Area Selective ALD
Room Tamna Hall A - Session AS1-WeM

Area Selective Deposition II

Moderators: Stacey Bent, Stanford University, **Anjana Devi**, Ruhr University Bochum

8:00am **AS1-WeM-1 Area-selective ALD of ZnS on Atomic Layer Etched (ALE) Substrates via Growth Modulation**, ***Taewook Nam,*** Sejong University, Republic of Korea **INVITED**

Area-selective atomic layer deposition (AS-ALD) has become essential for advanced semiconductor manufacturing by enabling precise bottom-up material deposition and reducing process complexity. Various approaches have been developed to achieve selective deposition, including surface activation, growth inhibition using self-assembled monolayers, and growth-etch back processes. These strategies are particularly crucial for fabricating self-aligned features in advanced technology nodes, where traditional lithography and etching face increasing challenges in meeting the demands of device scaling.

Thermal atomic layer etching (ALE) is a method for thin film removal based on sequential surface modification and volatile release reactions. After thermal ALE, atomic layer deposition (ALD) may be needed to deposit another material on the etched surface. Many thermal ALE procedures are defined by sequential fluorination and ligand-exchange reactions. These reactions can leave the surface terminated with fluoride and methyl or chloride species, respectively. These terminated surfaces may inhibit ALD. Additional chemical treatment may be required to reactivate the surface for normal ALD growth.

In this study, zinc sulfide (ZnS) ALD was conducted on Al_2O_3, SiO_2, HfO_2, and native oxide on Si substrates before and after ALE. The ALE was performed at 300 °C using sequential HF and $Al(CH_3)_3$ (TMA) exposures. ZnS ALD was conducted at 300 °C using diethylzinc (DEZ) and hydrogen sulfide (H_2S) exposures. The ZnS ALD thicknesses were monitored using in situ spectroscopic ellipsometry. When ZnS ALD was performed on as-deposited Al_2O_3 ALD films, the ZnS ALD films grew immediately with no noticeable nucleation delay. In contrast, the ZnS ALD growth was completely inhibited until 50 ALD cycles after the Al_2O_3 film was etched using sequential HF and TMA exposures. Similar results were observed for the other metal oxide substrates.

Various chemical treatments were explored to reactivate the metal oxides after ALE for normal ZnS ALD. The surface species present after ALE using HF and TMA exposures are fluoride or methyl species. These species lead to a nucleation delay for ZnS ALD. These surface species can react with exposures of H_2O_2 or H_2O to add hydroxyl groups to the surface. The ZnS ALD had only a slight nucleation delay using H_2O_2 exposures after ALE. This study reveals that ZnS ALD growth occurred almost immediately after H_2O_2 reactivation of the etched Al_2O_3 substrate. Results will also be shown for different chemical treatments for the various metal oxide substrates.

8:30am **AS1-WeM-3 Passivation of Nitride Surface Using Aldehyde Inhibitor for Area Selective Atomic Layer Deposition of SiNx on Oxide Surface**, ***Summal Zoha***, *Ngoc Le Trinh, Bonwook Gu, Han-Bo-Ram Lee,* Incheon National University, Republic of Korea

In recent years, area-selective atomic layer deposition (AS-ALD) has emerged as a superior technique for precise and selective thin-film deposition, surpassing conventional methods. AS-ALD has demonstrated promising potential for 2D and 3D nanoscale patterning by using inhibitor molecules to tailor surface properties. This approach enables thin-film deposition exclusively on desired growth surfaces (GS) while preventing unwanted growth on non-growth surfaces (NGS). Among various inhibitors, small molecule inhibitors (SMIs) have received significant attention for their effective inhibition despite their small size. The choice of surface inhibitor is crucial in determining the selectivity between growth and non-growth surfaces, as well as the degree of surface passivation. In this study, an aldehyde-based inhibitor, trimethylhexanal (TMH), was utilized for AS-ALD to achieve selectivity between oxide and nitride surfaces. TMH displayed selective adsorption on a diluted hydrofluoric (DHF) acid-treated Si_3N_4 surface while leaving the SiO_2 surface unaffected. The DHF pretreatment facilitated favorable TMH adsorption on Si_3N_4 via interactions with NH and NH_2 surface groups, whereas the OH-terminated SiO_2 surface exhibited no TMH adsorption. Density functional theory (DFT) calculations confirmed the favorable adsorption energy of TMH on the nitride surface. To assess the blocking properties of TMH, SiN_x ALD was performed using silicon tetrachloride ($SiCl_4$) as the precursor and ammonia (NH_3) as the reactant. The results demonstrated that SiN_x could be selectively deposited on the SiO_2 surface with no detectable growth on the TMH-treated Si_3N_4 surface. This process shows great promise for 3D patterning in silicon devices, where AS-ALD is critical to meeting the demands of miniaturization.

