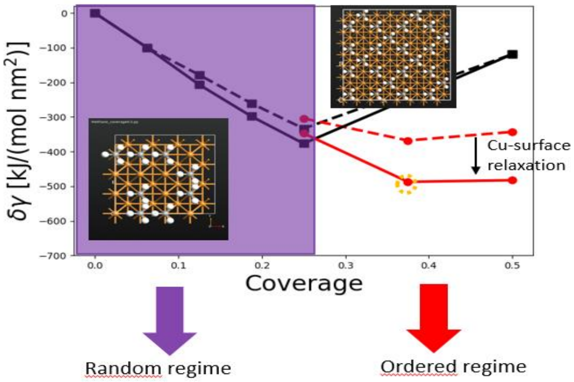

Figure 1: Free energy analysis of SAM formation on Cu surfaces.

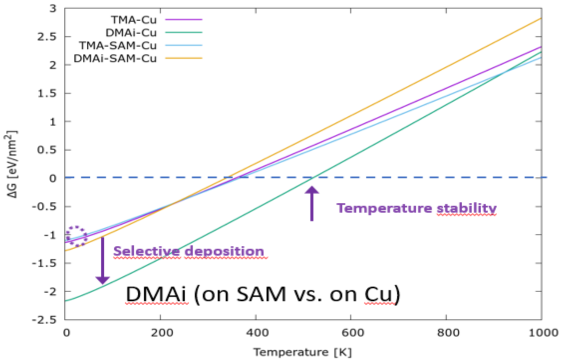

Figure 2: Selective deposition free energy of Alumina precursors on Cu and SAM-Cu.

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Thermally Assisted Area Selective
Atomic Layer Deposition

In our recent published work, we explore the possibility of achieving area selective ALD by applying temperature gradients on the substrate [1]. In this approach, the majority of the substrate is kept at a low temperature, which suppresses the surface chemical reaction, while a small area is heated to allow the reaction to locally proceed. A practical example of this technique is the ALD process of Si_2H_6, where instead of a co-reactant the elevated temperature induced by the laser itself is used to remove the ligands [2]. Controlling the size and the position of the heating spot on the substrate allows for 'writing' on the surface, with potential applications in the bottom-up fabrication of electronic devices like solar panels and OLED displays. We study the feasibility and window of opportunity of this technique by computational modeling. We first model the control of the temperature by various illumination protocols, and then model and simulate the nucleation and growth of spatially localized spots, as well as lines, of deposited material given an inhomogeneous temperature profile. We show that the temperature profile can direct substrate deposition and control the connectivity and size of the pattern deposited on the substrate.

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In situ studies of nucleation mechanisms during ALD of platinum-group metals

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Selective growth relies on differences in nucleation delay on the growth vs. non-growth area, and often involves an activation or deactivation step to enhance or block the nucleation. Therefore, an in-depth understanding of the nucleation mechanisms of ALD processes is required. This talk will discuss the nucleation of Pt, Pd and Ru ALD, as investigated with synchrotron-based in situ X-ray fluorescence (XRF) and grazing incidence small angle X-ray scattering (GISAXS). These techniques provide the metal loading, and the dimensions and spacing of the nuclei during the initial island growth mode. The nature of the surface chemical groups influencing the initial growth was further investigated in a vacuum cluster tool that allows for 'in vacuo' X-ray photoelectron spectroscopy (XPS) analysis.

For Pt ALD with $Me_3(MeCp)Pt$ and Pd ALD with $Pd(hfac)_2$ on SiO_2, we show that the choice of reactant (O_2 gas and various plasmas) has a clear impact on the initial nucleation density and on the extent of surface diffusion processes taking place during nucleation and growth. For Pt ALD with O_2 gas, the morphology during the 3D growth mode is largely governed by atom and cluster surface diffusion [1], while diffusion phenomena are suppressed during N_2 plasma-based ALD yielding smaller nuclei. In the case of Pd ALD, the highest areal density of nuclei is obtained for a three-step process that uses H_2 plasma followed by O_2 plasma, explained by the cleaning role of O radicals towards poisoning hfac ligands on the SiO_2 surface [2]. Removal of the site-blocking species can also be achieved by introducing exposures to TMA [3] or RuO_4, providing ways to enhance Pd nucleation.

For Ru ALD with RuO_4 and H_2, the strong oxidative nature of the RuO_4 precursor offers routes to selective ALD of Ru on H-terminated Si vs. SiO_2 [4]. RuO_4 can oxidize the Si-H surface, leading to immediate Ru deposition, while growth is inhibited on SiO_2. The growth on SiO_2 can be enhanced by exposing the surface to TMA, creating a methyl-terminated surface that becomes reactive towards RuO_4. Finally, an effective passivation strategy for RuO_4-based ALD will be introduced based on the use of patterned polymer films.

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Studies Toward Highly Selective Cobalt Metal ALD on Copper Features for Heterogeneous Chiplet Integration

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The continuous miniaturization of electronic devices necessitates the development of novel high-performance materials, processes, and integrated circuit architectures. Heterogenous chiplet-based architectures can provide design efficiency and electrical performance benefits through the three-dimensional integration of small modular chiplets. Such applications will require precise film growth for complex bonding in intricate architectures. Atomic layer deposition (ALD) provides self-limiting conformal thin film growth with sub-nanometer thickness control even in high aspect ratio features and on substrate pads with variable diameters and pitches. In this work, a novel thermal ALD process was developed affording inherently selective growth of low-resistivity cobalt (Co) metal thin films on copper (Cu) and ruthenium (Ru) substrates, with no film growth occurring on other metal, insulator, and ceramic substrates. Test beds containing µm-scale Cu patterns on silicon nitride (Si_3N_4) substrates were used to further demonstrate the selective Co depositions. Substrate selectivity ratios of >100:1 and ~30:1 Cu:Si_3N_4 were achieved when depositing <30 nm and >60 nm Co thin film thicknesses on Cu, respectively. The Co ALD process described herein is to be employed and characterized in further packaging application studies to fuse together Cu pads separated by <200 nm air gaps achieving electrical conductivity through them. These studies display the potential of this ALD process to be used toward simply and selectively depositing Co to bond Cu-Cu interconnects in chiplet integration applications.

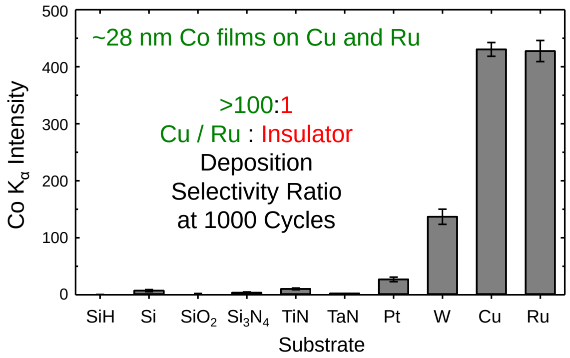

Figure 1 X-ray fluorescence (XRF) data displaying the inherent selectivity of the Co ALD process.

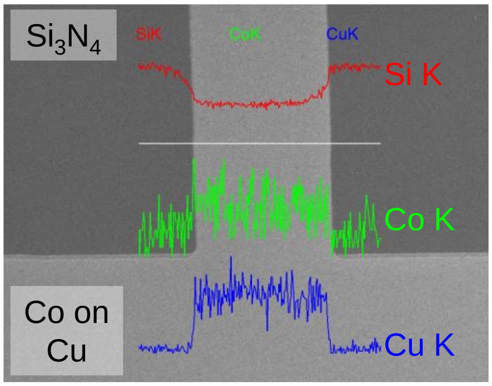

Figure 2 Energy-dispersive x-ray spectroscopy (EDS) scan lines displaying selective Co deposition on a 10 µm wide Cu strip on a Si_3N_4 substrate.

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Inhibitor-Free Nucleation Inhibition of ALD Titanium Nitride on Silicon Dioxide

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Area-selective atomic layer deposition (AS-ALD) is a potentially useful, bottom-up patterning and material manipulation technique for the nanoscale. Of particular interest in industry is the AS-ALD of titanium nitride (TiN). The conductive, superconductive, and thermodynamic properties of this material can be exploited for a variety of applications. High quality, thermal ALD of TiN is typically deposited using titanium tetrachloride ($TiCl_4$) and ammonia (NH_3) as precursors, at a temperature around 400°C. The ability to deposit this material thermally, rather than relying on plasmas that are limited by radical lifetime, allows for more conformal coating inside aggressively-scaled, high aspect ratio structures. Coupling this characteristic with the ability to deposit TiN on selective areas will have a significant impact on device scaling, throughput, and process complexity. Unfortunately, the relatively high deposition temperature may negate the use of most self-assembled monolayers (SAMs) and small molecule inhibitors (SMIs). An alternative path for AS-ALD of this material is via the intrinsic nucleation chemistry associated with bulk solid surfaces. For instance, functionalized and pristine carbon surfaces have previously been used as inhibiting materials for this and other ALD chemistries, with varying degrees of success.[1,2,3] An overview of these results will be briefly presented, followed by new results of TiN nucleation inhibition on functionalized silicon dioxide (SiO_2) surfaces. Ubiquitous in CMOS fabrication, the use of SiO_2 as an inhibiting material allows for enhanced process compatibility within a foundry setting, both in the front-end (FEOL) and the back-end (BEOL) of line stages. Results are achieved on the wafer-scale, using 200 mm tooling with processes that can easily be adapted for 300 mm. The functionalization process is single-step without correction, where cyclical inhibition treatments or etching steps are not used. Inhibition dependence on the functionalization processing parameters will be discussed. Using 500 cycles (20 nm) of ALD TiN as a testbed, this process allows for over 99% inhibition of the SiO_2 surface. The effect of this process on other material surfaces will also be explored, with the aim of identifying material sets that allow for AS-ALD with high quantitative selectivity.

