Area Selective Deposition
Room ETEC Atrium - Session ASD2-MoA

ASD Metrology, Surface Characterization and Modeling

Moderators: Adrie Mackus, Eindhoven University of Technology, Ralf Tonner-Zech, Wilhelm-Ostwald-Institute für Physikalische und Theoretische Chemie

3:45pm **ASD2-MoA-10 Development of Area-Selective ALD Processes Using In Situ Optical Diagnostics***, **Sumit Agarwal**,* Colorado School of Mines, USA **INVITED**

Area-selective atomic layer deposition (AS-ALD) can be achieved through either inherent growth selectivity or by blocking reactive sites on the nongrowth surface with inhibitor molecules. However, inherent growth selectivity is generally not observed on chemically similar surfaces since their surface functional groups may have similar reactivity with ALD precursors. Therefore, development of AS-ALD processes for chemically similar growth and nongrowth surfaces is challenging. In this presentation, we will demonstrate that *in situ* optical diagnostics such as attenuated total reflection Fourier transform infrared spectroscopy and spectroscopic ellipsometry can be used to study the reaction of inhibitor molecules with different growth and nongrowth surfaces, and to understand how and when nucleation of ALD occurs on the nongrowth surface.

SiO_2 and SiN_x are the most extensively used dielectric materials in semiconductor manufacturing. Previously, we showed that area-selective ALD of Al_2O_3 can be achieved on SiN_x by passivating the SiO_2 surface with aminosilanes. We will show that the aminosilanes react with both the SiO_2 and SiN_x surfaces, but the coverage of aminosilanes on the SiN_x surface is incomplete, which does not prevent ALD of Al_2O_3 from dimethylaluminum isopropoxide (DMAI) and H_2O, but simply introduces a nucleation delay of 5-10 cycles. However, selective growth of Al_2O_3 on SiN_x was limited to 2-3 nm at which point DMAI started to react with the SiO_2 surface to nucleate film growth. Based on these initial studies, our hypothesis was that there are residual –SiOH groups that remain on the SiO_2 surface that react with DMAI to initiate growth of Al_2O_3. To extend the nucleation delay on SiO_2, we created a set of plasma-deposited SiO_2 surfaces with a controlled density of surface –SiOH groups by first preheating from the deposition temperature of 150 °C up to 500 °C, and then by cooling the substrate to a lower temperature prior to ALD of Al_2O_3. We used aminosilanes with different size head groups and leaving groups to optimize the surface passivation of SiO_2. Finally, we will show how this optimization influences the nucleation delay for ALD of SiO_2.

Acknowledgements: We would like to thank EMD Electronics for funding this work.

4:15pm **ASD2-MoA-12 Characterization of Thin and Selective Film Depositions on v-Groove ASD Test Structures***, **Thomas Werner**,* Chipmetrics Oy, Germany*; Jussi Kinnunen, Feng Gao,* Chipmetrics Oy, Finland*; Rachel Nye de Castro,* Lam Research*; Karsten Lamann,* Tascon GmbH, Germany*; Lysann Kassner, Mathias Franz,* Fraunhofer ENAS, Germany

With the growing interest in introducing ASD processes at advanced technology nodes, many developers are faced with the question of the availability of suitable test structures. The challenge lies both in the very small feature sizes of modern semiconductor structures, typically below 100 nm, and in the combination of different materials serving as substrates for the ASD process under development. Chipmetrics has developed a patented approach in which various layers are deposited into a V-shaped silicon trench etched directly into silicon. After the trench is filled, the layers are planarized by CMP, resulting in a highly planar surface with alternating lines of different materials with widths below 100 nm. Owing to the wet-chemical patterning of the trenches, the lines exhibit very low line edge roughness, which has a positive impact on the evaluation of the results. Ultimately, this results in an array of planar lines of different materials, enabling an efficient evaluation of ASD results. The approach allows the combination of different dielectrics or combinations of metals and dielectrics.Another important aspect in the evaluation of ASD experiments is the use of suitable measurement techniques. For this purpose, various surface analysis methods (SEM-EDX, TOF-SIMS, TEM) for characterizing the described ASD structures were investigated and evaluated. Initial results from ASD experiments are presented, along with an outlook on the next development goals.

4:30pm **ASD2-MoA-13 Co-optimized Process and Metrology Accelerates Molybdenum Contact Development***, **Zhebo Chen**,* Applied Materials

Z. Chen, M. Shifrin, M. Gage, S. Deshpande, Y. Huang, J. Tang, B. Brown, W. Lei, S. Patel, Y. Hwang, S. Zhang, R. Wang, Y. Lei, J. Lu, A. Jansen, K. Rachakonda, X. Tang, A. Gen, E. Itzkovitz

Applied Materials Inc., 3050 Bowers Ave., Santa Clara, California, USA

As device scaling continues and connections to the transistors become even thinner, traditional tungsten (W) contacts face challenges in their ability to efficiently conduct electrons. Molybdenum (Mo or “Moly”), with its lower electrical resistivity at smaller dimensions, emerges as a promising alternative for next-generation contact applications in both logic and memory devices. Since contacts form the smallest connections between interconnects and transistors, maintaining low resistance is critical to ensure maximum device performance and efficient power consumption.