8:45am **AS1-WeM-4 Blocking Effects of Small Molecule Inhibitors in Atomic Layer Deposition: An Off-lattice Kinetic Monte Carlo Study**, ***Zhaojie Wang,*** *Yanwei Wen, Rong Chen, Bin Shan,* Huazhong University of Science and Technology, China

Small molecule inhibitors (SMIs) hold great promise for their compatibility with area-selective atomic layer deposition (AS-ALD) due to their gas-phase dosing scheme. However, it is quite challenging to describe the complex steric hindrance of inhibitors in simulations. In this work, an off-lattice kinetic Monte Carlo (KMC) simulation method is developed to evaluate the performance of SMIs. The heat-driven conformation transformations are considered in our method. During our simulation, the shape of each molecule is constantly changing to describe its dynamic steric hindrance, which is achieved by constantly refreshing its conformation following the Boltzmann distribution. The results show that the saturated deposition density of long-chain thiol inhibitor 1-mercapto octane on the substrate (~1.4/nm^2) is relatively lower than ethanethiol (~2.0/nm^2) due to its larger size, and the branched isomer 2-Ethyl-1-hexanethiol has an even lower deposition density (~1.1/nm^2). When DMAI is used as an ALD precursor, 1-mercapto octane has a better blocking effect than shorter thiol inhibitors despite its lower deposition density, which emphasizes the large steric hindrance provided by the long chain. Benzene-containing inhibitors show better DMAI-blocking performance than thiols due to their stronger binding strength to the substrate. Meanwhile, the desorption of SMIs gets faster after the simulation temperature increases from 100 to 130°C, resulting in a more rapid blocking failure. This work provides a reasonable method to study the molecular steric hindrance of SMIs and can be applied to large-scale molecular screening of potential inhibitors.

9:00am **AS1-WeM-5 Controlling the Surface Chemistry of Silicon Nitride Using a Plasma Pretreatment for Area-Selective Deposition**, ***Marc Merkx,*** *Pengmei Yu,* Eindhoven University of Technology, Netherlands*; Jhon González,* Universidad Tecnica Federico Santa Maria, Chile*; Ilker Tezsevin,* eindhoven University of Technology, Netherlands*; Rachel Nye de Casto, Dennis Hausmann,* Lam Research Corporation*; Erwin Kessels,* Eindhoven University of Technology, Netherlands*; Tania Sandoval,* Universidad tecnica Federico Santa Maria, Chile*; Adriaan Mackus,* eindhoven University of Technology, Netherlands

Selective deposition on SiO_2/SiN_x patterns, where either oxide-on-oxide or nitride-on-nitride deposition is desired, is currently considered as the “holy grail” in the field on area-selective deposition (ASD). Unlike other silicon-based materials (e.g., Si, SiO_2), SiN_x can be terminated with a large variety of surface groups e.g., (NH_2, NH, N, SiH). As a result, the surface chemistry of a SiN_x surface is very sensitive to the manner in which the layer was deposited, and to how the layer was treated after deposition. In addition, in case of air exposure, this surface chemistry becomes even more complex due to (partial) oxidation of the layer (which adds OH groups). For ASD, the surface chemistry of the SiN_x strongly affects the (selective) adsorption of the inhibitors and precursors. In this contribution, it will be discussed how plasma pretreatments can be used to control the surface chemistry of a SiN_x surface and correct for any unwanted oxidation, as well as how the obtained surface chemistries affect inhibitor adsorption on a SiN_x surface.

Three different plasma chemistries were explored: N_2, H_2, and NH_3 plasma. In-situ reflection adsorption infrared spectroscopy (RAIRS) results show that the N_2 and NH_3 plasma pretreatments were effective in removing the OH groups introduced by air exposure, whereas the H_2 plasma was insufficient and only partially removed the OH groups. The N_2 plasma was observed to result in a largely N-terminated SiN_x surface, while the NH_3 plasma resulted in a largely NH_2-terminated surface. The effect of the plasma pre-treatments on the adsorption of trimethylacetaldehyde (TMAAH) and acetylacetone (Hacac) inhibitor molecules onto the SiN_x was studied using in-situ RAIRS and density functional theory (DFT) calculations. Our results show that the SiN_x surface termination strongly affects whether and how strongly the inhibitors adsorb on the SiN_x surface. Importantly, Hacac was found to require a N-terminated SiN_x surface for adsorption, while TMAAH adsorbs most strongly on a NH_2-terminated surface. Therefore, these results demonstrate the importance of understanding and controlling the surface chemistry for ASD.