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Selective Area Deposition of Semiconducting Carbon Nanotubes Using Chemical and Topographical Features

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Semiconducting carbon nanotubes (CNTs) have incredible promise for next-generation high-speed, low-power logic circuits. Recent advances have made it possible to purify highly monodisperse CNTs with atomically identical structures using polymer wrappers that differentiate among CNTs in solution, overcoming a historical roadblock. The remaining challenge is in selectively depositing and organizing CNTs into dense parallel arrays on substrates. We report the combination of chemical contrast patterns, topography, and pre-alignment of s-CNTs via shear to achieve selective-area deposition of aligned arrays of CNTs. Alternate stripes of surfaces favorable and unfavorable to s-CNT adsorption were patterned with widths varying from 2000 nm down to 100 nm. When the chemical and topographical contrast patterns are reduced to less than the width of individual nanotubes (≤ 500 nm), confinement effects become dominant enabling the selective-area deposition of much more tightly aligned CNTs (~7 degrees). At a trench width of 100 nm, we demonstrate the lowest standard deviation in alignment degree of 7.6 ± 0.3° at a deposition shear rate of 4,600 s^{-1}, while maintaining an individualized s-CNT density > 30 CNTs μm^{-1}. Chemical contrast alone enables selective area deposition but chemical contrast in addition to topography enables more effective selective area deposition and stronger confinement effects, with the advantage of removal of nanotubes deposited in spurious areas via selective lift-off of the topographic features. These findings provide a methodology that is inherently scalable, and a means to deposit spatially selective, aligned s-CNT arrays for next-generation semiconducting devices.

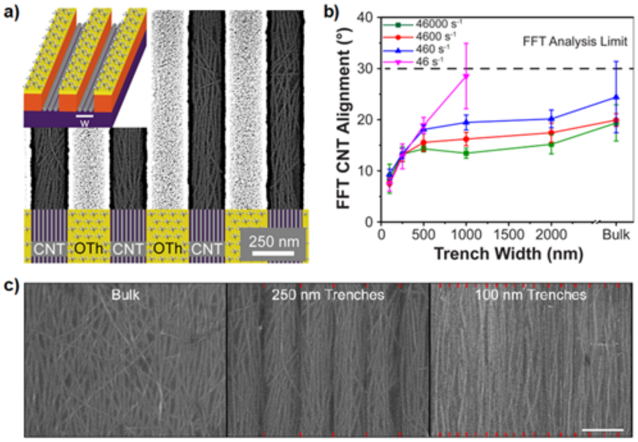

Fig. 1: a) SEM image of s-CNT arrays in 250 nm wide trenches. (b) 2D FFT analysis of alignment as a function of both trench width and shear rate. (c)SEM images at constant deposition shear rate for bulk, 250 nm, and 100 nm wide trenches bar is 250 nm and same for all images.

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Surface Engineering for Selective Deposition on Patterned C/SiO_2 Materials

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Production challenges have become increasingly prominent in the semiconductor industry due to interest in manufacturing smaller chips for next-generation devices. Area-selective atomic layer deposition (AS-ALD) is a bottom-up thin film deposition technique that allows for the direct growth of material on a specific area of a substrate (i.e., growth region). The non-growth region can be selectively functionalized with surface inhibitors (e.g., small molecule inhibitors and self-assembled monolayers (SAMs)) to prevent growth. Through chemical binding to the non-growth surface, SAMs have proven effective in protecting this region from ALD growth. The materials of focus for this project include three carbon-based materials synthesized via plasma-enhanced chemical vapor deposition (PE-CVD), photoresist (PR) and spin-on carbon. The challenging carbon/SiO_2 system, of interest because of its role in self-aligned multiple patterning capabilities, is used to show how self-assembled monolayers can be applied for ALD processes to direct growth. The carbon materials serve as the desired growth regions, whereas SiO_2 is the non-growth region. Our studies show moderate selectivity for both aluminum oxide and hafnium oxide ALD (precursors of trimethylaluminum/water and tetrakis(dimethylamido)-hafnium/water are used, respectively) when octadecyltrimethoxysilane (OTMS) SAMs are used to block SiO_2 but not C. For instance, after 25 cycles of HfO_2 ALD, a selectivity of 71% is achieved for deposition on the spin-on carbon material. The selectivities for both PR and PE-CVD carbon substrates reach around 50% after 25 cycles of HfO_2 ALD, and results suggest that surface species in those two types of carbon substrates may lead to some undesired uptake of the SAM. Optimized SAM formation on the SiO_2 substrate is being studied to help provide better selectivities on the carbon growth regions to achieve area selective deposition of dielectric on C/SiO_2 patterns.

Area Selective Deposition of HfO_2 through ALD and Selective ALE Supercycles

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ASD combines the chemical information of the surface and deposition material to promote growth on one surface while impeding growth on another to enable reliable patterning for nanoscale devices and complex architectures.

In this work, ASD is accomplished by incorporating atomic layer etching (ALE) steps into atomic layer deposition (ALD) steps to suppress unwanted growth. HfO_2 ALD is performed using TDMAH and H_2O, while HfO_2 ALE is performed using WF_6 and BCl_3, a novel etch system. We evaluated HfO_2 ALD and ALE on various surfaces, including hydroxyl-terminated Si (Si-OH), hydrogen terminated Si (Si-H), thermal silicon dioxide (SiO_2), Ru with native oxide (RuO_x), Co with native oxide (CoO_x), and low-k material (SiCOH). The growth on each surface was studied using *ex-situ* spectroscopic ellipsometry and *ex-situ* x-ray photoelectron spectroscopy.

Previously, our group reported a supercycled ALD/ALE process for TiO_2 ASD on SiO_2 vs Si-H due to an ALD nucleation delay on Si-H. This work focuses on an ALD/ALE process for HfO_2 at 275°C, but utilizes surface selective ALE. Figure 1 shows the HfO_2 film thickness on each starting substrate as a function of the number of supercycles. Film growth behavior on RuO_x and SiCOH substrates with ALD/ALE supercycling behaves similarly to the behavior on Si-OH and SiO_2 substrates. While the ALD growth rate is consistent on all surfaces studied here, the ALE etch rate is surface dependent and changes with HfO_2 film thickness. XPS confirms HfO_2 ASD on CoO_x and Si-H vs Si-OH and SiO_2.

These results demonstrate a new system for HfO_2 ALE as well as HfO_2 selective deposition through integrated ALD/ALE. We believe these findings provide valuable insight into selective deposition processes using surface selective ALE for bottom-up nanofabrication.

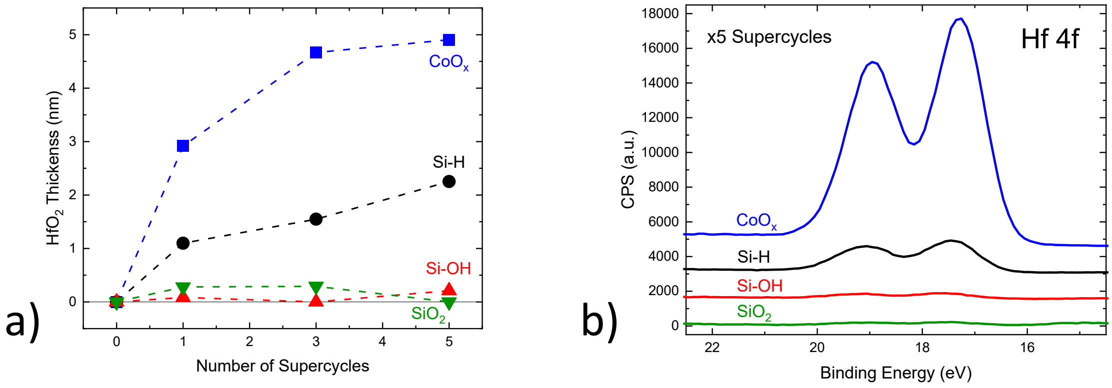

Figure 1. a) HfO_2 film thickness from ellipsometry measurements as a function of supercycle on Si-OH, Si-H, SiO_2, and CoO_x substrates deposited at 275°C. Each supercycle consists of 20 ALD cycles followed by 20 ALE cycles. b) XPS Hf 4f high resolution scans of HfO_2 films on Si-OH, Si-H, SiO_2, and CoO_x substrates after 5 supercycles showing elevated Hf content on CoO_x and Si-H substrates vs Si-OH or SiO_2.