The industry’s gold standard has been Applied’s Selective W, which lowers contact resistance by 40% compared to conventional W. Applied’s Selective Mo metallization technology can achieve an additional 15% lower resistance compared to Selective W in the tiniest features, supporting continued device scaling for gate-all-around transistors.In this presentation, we discuss Applied’s latest innovations for low resistance contacts, and how we co-optimize deposition, planarization, and inspection to enable a complete ecosystem of solutions to advance device scaling.

By combining Applied’s advanced eBeam process and metrology tools with the Maydan Technology Center’s rapid development environment, a novel Moly contact metrology system was created that leverages the Applied PROVision™ eBeam system. Close collaboration between the process and metrology teams enabled Applied to accelerate learning cycles, generating massive amounts of localized, on-device data in less than an hour with massive eBeam metrology.

4:45pm **ASD2-MoA-14 Hydrogenolysis of Aniline on Transition Metal Surfaces: Effects of Temperature and Electronic Structure***, **Matías Picuntureo**,* Universidad Técnica Federico Santa María, Chile*; Marc J. M. Merkx,* Eindhoven University of Technology, Netherlands*; Christopher Jezewski, Scott B. Clendenning,* Intel Corporation*; Adriaan J.M. Mackus,* Eindhoven University of Technology, Netherlands*; Tania E. Sandoval,* Universidad Técnica Federico Santa María, Chile

Area-selective atomic layer deposition (AS-ALD) enabled by small-molecule inhibitors (SMIs) relies on the formation of stable passivation layers that suppress ALD nucleation on selected surfaces. Recent temperature-dependent selectivity measurements for aniline-based inhibitors indicate that, at elevated temperatures, aniline undergoes hydrogenolysis on metal surfaces, leading to the accumulation of benzene-like fragments that constitute the dominant inhibitory species in the passivation layer. However, the atomistic mechanisms controlling their formation, stability, and surface selectivity across technologically relevant metals remain incompletely understood.

In this study, we use a combination of theoretical and experimental characterization to explore the hydrogen-assisted transformation of aniline molecules into carbonaceous species that enhance inhibition on transition-metal surfaces (Co, Ru, Mo, and W). These surfaces are selected for their relevance to advanced interconnect architectures. Temperature-dependent selectivity measurements reveal a clear metal-specific crossover in inhibition efficiency: Co and Ru exhibit higher selectivity at low temperatures, while W and Mo become highly selective at elevated temperatures ($S > 0.96$ for 6 nm films at 200 cycles). Kinetic and free energy analyses of density functional theory rationalize these trends by showing that hydrogen-assisted C-N bond cleavage in aniline becomes increasingly favorable in W and Mo with temperature, leading to the formation of stable benzene-like fragments, whereas in Co the reaction is already exergonic at low temperatures and in Ru it remains intermediate. The calculated decrease in the C-N cleavage barrier after hydrogenation, particularly pronounced in W, and the corresponding stabilization of the hydrogenolysis products correlates with the experimentally observed change from optimum Co/Ru selectivity at low temperature to W/Mo at higher temperature, supporting a mechanism in which aromatic fragments derived from hydrogenolysis constitute the active passivation layer. Overall, these results provide fundamental understanding into the mechanism of hydrogen-assisted surface reactions (hydrogenolysis) of aromatic SMIs and its effect on temperature-dependent selectivity. Moreover, our results indicate that selectivity values change drastically across all metals studied and suggest that catalytic reactions may offer a pathway for metal differentiation that can be further explored for AS-ALD on multicolored surfaces.

5:00pm **ASD2-MoA-15 Organic Functionalization of H-terminated Si Surfaces to Inhibit Atomic Layer Deposition of Al_2O_3**, ***Andrew Kaye***, Colorado School of Mines; *Bhushan Zopé,* Intermolecular, Inc.*; Xinjian Lei, Ronald Pearlstein, Haripin Chandra,* EMD Electronics*; Sumit Agarwal,* Colorado School of Mines

