Area Selective ALD
Room Regency Ballroom A-C - Session AS1-TuM
Surfaces and ASD

Moderators: Dr. Jeffrey W. Elam, Argonne National Laboratory, Dr. Adrie Mackus, Eindhoven University, Netherlands

8:00am **AS1-TuM-1 Advances in the Industrial Adoption of Selective ALD Processes*, David Thompson,*** Applied Materials, Inc. **INVITED**

Since the initial adoption of atomic layer deposition in capacitor dielectrics for DRAM, and for gate dielectrics in logic at 45 nm, ALD has played a transformative role in enabling a wide variety of integration, without which the industry would have been unable to scale.However, over the last 15 year the number of steps required to process a chip has dramatically increased and integration has become increasingly complicated.

Selective deposition can offer enabling and/or simplified integration approaches, and while there has been strong adoption of some selective processes (e.g. selective epitaxy of Si and selective capping of copper with CVD Co), there remains a tremendous opportunity for the industry to solve many integration problems with selective ALD processes.

This talk will focus on several high value problems that can be addressed by selective ALD, and the additional steps required to enable these selective processes.A specific case study on leveraging selective ALD to enable higher chip speeds through reducing RC delays by leveraging an integration scheme enabling selective ALD TaN will be examined.In this particular case, the selective barrier can reduce via resistance by >50% with no reliability degradation.

Finally, the lessons learned in enabling the selective ALD TaN process will be highlighted as they relate to enabling the many other selective ALD applications that promise to continue enabling device manufacturers roadmaps.

8:30am **AS1-TuM-3 Control of Silanol Density in Silicon Oxide Surfaces via Gas-Phase Treatments to Control Metal Atomic Layer Deposition*, Mohammed Alam,*** University of California at Riverside*; F. Zaera,* University of California - Riverside

Controlling the deposition of metal films grown on oxides by atomic layer deposition (ALD) requires stringent control over the surface nucleation sites, typically hydroxyl groups. The hypothesis driving this project is that preliminary surface modification steps may be used to alter the hydroxyl surface density and with that, the properties of the ALD metal films. In the case of area-selective ALD, for example, the use of surface modifiers such as silylation agents has been implemented to deactivate all silanol sites on the non-growth surface in order to spatially direct film deposition onto the growth surface. The extent of silylation may also be controlled to tune the ALD in terms of the film density. Partial silylation can help deposit metal nanoparticles of varying sizes by immobilizing them thereby preventing their aggregation and sintering at high temperatures.

The medium in which surface modification reactions, such as silylation, are carried out in is vital to achieve control over the efficiency of the process of blocking nucleation sites. A liquid-phase environment affords little control over the surface modification process and may result in the formation of defects within the organosilane layer. These drawbacks may be eliminated by conducting the modification step in the gas phase, as was tested in this work.

In our XPS study, Si-OH sites in silica surfaces were blocked in a controlled fashion via gas-phase silylation using *N,N*-dimethyltrimethylsilylamine. The silylation efficacy was assessed by evaluating the kinetics of metal oxide ALD on the resulting substrates. The results from gas-phase silylation were compared to a set of experiments in which the modification step was performed in the liquid-phase. In both cases, the SiO_x/Si(100) surface becomes fairly unreactive during the initial stages of TiO_2 or HfO_2 ALD and remains passivated up to 5 TiO_2 cycles; the passivation is less effective with HfO_2. Nucleation sites are eventually re-activated with increasing cycles, but partial surface passivation is maintained up to 50 cycles. These results suggest that the metal precursor can eventually chemisorb onto defect sites in the silylated layer after sufficient interaction with the surface, propagating film growth. Moreover, as the results obtained with gas- vs. liquid-phase silylation are comparable in terms of ALD passivation, it is concluded that there is an intrinsic limitation to the degree of passivation achievable using this surface modification scheme. Finally, preliminary NMR results with porous silica indicate that the extent of silylation can be tuned to modify the ratio of free vs. capped nucleation sites.