Selective Deposition of Dielectric on Dielectric using Low Temperature ALD SiO_2 from a Halogen-free Precursor

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Selective deposition of dielectric on dielectric (DoD) requires minimal deposition of a dielectric material on a metal surface, such as Cu or Co, while allowing growth of a dielectric film on dielectric surface, such as SiO_2 or SiOC low k films. Passivation of the metal surface with a hydrophobic self-assembled monolayer (SAM) can be utilized to inhibit deposition on the metal surface, but this method limits the dielectric deposition temperature to less than 250°C and does not work well with a strong oxidizer due to potential damages to the SAM layer. However, it is very challenging to deposit a SiO_2-based low-k dielectric at low temperatures without using ozone or O_2 plasma.

It has long been known that SiO_2 can be deposited at low temperatures using certain silicon halides and water in presence of a catalyst such as ammonia or amines [1]. Non-halogenated silicon precursors are more desirable to avoid halide contamination and to achieve better electrical properties. In this work, we have deposited SiO_2 by ALD using a halogen-free precursor FX-Si and co-trapped water and trimethylamine as co-reactants. The growth rate is strongly temperature dependent as shown in Figure 1. Furthermore, we have demonstrated good selectivity of this ALD SiO_2 process at 150°C against Cu surface passivated with a vapor-phase thiol SAM up to about 100 Å of SiO_2 on the dielectric as shown in Figure 2.

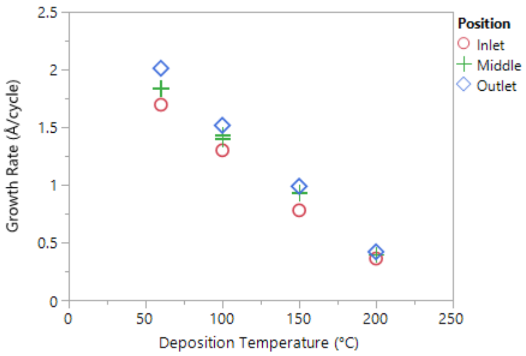

Figure 1 Temperature Dependence of SiO_2 Growth Rate on Native Oxide

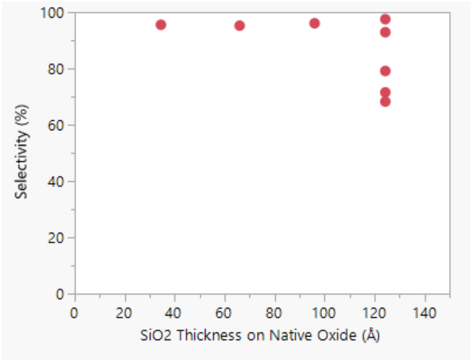

Figure 2 Selectivity of SiO_2 on Cu with a Thiol SAM Inhibitor at 150°C

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Understanding the Breakdown of Self-Assembled Monolayer Inhibitors in Area-Selective Atomic Layer Deposition

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Self-assembled monolayers (SAMs) have been widely used as the inhibitors to block a variety of metal and metal oxide ALD processes. However, as the selective deposition process continues, selectivity between growth and nongrowth surfaces will gradually be lost due to the nucleation of ALD on nongrowth surfaces protected by SAMs. Hence, investigating how the SAM inhibitors break down during ALD is essential to better understand the AS-ALD process and to develop a more robust AS-ALD system. In this work, octadecyltrichlorosilane (ODTS) on native SiO_2-covered Si is chosen as a model SAM system and Al_2O_3 and ZnO ALD selected as model ALD systems to study the changes in crystallinity and structure, such as thickness and roughness, of SAM inhibitors after ALD. We show that the ODTS SAM remains relatively undamaged until a significant amount of ALD breakthrough nucleation occurs. We further show that the undesired ALD materials form different morphologies on the top of SAM surfaces. ZnO ALD forms dispersed nanoparticles, while a relatively continuous film is deposited on the SAM for Al_2O_3 ALD. In addition, ODTS SAM on a different substrate, single crystal sapphire, is investigated. Similar results are also observed on ODTS-sapphire samples, suggesting that these effects are substrate independent. This study provides a systematic understanding of the breakdown of ODTS SAMs during AS-ALD processes and describes how ALD nucleates on SAM surfaces, insights that will be instrumental in developing more robust AS-ALD systems for future research.

Area-Selective Deposition of Ruthenium on Copper/Dielectric Surfaces for Nano Interconnect Applications

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Multiple level of metal interconnects at the back end of line (BEOL) in integrated circuits (ICs) are interconnected vertically through vias. As the technology node is moving beyond the 2nm node, conventional copper vias surrounded by a barrier layer can offer very high resistance along with the risk of electromigration. [1] In this work, Metal on Metal (MoM) Area-selective deposition (ASD) is investigated for hybrid interconnect applications to reduce this via resistance by a barrierless bottom-up via fill with alternative metals like Ru. We found that Ru ASD on low-k dielectric/Ru nanopatterns by Ru Chemical Vapor Deposition (CVD, Carbonyl Alkyl Cyclohexadiene Ru) with NH_3 at 150˚C gives good yields. However, for Ru ASD with the same CVD process conditions with Cu as a growth surface, we observe more Ru nanoparticles on the low-k dielectric making selectivity more challenging. To better understand Ru ASD with Cu as a growth surface, we study the surface dependence of Ru CVD on blanket low-k dielectric and Cu wafers treated with and without Dimethylamino-trimethylsilane (DMA-TMS). DMA-TMS is known for improving selectivity by inhibiting deposition on dielectric non-growth surfaces, which is in line with our result.[2] Fig.1 shows the growth curves for Ru CVD for various process conditions (150˚C with NH_3 as co-reagent, 150˚C with H_2 as co-reagent, 250˚C with H_2 as co-reagent). The selectivity for Ru CVD is highly dependent on the bottom metal and co-reagent. H_2-based Ru CVD gives the best selectivity for Cu growth surfaces, whereas NH_3 based Ru CVD gives the best selectivity for Ru and TiN growth surfaces. And surprisingly, the selectivity for Cu/low-k dielectric for Ru CVD with NH_3 as a co-reagent is Metal on Dielectric (MoD) instead. This selectivity found on blanket wafers study can be further improved by implementing it on nanoscale patterns [2]. The insights from the study of surface dependence of Ru CVD for different process conditions and co-reagents can not only pave the path for low resistive vias but can be applied beyond metal interconnect application.

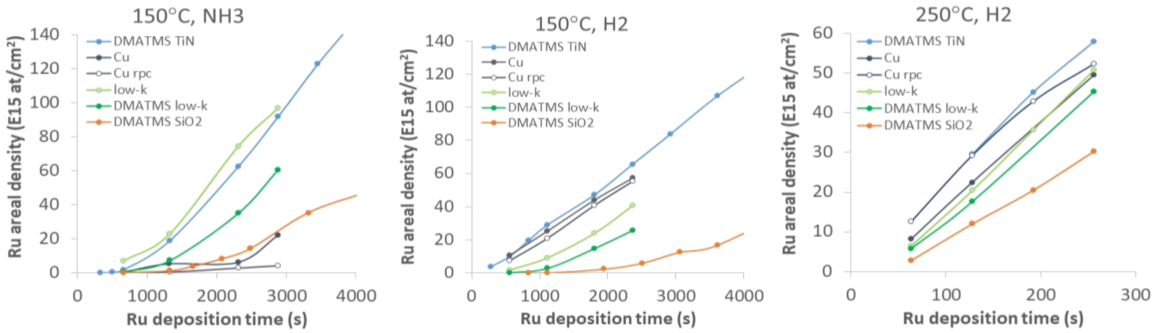

Figure 1 Ru growth curves on different surfaces and with different CVD co-reagent conditions (a) 150˚C, NH_3 (b) 150˚C, H_2 (c) 250˚C, H_2

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[1] https://www.imec-int.com/en/articles/view-logic-technology-roadmap

[2] F. Grillo and J. Soethoudt et al, Chem. Mater. 2020, 32, 22, 9560–9572

Low Temperature Area Selective Deposition via Simultaneous Deposition and Etching

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Downward scaling of semiconductor devices imposes restrictions on the tolerance for feature misalignment. Stochastic lithographic patterning methods introduce significant pattern variability, which will limit their application in industrial-scale processing in the coming decades. Alternatively, bottom-up patterning methods take advantage of differences in surface chemistries to direct precursors to desired regions of a substrate, allowing for selective deposition. Understanding the nuances of area-selective deposition, a bottom-up patterning method, will be crucial in the development of efficient processing. Our lab has demonstrated selective W deposition on Si-H by etching neighboring TiO_2 features [1]. Because W-ALD and TiO_2-CVE share $WF_{6(g)}$ as a precursor and use similar processing temperatures, the two reactions can be combined into a single processing step (Fig. 1). This results in selective W growth on Si-H regions because TiO_2 features consume the deposition precursor, thereby avoiding undesired nucleation. Herein, we investigate selectivity loss mechanisms during simultaneous deposition and etching by sequentially dosing SiH_4 and WF_6 gases onto 100-nm thick TiO_2/Si-H lines (Fig. 2a). We find that the extent of selective W-ALD is dictated by the sacrificial etching kinetics. When the etching rate is too fast at 280°C (Fig. 2b), the selectivity of W-ALD is poor. SEM imaging shows that in this case, fast etching results in a rough TiO_2 feature due to the formation of a porous WO_xF_y/TiO_yF_z layer. This layer prevents efficient SiH_4 purging and allows parasitic W growth on TiO_2. STEM EDS mapping reveals that the feature profile evolution of TiO_2 can be smoothed at lower processing temperatures. For example, at 250°C (Fig. 2c) selectivity of W deposition is significantly improved.