After exposure to the ambient, Si surfaces form a native oxide layer, which changes the surface termination. Typically, native oxides are removed from these surfaces by etching in dilute HF, but it is desirable to remove these native oxides *in vacuo*. Using *in situ* attenuated total reflection Fourier-transform infrared spectroscopy, we first show that SiO_2 films that were plasma-deposited at 150 °C can be etched using atomic layer etching (ALE) based on half-cycles of HF vapor followed by a H_2O plasma. During ALE, we observed a net decrease in the Si−O−Si phonon mode. However, using a similar chemistry for ALE of an RCA oxides on Si(100) surfaces did not result in complete etching. Therefore, the H content and density of the SiO_2 film is important for ALE of SiO_2. Next, we show that a H_2 plasma can remove an RCA oxide from Si(100) to form a H-terminated Si surface with some O atoms remaining, as stretching modes for surface $-SiH_x$ species that are back-bonded to O atoms and isolated Si−OH remain on the surface. These isolated Si−OH groups likely appear in the infrared spectra as the density of hydrogen-bonded Si−OH decreases upon reaction with the H_2 plasma, resulting in the net formation of the isolated modes (see Figure 1). In a separate set of experiments on a plasma-deposited hydrogenated Si surface, we observed the reaction of surface $-SiH_x$ species with 3,5,5-trimethylhexanal (TMH) at 150 °C resulting in surface alkoxides, which was apparent from the increase in absorbance for the Si−O−C stretching mode (see Figure 2). No reaction byproducts are produced in this reaction (see Figure 3). The alkoxide was shown to be thermally stable up to ~200 °C (see Figure 2). Using *in situ* ellipsometry we show that there is an inherent nucleation delay of Al_2O_3 ALD on H-terminated Si compared to SiO_2 surfaces for up to ~10 ALD cycles. However, pre-functionalization of the H-terminated surface with TMH did not increase the nucleation delay for ALD of Al_2O_3 using dimethylaluminum isopropoxide (DMAI) and H_2O. Our infrared spectra show that DMAI likely breaks Si−Si bonds allowing ALD to occur. We will show strategies for increasing the degree of surface passivation to further increase the nucleation delay for ALD of Al_2O_3 by increasing the surface coverage and passivating the strained Si−Si bonds with atomic hydrogen prior to exposure to an aldehyde. The H_2 plasma step for removal of surface SiO_x on Si will likely also passivate the strained Si−Si bonds.

5:15pm **ASD2-MoA-16 Adsorption Behavior of ALD Precursors on Si, SiO_2 and SiN: Simulation and Experimental Investigation**, ***Genki Hayashi***, *Zeyuan Ni, Yumiko Kawano, Shinichi Ike, Shuji Azumo, Tetsuya Goto,* Tokyo Electron Technology Solutions Limited, Japan

Area-Selective Deposition (ASD) is an important process in semiconductor manufacturing [1]. It utilizes the differences in the surface chemical reaction between a precursor and different substrates. Surface reaction simulations are useful tools for searching for appropriate ASD precursors. In this study, we investigated the validity of adsorption energy calculation by comparing the calculation with the process outcomes.

We calculated the adsorption energies of Trimethylaluminium (TMA) and Triethylindium (TEIn) on H-terminated Si, OH-terminated SiO_2, and NH- and F-terminated SiN substrates using the Machine Learning Potential [2] (Fig1). In the calculations, we considered several adsorption structures including both physisorption and chemisorption, and we picked up the lowest adsorption energy in Fig1. It is noted that fluorine appeared on the SiN surface after the DHF dip as shown in Fig2(XPS results), which agrees with the previous report [3]. For both TMA and TEIn, the calculated adsorption energy was lower in order of the SiO_2(-OH), SiN(-NH), Si(-H), and SiN(-F) cases. These results indicate that TMA and TEIn are most likely to adsorb on SiO_2. The surface affinity of TMA and TEIn on SiN substrates might depend on the surface density of -NH and -F terminations.

To compare the calculation results with experiments, we introduced TMA and TEIn onto Si, SiO_2, and SiN substrates in a vacuum chamber. We dipped the samples into 0.5% DHF for 60 seconds before the molecule introduction in order to remove the native oxide. We set the condition of the molecule introduction so that the molecule did not decompose in the chamber and adsorption equilibrium was achieved. Fig3(a) shows the XPS spectra (Al 2p) of these substrates after TMA exposure and Fig3(b) shows the XPS spectra (In 3d) of these substrates after TEIn exposure. The largest amounts of both Aluminum and Indium were observed on the SiO_2 substrate, which agrees with the expectations from the simulation results. For SiN substrate, the amounts of Aluminum and Indium were lower than on SiO_2 and larger than on Si. Since -F and -NH termination might coexist, the surface affinity of TMA and TEIn is considered to be averaged. We need to quantify the surface densities of -NH and -F termination in order to investigate the adsorption of TMA and TEIn in more detail. Based on these results, the adsorption energy calculation can be a useful tool to estimate the adsorption selectivity in developing ASD.

[1]G. N. Parsons and R. D. Clark, Chem. Mater. 2020, 32, 4920−4953.

[2]S. Takamoto, et al., Nat Commun 13, 2991 (2022).

[3]L-H. Liu et al., J. Phys.: Condens. Matter 28 (2016) 094014.

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