9:15am **AS1-WeM-6 Area Selective Atomic Layer Deposition of Ruthenium with Pinacolborane as a Small Molecule Inhibitor**, *Mikko Ritala,* ***Sundas Ismaeel,*** University of Helsinki, Finland

With the miniaturization of microelectronic devices, it is important to find efficient small molecule inhibitors (SMI) and processes to achieve selective growth between different materials on substrate surfaces. Ru has advantages over Cu in terms of bulk resistivity, electron mean free path (λ), processing, and electromigration which makes it a good candidate for narrow interconnect lines in the future [1, 2, 3]. Area Selective Atomic Layer Deposition (AS-ALD) of Ru would be useful in making interconnects bottom-up inside 3D features without the formation of voids. AS-ALD can also eliminate misalignment between different layers of interconnect metallization [4]. This study investigates pinacolborane as an SMI on native SiO_2, Pt, TiN, HfO_2, and ZrO_2 surfaces. After exposure to pinacolborane vapor, Ru ALD followed using bis(cyclopentadienyl)ruthenium ($RuCp_2$) and O_2 at 340°C. The results from energy dispersive X-ray spectroscopy (EDS) indicate that the Ru film growth is inhibited on TiN, HfO_2, and ZrO_2, making them non-growth surfaces (NGS) but film grows normally on native SiO_2 and Pt, making them growth surfaces (GS). The optimization of temperature and effective pinacolborane dose is essential for achieving maximum selectivity.

References

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9:30am **AS1-WeM-7 Inherent Area-Selective Deposition of Low-Resistivity Molybdenum Carbide Films by Thermal Atomic Layer Deposition**, *Jeong Hwan Han,* ***Ji Sang Ahn,*** Seoul National University of Science and Technology, Republic of Korea

With the ongoing downscaling of logic and memory devices, one of the main challenges has emerged such as edge placement error issues resulting from top-down patterning. To overcome the limitations of lithography, a recent focus in bottom-up patterning is based on area-selective atomic layer deposition (AS-ALD). Numerous studies have investigated AS-ALD that employed precursor inhibitors such as SAMs or SMIs to prevent precursor adsorption in non-growth areas. However, there is an increasing need for research into inherent AS-ALD strategies, which exploit the intrinsic properties of substrates with the chemical adsorption of the precursor to enable selective adsorption at targeted surface sites. Molybdenum carbide (MoC_x) has attracted as promising materials for metallization, particularly as bottomless diffusion barriers, liners, capping layers, and interconnects, due to their high melting points, low resistivity, excellent thermal stability, and low reactivity with Cu and its area selective deposition methods have been requiring.

In this work, we developed conductive MoC_x films via thermal ALD without the use of halogen-based precursors, at the deposition temperatures of 200−300℃. This process enabled area-selective growth of MoC_x films on metallic substrates (TiN, Ru, Cu) over oxide substrates (SiO_2, Al_2O_3) by utilizing the intrinsic chemical adsorption of the precursor. We investigated the crystallinity, chemical bonding states, impurity, and resistivity of the MoC_x films, and evaluated the selectivity between substratesthrough analysis of Mo areal density and film thickness. Moreover, the selective growth of MoC_x films on metallic substrates was demonstrated on metal/dielectric patterns using auger electron spectroscopy (AES) mapping and energy-dispersive X-ray spectroscopy (EDS) analysis, indicating the feasibility of implementing this process in practical device applications. To elucidate substrate-dependent surface chemistry in MoC_x AS-ALD, density functional theory (DFT) calculations were conducted, revealing the relative adsorption energies of Mo precursor between metal and dielectric substrates. In conclusion, a newly developed inherent AS-ALD of MoC_x films presents a promising alternative to top-down processes, offering a simplified workflow and potential conducting materials for advanced metallization.

9:45am **AS1-WeM-8 Enhancing Area Selective Deposition Through Sub-saturated ALD: A Pathway to High Volume Manufacturing**, ***Nupur Bihari,*** Lam Research Corporation

Area Selective Deposition is a key technique in semiconductor fabrication processes, enabling the deposition of thin films in a controlled, pattern specific manner. Achieving a high level of selectivity, i.e., no growth on “non-growth surface” and high-density continuous growth on the “growth surface” is essential for ensuring good device yield. Traditional Atomic Layer Deposition processes often face limitations in selectivity due to the inherent challenges in controlling surface chemistry and reaction kinetics.

This talk will explore an approach to enhancing area selectivity through a subsaturated ALD process. By carefully controlling the precursor selection, flux and reaction time to operate in a subsaturated regime, we can significantly reduce unwanted deposition on non-target areas while ensuring high quality film growth on desired regions. This method leverages the intrinsic self-limiting nature of ALD while mitigating issues such as precursor overexposure and undesired nucleation, resulting in improved spatial uniformity and deposition control.

The talk will present experimental results demonstrating the superior selectivity and film quality achieved with sub-saturated aluminum oxide ALD in a dielectric on dielectric (DoD) process compared to a traditional, saturated process. We will also discuss the underlying mechanistic insights, including the role of surface coverage, precursor dynamics and impact of process parameters such as temperature, dilution and pressure. Additionally, a known challenge with ASD – metrology will be discussed. Lam’s successful attempts at image processing to understand large scale selectivity over an entire die will be presented. With the need to shorten the time from R&D to High Volume Manufacturing (HVM), this fast, quantitative metrology is key to rapid validation of new processes.The quick turnaround image processing method allows for testing of marginal processes enabling a larger number of experiments in a short period of time.

This work provides future directions for optimizing selectivity and process uniformity at smaller pitches across a wide range of semiconductor applications.

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