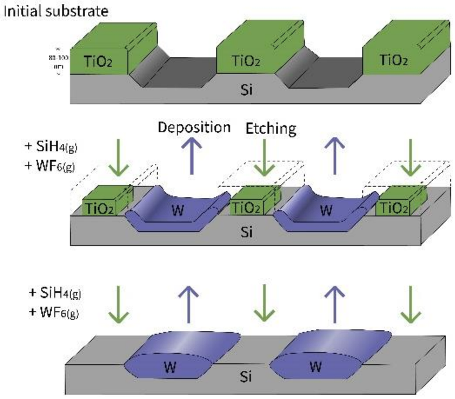

Figure 1 Schematic of ASD mechanism

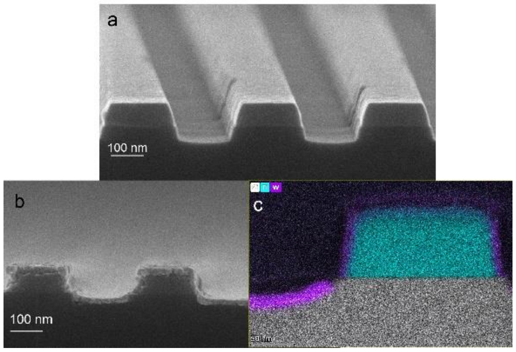

Figure 2 (a) initial substrate (b) 280°C, (c) 250°C

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[1] S.K. Song, et al., ACS Nano. **15**, 7(2021).

Mechanisms of precursor blocking by aniline inhibitor molecules during area-selective ALD of TaN

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Aniline has been established to be a promising inhibitor molecule for enabling area-selective atomic layer deposition (ALD) with metal/dielectric selectivity.[1] As compared to other small molecule inhibitors (SMIs), much thicker films can be deposited selectively, which raises the question of what makes aniline a good inhibitor. In this contribution, precursor blocking using aniline as the inhibitor is studied on a mechanistic level. In addition, our toolbox for area-selective ALD is expanded to enable the selective deposition of TaN.

Density functional theory (DFT) calculations show that that aniline adsorbs either with the amine group to the surface through a δ-bond or with the phenyl ring through a π-bond (Figure 1a). Both adsorption configurations bind sufficiently strong to the surface such that inhibitor desorption does not play a role. Furthermore, even the more weakly bonded δ-configuration is inert toward incoming precursor molecules, and therefore both adsorption configurations of aniline can block precursor adsorption. Hence aniline provides a stable and effective physical barrier for precursor adsorption.

An area-selective TaN ALD process was developed using aniline as inhibitor, ter-butylimidotris(dimethylamino)tantalum (TBTDMT) as the precursor, and an Ar-H_2 plasma as the co-reactant. As shown in Figure 1b, ~2 nm TaN can be deposited selectively with a selectivity of 90% on SiO_2, considering Ru as the non-growth area. These and other experimental results will be presented to provide insight into the mechanisms of precursor blocking, thereby contributing to the identification of promising inhibitor molecules for future development of area-selective ALD processes.

[1] Merkx *et al.*, *Chem. Matter* **32**, 7788 (2020).

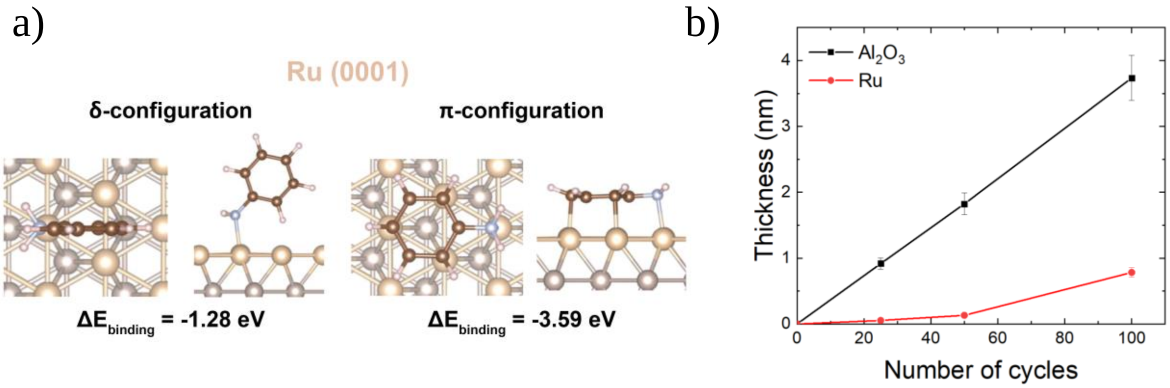

Figure 1: (a) Favorable adsorption configurations for aniline on Ru as found by DFT calculations. (b) TaN nucleation curves as measured by XPS on Al_2O_3 and Ru starting surfaces. The thickness was based on XPS and ellipsometry results.

Area-Selective Atomic Layer Deposition of Palladium via Area Activation

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Atomic layer deposition (ALD) of palladium is commonly carried out using Pd(hfac)$_2$ and a reducing coreactant such as formalin, H_2 or hydrogen plasma. When formalin is used, palladium nucleation is inhibited on oxide substrates due to surface site blocking by formalin [1]. On the other hand, Pd can be successfully grown on various substrates at as low as 80 °C using a hydrogen plasma [2]. Palladium can also be grown at low temperatures using H_2 gas; however, the substrate must enable the surface dissociation of H_2 to promote nucleation [3]. In this work, a route to low temperature deposition of Pd with H_2 on oxide surfaces (SiO_2) is investigated using a (<2 nm) seed layer. First ASALD is utilized to prepattern a transition metal oxide (NiO) and subsequent low-temperature (<175 °C) reduction with atomic hydrogen yields a metallic surface capable of H_2 dissociation, thus promoting Pd deposition.

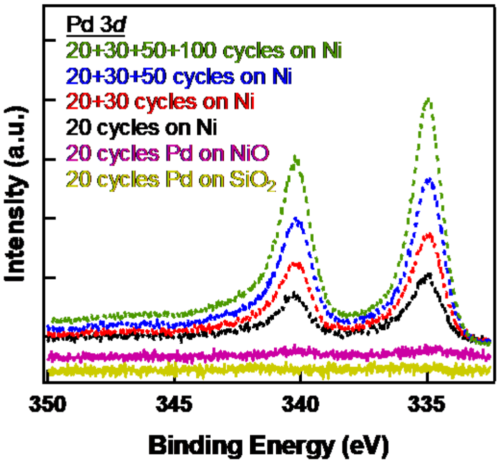

Figure 1: XP spectra of Pd deposition at 125 °C on Ni (black, red, blue, green), NiO (magenta) and SiO_2 (yellow)

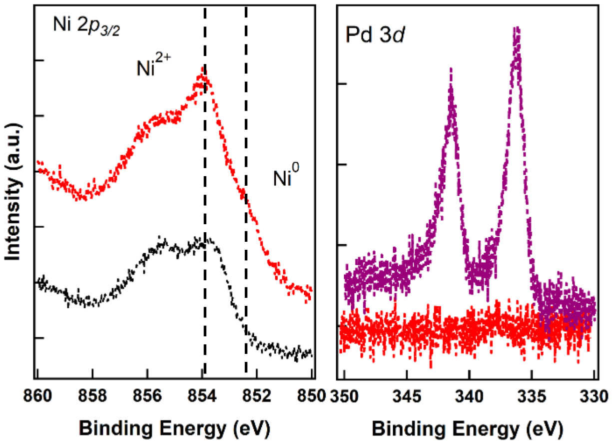

Figure 2: XP spectra of Ni 2$p_{3/2}$ (left) and Pd (right) of the starting NiO surface (black), after H atom (partial) reduction (red) and after 20 cycles Pd ALD at 125 °C (purple)

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[3] J. J. Senkevich et. al. Chem. Vap. Deposition. **2003**, 9, No. 5

Area Selective Atomic Layer Deposition of Ruthenium using Ru(EtCp)$_2$ Inhibitor

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Since the dimensions of electronic devices are required to be reduced to maintain the device performance, area-selective deposition (ASD) has shown great potential to overcome the current fabrication challenges, such as pattern transfer in 3D structures and simplifying the processes by excluding lithography and etching. In most of the ASD researches, it has been commonly employed that an inhibitor which has a chemoselectivity toward the precursor and reactant in the following atomic layer deposition (ALD) process deactivates a specific surface. If the inhibitor is properly removed after ASD, however, contamination from the inhibitors could degrade the final film property. Thus, an homogeneous inhibitor to the precursor with clean removal is required. In this work, we introduced ASD Ru using a homogeneous Ru inhibitor, bis-(ethylcyclopentadienyl)ruthenium (Ru(EtCp)$_2$). Because the Ru(EtCp)$_2$ inhibitor is originally used as a Ru precursor for Ru ALD with O_2 counter reactant, dicarbonyl-bis(5-methyl-2,4-hexanediketonato) Ru(II) ("Carish") and H_2O were selected as Ru precursor and counter reactant, respectively, for chemoselectivity. The density functional theory (DFT) calculation results showed that the Ru(EtCp)$_2$ does not chemically react with Carish, and the Monte Carlo simulation showed physical steric hindrance effects of Ru(EtCp)$_2$ toward Carish adsorption. Ru(EtCp)$_2$ can block the growth of ALD Ru up to 200 cycles with high selectivity over 90 %. ASD with homogeneous inhibitors proposed in this study could be applied for various unit processes in semiconductor fabrication due to its high compatibility.

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Integrated Selective Deposition of SiCOH on SiCOH for Fully Aligned Via structure in interconnects.

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For interconnect levels below 36nm pitch, the lithographic critical dimension (CD) uniformity/overlay variations require new integration schemes to maintain 'minimum' insulator spacing between via and line below. Fully aligned via (FAV) integration scheme is demonstrated at 36 nm metal pitch with extendibility to the 3nm node and beyond [1]. Materials with a higher dielectric constant metal oxide such as selective AlOx (k~8) have been used for FAV structure in recent work [2,3]. In this paper, we demonstrate selective deposition of low k SiCOH on top of SiCOH at 32 nm pitch to form FAV) structure. The selective process involves multiple steps – a.)surface treatment b.)selective Self assembled Molecules (SAM) bonding to Co/Cu metal surface, c.)deposition of partial selective CVD SiCOH & UV Cure, and d.)removal of overgrown SiCOH at temperature below 300°C (Figure 1). Selective SiCOH thickness up to 7 nm is demonstrated on top SiCOH over Co capped Cu-SiCOH patterned structures across varying pitches/spacings (Figures 1-2). FAV structure electrical yields (>70%) were obtained on 32/36 nm pitch structures post selective deposition processing.

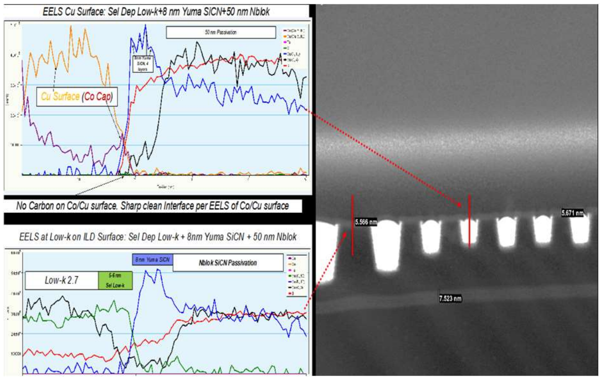

Figure 1- Selective deposition of SiCOH : STEM and EELS of sub-40nm FAV structure

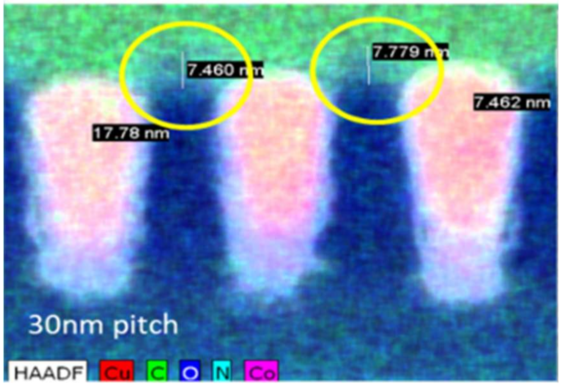

Figure 2 – EDX/EELS spectra of 7-8 nm Selective SiCOH on FAV structure

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[1] B. D. Briggs et al., "Fully aligned via integration for extendibility of interconnects to beyond the 7 nm node," in IEDM Tech. Dig., Dec. 2017 pp. 338-341

[2] S. Van Nguyen et al., "Selective deposition of AlOx for Fully Aligned Via in nano Cu interconnects," in Proc. IEEE Int. Interconnect Technol. Conf., paper S7-4, Jul. 2021 Kyoto, Japan

[3] H.P. Chen, et al. "Fully Self-Aligned Via Integration for Interconnect Scaling Beyond 3nm Node", International Electron Device Meeting 2021, paper 22.1, San Francisco, CA, USA

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Dual-Material Area-Selective Depositions for Advanced Nanopatterning: Poly(3,4-ethylenedioxythiophene) (PEDOT) and Tungsten (W) on Si-H/SiO_2 Substrates

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With the advent of sub-10 nm technology nodes, area-selective deposition (ASD) has received considerable interest as an efficient vapor-phase "bottom-up" technique owing to its self-aligned nature. [1] However, most reported ASDs have dealt with individual dielectric or metal depositions despite the recent notable advances. [2] Therefore, it is necessary to develop a process route that integrates multiple ASD processes for more efficient nanofabrication. In this study, we demonstrated dual-material ASDs by integrating two separate intrinsic ASD processes of: 1) poly(3,4-ethylenedioxythiophene) (PEDOT) on SiO_2 (not Si-H) [3] and 2) tungsten (W) on Si-H (not SiO_2) [4]. Since the surface chemistry strongly influences the initial nucleation stage, the process sequence must be considered to maintain selectivity at each ASD step (Figure 1). In this vein, we deposited PEDOT first on SiO_2 (vs Si-H) at 125 ^{o}C using 3,4-ethylenedioxythiophene (EDOT) as a monomer and antimony pentachloride ($SbCl_5$) as a volatile liquid oxidant *via* oxidative chemical vapor deposition (oCVD). Subsequently, W deposition was carried out on Si-H (vs PEDOT) at 220 ^{o}C using sequential exposure of silane (SiH_4) and tungsten hexafluoride (WF_6) *via* atomic layer deposition (ALD). With the determined reaction sequence, we successfully extended our dual-material ASDs to nanoscale Si-H/SiO_2 patterend substrates (Figure 2). Overall, we anticipate our study to pave the way for more efficient bottom-up nanopatterning.

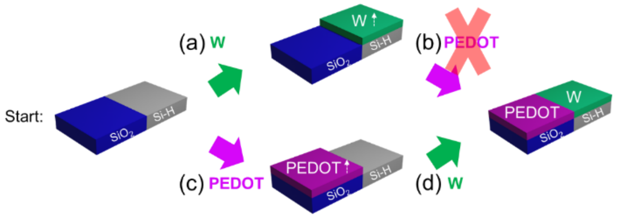

Figure 1. Schematic of the possible sequences in achieving dual-material orthogonal ASD of PEDOT on SiO_2 and W on Si-H.

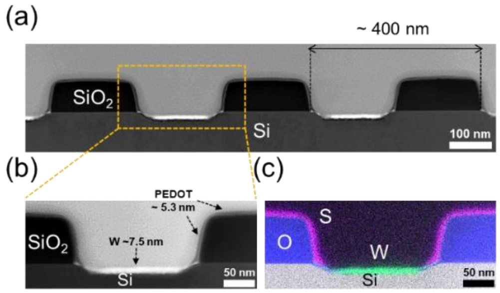

Figure 2. Cross-Sectional STEM-EDX images of PEDOT and W ASDs on topographical Si-H/SiO_2 patterns with ~ 400 nm full-pitch.

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[1] R.; Clark, K. Tapily,; K. -H. Yu,; T.; Hakamata, S. Consiglio,; D. O'Meara,; C. Wajda,; J. Smith,; G. Leusink, APL Materials. **6**, 058203 (2018)
[2] G. N. Parsons,; R. Clark, Chem. Mater. **32**, 4920-4953 (2020)
[3] J. S. Kim,; G. N. Parsons, Chem. Mater. **33**, 9221-9230 (2021)
[4] B. Kalanyan,; P. C. Lemaire, Chem Mater. **28**, 117-126 (2016)

ASD of Conjugated Polymers: Direct Comparison of Selectivity via CVD vs MLD

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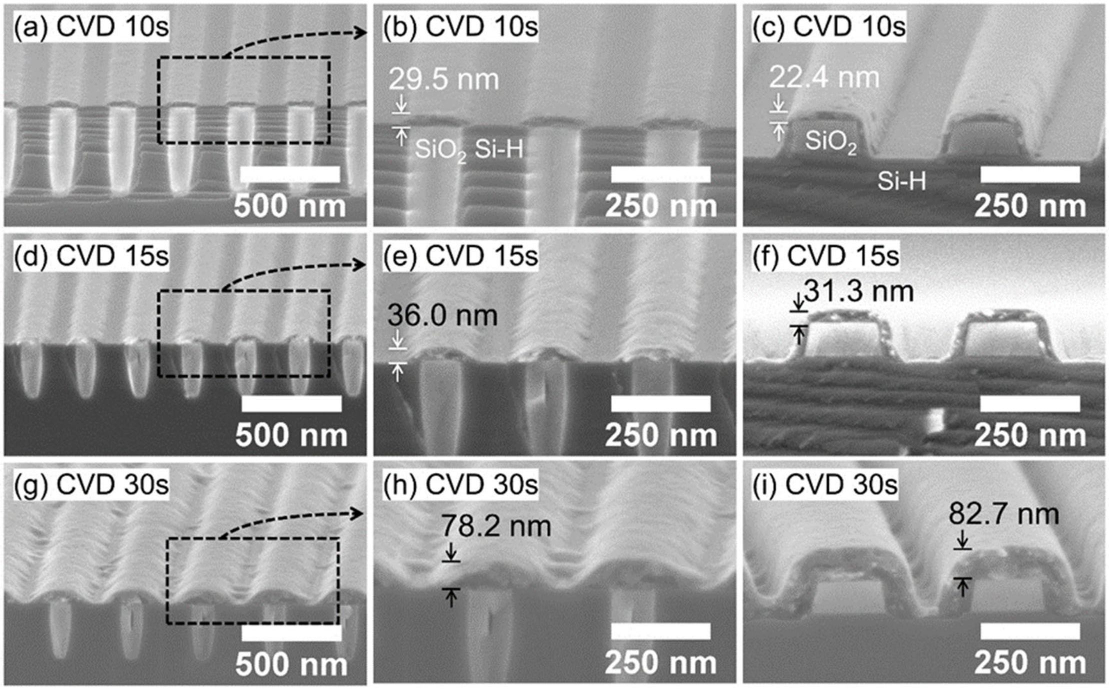
Area-selective deposition (ASD) of polymers is expected to be useful for self-aligned patterning of nucleation inhibitors, sacrificial layers, and air-gap materials during future bottom-up nanoscale materials fabrication. This work describes a simple, rapid, and effective method to achieve inherent ASD of poly(3,4-ethylenedioxythiophene) (PEDOT) on SiO_2 vs hydrogen terminated silicon (Si-H) substrates via molecular layer deposition (MLD) and chemical vapor deposition (CVD) using 3,4-ethylenedioxythiophene (EDOT) as a reactive monomer and $SbCl_5$ as an oxidant for polymerization. Film thickness measured by spectroscopic ellipsometry (SE) indicates the MLD process can obtain ~35 nm with selectivity of 90%, *i.e.* $t_{S=0.90} \approx 35$ nm, which is better than many other reports of inorganic or organic material ASD. Furthermore, we show that under CVD conditions, the selectivity is further improved *i.e.* $t_{S=0.90} \approx 55.4$ nm, and that CVD can achieve ASD at an overall rate more than 100 X faster than MLD for the same ASD thickness, allowing 30 nm of ASD to be achieved in less than 10 seconds of process time. The selective growth of PEDOT on SiO_2 vs. Si-H is ascribed to localized reduction of the $SbCl_5$ on the Si-H surface, thereby inhibiting EDOT polymerization in that region. The high selectivity allows us to observe and analyze lateral "mushroom" overgrowth and compare ASD growth rates on blanket vs patterned wafers. Overall, results suggest that CVD may have advantages over MLD or ALD for ASD.



J.-S. Kim and G.N. Parsons Chem. Mater. 33, 9221−9230 (2021)

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Area-selective etching of polymers, a novel approach to self-aligned patterning of thin films

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Area-selective thin film deposition processes have been actively developed and studied for making semiconductor devices because of the increasing problems met with lithography techniques at feature sizes in the sub-10 nm range. Here, an entirely new approach is taken to self-aligned thin-film patterning: area-selective gas-phase etching of polymers. In these etching processes the selectivity arises from the materials underneath the polymer layers. Both O_2 and H_2 can be used as an etchant gas. Etching gas molecules diffuse through the polymer film, and if they meet a catalytic surface underneath, the molecules become dissociated into their respective atoms, which then readily react with the polymer etching it away. On noncatalytic surfaces, the polymer film remains. As the first demonstration, polyimide and poly(methyl methacrylate) (PMMA) were selectively oxidatively removed at 300 °C from Pt and Ru, while on SiO_2 they stayed (Fig. 1). CeO_2 also showed a clear catalytic effect for the oxidative removal of PMMA. In H_2, the most active surfaces catalyzing the hydrogenolysis of PMMA were Cu and Ti.

When innovatively combined with area-selective thin film deposition or, for example, lift-off patterning processes, self-aligned etching of polymers opens entirely new possibilities for the fabrication of the most advanced and challenging semiconductor devices. An example is given where the area-selective etching of polyimide from Pt was followed by area-selective ALD of iridium using the patterned polymer as a growth-inhibiting layer on SiO_2, eventually resulting in dual side-by-side self-aligned formation of metal-on-metal and insulator (polymer)-on-insulator. A sharp edge between the two regions (Fig. 2) shows that there is no significant spillover effect from the catalytic to the noncatalytic areas. What is also important to emphasize is that, unlike area selective deposition, area-selective etching does not have to be even close to perfectly selective - it is enough that polymer remains on the noncatalytic surface and the remaining polymer can block the following growth.

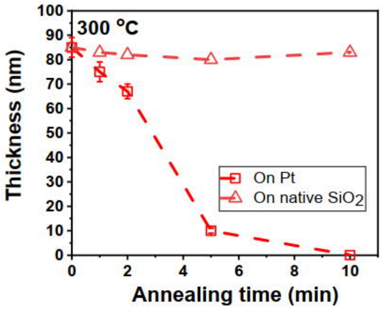

Figure 1 Etching of polyimide in air on Pt vs. native SiO_2.

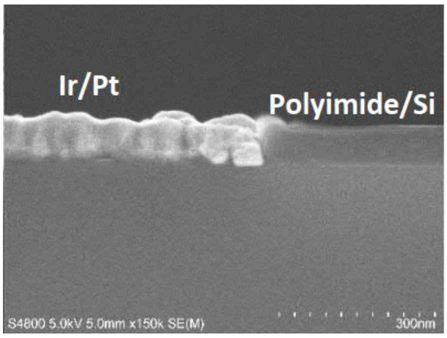

Figure 2 SEM cross section of a line edge made by area-selective etching of polyimide followed by AS-ALD of Ir.

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[1] C. Zhang, M. Ritala and M. Leskelä, Coatings **11**, 1124 (2021).

Area-Selective Atomic Layer Deposition Using Nitrogenous Aromatic Small Molecule Inhibitors

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With continued semiconductor device downscaling, the current top-down approach to nanopatterning is beginning to face challenges in pattern resolution and alignment. One promising alternative processing technique being explored is area-selective atomic layer deposition (AS-ALD), due to the angstrom-level thickness control and high conformality that the technique provides. A novel means of facilitating AS-ALD on chemically distinct surfaces is by using small molecule inhibitors (SMIs) to deactivate one surface towards nucleation. There are two notable potential benefits of using SMIs compared to other AS-ALD techniques. SMIs can be vapor-phase delivered which can allow for regeneration of the inhibitor layer *in operando* – further prolonging the nucleation delay. Additionally, due to the relatively low steric bulk of SMIs, they could be used to facilitate AS-ALD in sub-10 nm, high aspect ratio features. Several types of SMIs have been studied including silanes, alkynes, β-diketonates, thiols, and aromatics; however, there are currently few investigations into a related series of SMIs to better understand how certain aspects of the SMI chemistry impact the selectivity achievable for a given process.

In this work, three distinct nitrogenous aromatic SMIs are used to facilitate the AS-ALD of a dielectric on a dielectric in the presence of a metal. The specific SMIs studied are pyrrole, aniline, and pyridine. The substrates of interest are SiO_2 as the dielectric and Cu as the metal. Several dielectric ALD chemistries are tested including trimethyl aluminum (TMA) and dimethyl aluminum isopropoxide (DMAI) for Al_2O_3 deposition, diethyl zinc for ZnO deposition, and tetrakis (dimethylamido) hafnium (TDMAHf) for HfO_2 deposition. Blocking results indicate that conventional precursors such as TMA and DEZ are difficult to block with these SMIs; however, DMAI has been successfully blocked by each SMI, in some cases for as high as 30 cycles – leading to nearly 100% selectivity for over 3 nm of Al_2O_3 deposition on SiO_2. The mechanisms by which selectivity is lost and by which the SMIs saturate the substrate are being investigated using x-ray photoelectron spectroscopy (XPS), infrared reflection absorption spectroscopy (IRRAS), and atomic force microscopy (AFM) in order to elucidate how the SMI chemistry determines the selectivity of the process.

Area-Selective Atomic Layer Deposition of $Ge_2Sb_2Te_5$ on nanopatterned substrate

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Atomic layer deposition (ALD) is one of the techniques that enable conformal deposition over complex three-dimensional (3D) structures with high aspect ratio. ALD has therefore gained attention for depositing phase change materials for memory device applications. $Ge_2Sb_2Te_5$ is a widely investigated phase change material, accompanied by a bottom electrode (TiN or W) and dielectric material (SiO_2) for isolation in the memory device. Area-selective deposition of $Ge_2Sb_2Te_5$ on the bottom electrode could greatly simplify the fabrication of these complex 3D devices. This work therefore aims to study area-selective deposition of $Ge_2Sb_2Te_5$ on TiN towards SiO_2 via ALD. The dimethylamino-trimethylsilane (DMA-TMS) surface pre-treatment was investigated, as this treatment selectively alters the SiO_2 surface properties and passivates the SiO_2 surface.[1] Alternating subcycles of GeTe and Sb_2Te_3 were used to deposit $Ge_2Sb_2Te_5$ using $GeCl_2$. $C_4H_8O_2$, $SbCl_3$ and $((CH_3)_3Si)_2Te$ as precursors. $Ge_2Sb_2Te_5$ growth occurred readily on blanket TiN substrates, and the DMA-TMS did not affect the growth behaviour. The growth-per-cycle was found to be 0.38 nm/cycle and the 2-2-5 composition of a $Ge_2Sb_2Te_5$ film of 20 nm was confirmed by Rutherford Backscattering Spectrometry (RBS) (figure 1). Next, nanopatterns comprising TiN areas and SiO_2 lines were used to deposit $Ge_2Sb_2Te_5$ with and without DMA-TMS pre-treatment (figure 1). The $Ge_2Sb_2Te_5$ deposition was conformal on nanopatterns having no treatment of DMA-TMS. In contrast, with the introduction of a DMA-TMS pre-treatment, $Ge_2Sb_2Te_5$ deposition occurred selectively on the TiN areas, while the SiO_2 lines were passivated. The scanning electron microscopy (SEM) images show no sidewall deposition on SiO_2. The deposited $Ge_2Sb_2Te_5$ on nanopatterns have 2-2-5 composition similar to blanket TiN (figure 1). The selectivity was found to be 0.96 for a thickness of 12.6 ± 1.8 nm on TiN, using RBS and particle induced X-ray emission (PIXE) measurement which shows that high selectivity of $Ge_2Sb_2Te_5$ can be achieved via area selective deposition.

[1] J. Soethoudt, S. Crahaij, T. Conard, and A. Delabie, Journal of Materials Chemistry C **7**, 11911 (2019).

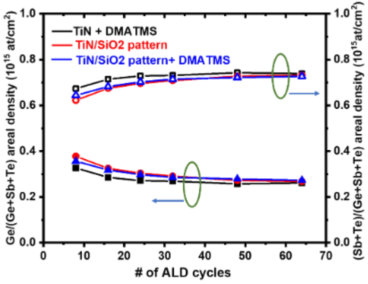

Figure 1 RBS areal density of Ge/(Ge+Sb+Te) and (Sb+Te)/(Ge+Sb+Te) as a function of ALD cycle number

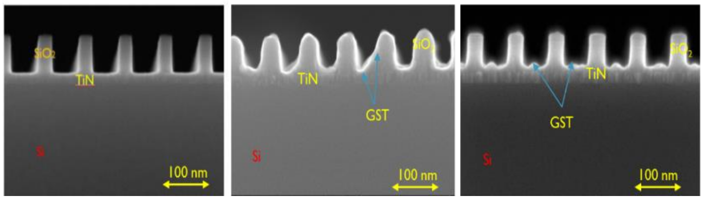

Figure2 Pristine nanopatterns (left), GST deposited on pristine nanopatterns (middle) and on DMATMS treated nanopatterns (right) after 32 cycles

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Minimization of Hydrogen Plasma Damage (ASD 2022)

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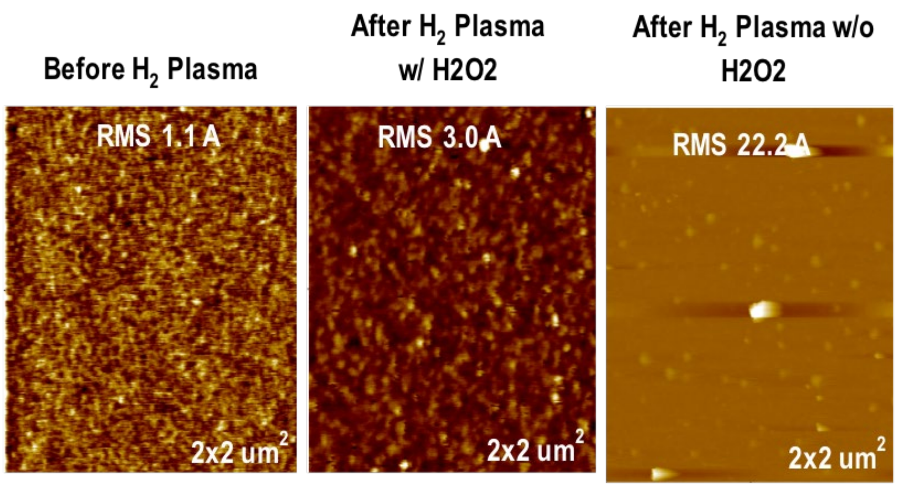
Hydrogen Plasma is used create energy and a reducing environment for growth ALD metals, nitrides, and selective removal of surface species. Oxide films exposed to hydrogen plasma initially lose oxygen and subsequently blister and particulate. Plasma damage prevents the selective use of hydrogen plasma where oxide structures would be exposed without protective mask layers. It is hypothesized that the damage to the oxide is initiated by the removal of the protective surface oxide by hydrogen radicals. Once the hydroxyl layer is removed, exposed the metal atoms are free to realign in the reducing environment. If the hydroxyl layer could be maintained during hydrogen plasma exposure, metal or organic layers could be processed by hydrogen plasma while the oxide layers are protected.

To determine if plasma damage can be prevented, ZrO_x thin films were exposed to hydrogen plasma. During the plasma exposure, low levels of hydrogen peroxide gas were injected into the environment. Data present includes XPS surface analysis and quantified AFM data showing particle, size height and distribution.

Results indicate that H_2O_2 doping in H_2 Plasma: reduced particle count by 90%; reduced by largest particle size by 90%; reduced rate of particle agglomeration, reduced rate of surface roughing; and prevented base Si wafer exposure. Continued plasma exposure demonstrated Ostwalt ripening of particles in H_2 plasma without H_2O_2.



Before H_2 Plasma

After H_2 Plasma w/ H2O2

After H_2 Plasma w/o H2O2

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6th Area Selective Deposition Workshop (ASD 2022)

Direct patterning of ZnO deposition by atomic-layer additive manufacturing using a safe and economical precursor

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Area-selective deposition (ASD) enables bottom-up nanofabrication with individual atoms as building blocks, exploiting chemical control to deliver self-aligned fabrication without dedicated lithographic steps. However, the need for pre-patterned substrates, which is inherent to ASD, the generation of defects outside of the desired growth area and the limited selection of substrate materials represent limitations to applications of ASD.

To overcome these limitations, we have invented atomic-layer additive manufacturing (ALAM): a direct-patterning atomic layer 3D-printing method based on a microfluidic nozzle design which can deposit arbitrary patterns of materials with atomic precision using the underlying chemical principles of ALD. With respect to methods reliant on lithography, ALAM increases flexibility, reduces manufacturing cost and time, while delivering atomic resolution (on the vertical axis). The deposition chemistry of ALAM is similar to conventional ALD and all the commercially available gaseous precursors used in g-ALD are compatible with ALAM. Additionally, the minimized precursor consumption of ALAM allows us to explore new reactions with precursors which are typically less preferred in ALD because of their low vapor pressure or limited reactivity.

Here, we establish ZnO ALAM using as precursors water and $Zn(DMP)_2$ (DMP = dimethyl-aminopropyl), which differs from the well-studied diethylzinc ($ZnEt_2$) by its lower vapor pressure and lower reactivity. Lines and patterns of ZnO deposited by ALAM are continuous, display sharp edges, and offer residual-free surfaces. The solid is crystalline and the crystallites can be either isotropically or preferentially oriented depending on the application, as chosen based on the growth conditions. We demonstrate and applicability of ZnO ALAM direct patterning by fabricating a metal oxide field effect transistor and characterizing the device performance. Taken together, these results highlight how ALAM can be more flexible and facile than ASD on lithographically defined patterns, and simultaneously more economical and safer than classical ALD.

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Random sequential adsorption simulations of small molecule inhibitor packing during area-selective atomic layer deposition

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Small molecules inhibitors (SMIs) can be used to functionalize surfaces during area-selective atomic layer deposition (ALD). The packing of inhibitor molecules, in terms of molecule arrangement and surface density, plays a key role in the blocking of ALD precursor adsorption. However, as a consequence of vapor-phase dosing, SMIs arrive one by one on random surface sites, and closed packing of inhibitor molecules is not likely to be achieved. In this work, random sequential adsorption (RSA) simulations[1] are used to explore the effect of molecular size and shape on the packing of SMIs on a substrate.

As a case study, small alcohol molecules were tested as potential inhibitors for area-selective ALD of SiO_2 by measurement of nucleation curves for ABC-type ALD cycles on Al_2O_3 surfaces (Fig. 1). In the experiments, ethanol resulted in the longest nucleation delay, however, it could not achieve the inhibition performance of acetylacetone (Hacac) inhibitor molecules studied in our previous work.[2] Therefore, ethanol and Hacac were used to develop a statistical model in order to investigate the performances of inhibitor molecules using RSA simulations. The two-dimensional footprints of the inhibitor molecules on the surface were determined based on the optimized geometries from density functional theory calculations. These footprints were used in RSA simulations to study the inhibitor packing (Fig. 2). As a measure for precursor blocking, the availability and the effective sizes of the free area (gaps) around the unoccupied surface sites after inhibitor saturation is also analyzed (Fig. 3). Our model shows that the packing of the inhibitors and a high inhibitor density are important for inhibitor selection in area-selective ALD.

[1] 1 R. Khan et. al, Chem. Mater. 30, 7603 (2018).
[2] M. J. M. Merkx et. al. Chem. Mater. 2020, 32, 3335−3345

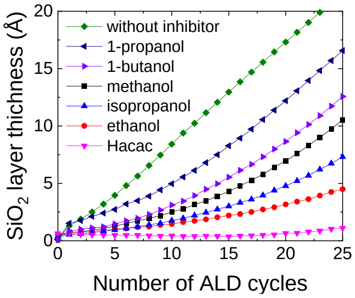

Figure 1. Nucleation curves for ABC-type SiO_2 ALD on Al_2O_3 using various alcohol molecules and Hacac as inhibitor.

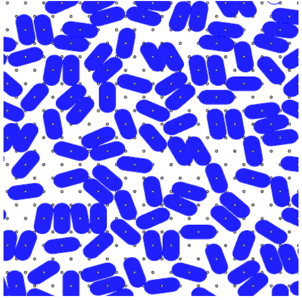

Figure 2. Packing of Hacac molecules on a hexagonal grid representing the Al_2O_3 (0001) surface.

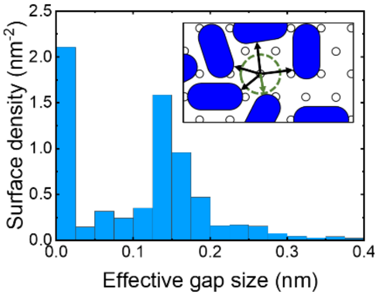

Figure 3. Determination of effective gap sizes (inset) and their surface densities after inhibitor dosing.

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Intrinsic Area-Selective Atomic Layer Deposition of Gallium Nitride in purely Thermal Mode

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Atomic layer deposition (ALD) is a thin film deposition technique exhibiting high conformality, large area uniformity and accurate film thickness control at sub-nm scale, enabled by the use of sequential self-limiting vapor-solid reactions. To overcome critical alignment requirements and reduce film patterning costs, interest is taken in reducing the amount of lithography steps by means of area-selective deposition [1].

Group III nitrides (AlN, GaN, InN and their alloys, III-N in short), in terms of bandgap, cover a spectral range from deep ultraviolet to near infrared and are thermally and chemically stable materials. This makes them suitable for the use in optical and high-power electronic devices [2]. Fabrication of mono-crystalline III-N substrates is expensive as it typically involves high temperatures and thick buffer layers. Fabrication of poly-crystalline variants are therefore a viable route to reduce fabrication costs and lower the thermal budget to ≤ 400 °C.

In this work, we demonstrate inherent area-selective atomic layer deposition (ASALD) of Gallium Nitride (GaN) films in purely thermal mode (400 °C) at a reactor pressure of 10 mbar, from trimethylgallium (TMG) and ammonia (NH_3). GaN is selectively grown on patterned substrates, consisting of areas of sputtered AlN and thermal SiO_2. Size of the areas varied from 2×2 μm^2 to 10×10 mm^2. Importantly, before ASALD of GaN on AlN can be established, ASALD of AlN [3] is required. Film growth is monitored in-situ by spectroscopic ellipsometry (SE) and verified by ex-situ SE and atomic-force microscopy. After 200 ALD cycles about 6.5 nm GaN is deposited on the patterned AlN, whereas less than 1.0 nm is deposited on the SiO_2 area. The selectivity is further verified using angle resolved X-ray photoelectron spectroscopy (ARXPS).

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[1] A. J. M. Mackus, M. J. M. Merkx, and W. M. M. Kessels, Chem. Mater. **31**, 2 (2019).
[2] D. A. Neumayer and J. G. Ekerdt, Chem. Mater. **8**, 9 (1996).
[3] B. Y. van der Wel, submitted for publication

Area-selective ALD using small molecule inhibitors of different sizes: steric shielding versus chemical passivation

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Area-selective atomic layer deposition (ALD) is gaining importance in the semiconductor industry for bottom-up device fabrication. For inhibiting film growth on the non-growth area, small molecule inhibitors (SMIs) provide particular interest due to their vapor-phase application and the resulting compatibility with industrial processing techniques.[1] We previously established that steric shielding is not sufficient for complete precursor blocking by SMIs, but that chemical passivation of surface sites plays a crucial role as well.[2]
In this contribution, we explore SiO_2 blocking on Al_2O_3 comparing three SMIs of different sizes: acetic acid (HAc), acetylacetone (Hacac), and 2,2,6,6-tetramethyl-3,5-heptanedione (Hthd). The aim is to unravel the contributions of steric shielding and chemical passivation to their performance. In-situ spectroscopic ellipsometry studies showed SiO_2 nucleation on Al_2O_3 was delayed for 30 [3], 44 and 58 cycles by Hacac, Hthd, and HAc, respectively as shown in Figure 1. The same trend was observed by evaluating the blocking of Si precursor adsorption using infrared spectroscopy (Figure 2,3). In combination with density functional theory and random sequential adsorption simulations, we found that both steric shielding and chemical passivation are required for effective precursor blocking by SMIs, but neither of them plays a dominating role (Figure 3). As compared to Hacac, HAc performs better due to its small size, yielding denser packing and thereby a higher degree of chemical passivation. Hthd benefits from its bulkiness, resulting in a higher contribution from steric shielding.

[1] A.J.M. Mackus *et al.*, Chem. Mater. 31, 2 (2019).
[2] M.J.M. Merkx *et al.*, 21st International ALD Conference (2021).
[3] M.J.M. Merkx *et al.*, J. Vac. Sci. Technol. A 39, 012402 (2021).

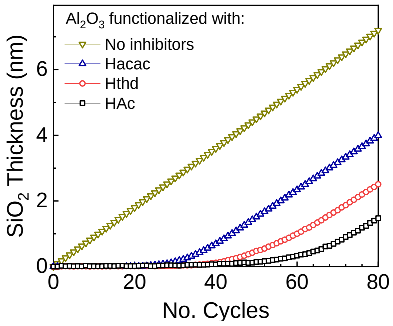

Figure 1 SiO_2 nucleation curves on Al_2O_3 without or with SMI surface functionalization.

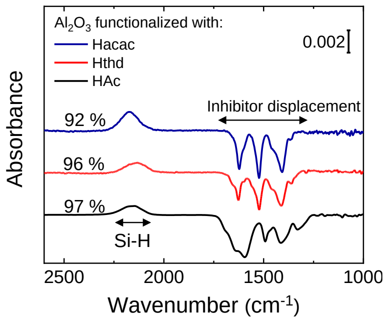

Figure 2 Precursor blocking by three studied SMIs determined from infrared spectroscopy.

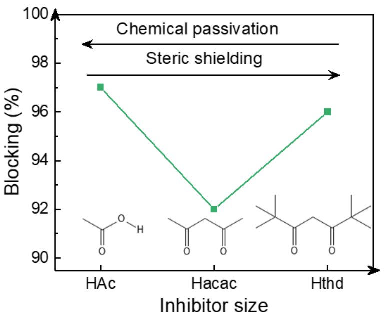

Figure 3 Precursor blocking from Figure 2 as a function of inhibitor size.

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Area Selective Deposition of HfO_2 ALD on Metal, Oxide and Nitride Using Organothiol Inhibitor

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With continuous progress in the field of nanofabrication and nanotechnology, the semiconductor industry has greatly flourished. However, efforts for further reduction in feature sizes of electronic interconnects in search of better and fancier devices, are still ongoing. The struggle to search for better area selective deposition (ASD) processes has led researchers to manipulate deposition surfaces using different passivation tools. In this regard, surface inhibitors have gained a lot of attention. In this study, an organothiol inhibitor has been utilized for ASD on metal, oxide, and nitride surfaces, Cu, SiO_2, and TiN, respectively. The inhibitor selectively adsorbs on the Cu and SiO_2 surfaces at 400 ºC, while the TiN surface remains unaffected after exposure to the inhibitor. Upon high-temperature exposure, the organothiol inhibitor is capable of decomposing to assist adsorption of its different parts on the Cu and SiO_2 substrates, thereby simultaneously inhibiting two surfaces through a single inhibitor. The inhibited substrates were examined for adsorption and inhibition using surface analysis tools including water contact angle (WCA) measurements, X-ray photoelectron spectroscopy (XPS), etc. Blocking results revealed promising blocking potential against HfO_2 ALD on Cu compared to other surfaces. Furthermore, the surface chemistry and reactivity have been explained by theoretical calculation using density functional theory.

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