8:45am **AS1-TuM-4 Inherently Area-Selective Atomic Layer Deposition of Device-Quality $Hf_{1-x}Zr_xO_2$ Thin Films through Catalytic Local Activation*, Hyo-Bae Kim,*** *J. Lee, W. Kim, J. Ahn,* Hanyang University, Korea

Area-selective atomic layer deposition (AS-ALD) has attracted tremendous interest as an alternative bottom-up patterning process to implement versatile fabrication of selectively formed thin films in both vertical and lateral direction in extremely downscaled 3D semiconductor devices. In this study, we report a methodology for achieving inherently selective deposition of $Hf_{1-x}Zr_xO_2$(HZO) thin films by catalytic local activation not only on noble metal surfaces like Ru and Pt, but also on the TiN surfaces. For achieving selective deposition on metal surfaces, O_2 gas was utilized as a mildly oxidizing co-reactant and cyclopentadienyl-tris(dimethylamido)hafnium(zirconium) precursors ($Hf(Zr)[Cp(NMe_2)_3]$) which require strong oxidizing agents were used to deposit HZO thin films. As a results of catalytic dissociation of O_2 molecules, we successfully achieved inherent selectivity greater than ~7 nm on both blanket Ru substrate and Pt/Si patterned substrates. Furthermore, it was demonstrated that the anti-ferroelectric HZO thin films with high dielectric constants of 31 and 34 can be fabricated selectively on TiN and Ru substrate, respectively, through the inherent AS-ALD method using catalytic local activation and ozone post-treatment. It should be noted that this intriguing approach for achieving inherent selectivity expands the potential utility of bottom-up nanopatterning processes for next-generation nanoelectric applications.

9:00am **AS1-TuM-5 Targeted Dehydration as a Route to Site-Selective Atomic Layer Deposition at TiO_2 Defects*, Jessica Jones,*** *E. Kamphaus, A. Martinson,* Argonne National Laboratory

Distinct reactivity of unique atomic arrangements (i.e. defects) on material surfaces allows for selective surface chemistry exclusively at those sites. We present an atomic layer deposition (ALD)-based technique of site-selective ALD (SS-ALD) targeting undesirable defect sites. Defects on the TiO_2 and other oxidized surfaces affect the electronic properties, interfaces, and performance of devices utilizing those interfaces. We present first principles calculations to predict the difference in hydration/hydroxylation of pristine TiO_2 terraces and minority atomic configurations including step edges and oxygen vacancies. In situ ellipsometry reveals the nucleation behavior of SS-ALD at process conditions precisely tuned for selective hydroxylation of surface defects. An island growth model for nucleation and atomic force microscopy (AFM) imaging are consistent with a site-selective growth mechanism that depends on defect density.

9:15am **AS1-TuM-6 Inhibitor-Free Area Selective Atomic Layer Deposition based on Atomic Layer Nucleation Engineering and Surface Recovery with a Feature Size of Nearly 10 nm*, Yu-Tung Yin,*** *C. Chou,* National Taiwan University, Taiwan*; W. Lee, C. Chuu,* TSMC, Taiwan*; C. Hou,* Academia Sinica, Taiwan*; T. Wang,* National Taiwan University, Taiwan*; J. Shyue,* Academia Sinica, Taiwan*; M. Chen,* National Taiwan University, Taiwan

While conventional photolithography faces more and more challenges to follow the progress of aggressive semiconductor scaling, area-selective atomic layer deposition (AS-ALD) has become a promising technique that can directly reduce the number of lithography and etching processes. In this study, novel concepts including the “atomic layer nucleation engineering (ALNE)” and “surface recovery (SR)” techniques, were proposed for the realization of AS-ALD without using any inhibitors. The AS-ALD process based on ALNE and SR results in nearly 100% selectivity of the oxide (Al_2O_3) and nitride (AlN) deposition between the dielectric (SiO_2) and the metal (Pt or W). For ALNE, by directly introducing the radio-frequency (RF) substrate bias after the exposure and purging of precursors in each ALD cycle, the difference in the binding energy of the precursor adsorbed on dielectric and metal surfaces give rise to the selectivity of film deposition. The relatively lower binding energy of the precursor on the metal surface, as compared with that on the dielectric surface, opens a processing window for the local substrate plasma to remove the precursor adsorbed on metal, which contributes to the inhibitor-free AS-ALD between SiO_2 and Pt. Furthermore, for those metals that are easily oxidized during the oxide deposition, the SR technique (i.e., by introducing the RF substrate bias again) is subsequently applied to dispose of the oxidized layer on the metal surface. Accordingly, the ALNE method achieves the high-selectivity AS-ALD over 100 ALD cycles for Al_2O_3 and AlN between the SiO_2 and Pt surfaces. For tungsten (W) which is easily oxidized during the exposure of oxidant in the ALD process, the AS-ALD of Al2O3 without any selectivity loss over 100 ALD cycles is realized between the SiO2 and W surfaces. In addition, the AS-ALD

process based on the ALNE and SR treatments has been further demonstrated on the SiO_2/W patterned substrates with the scaling of the feature size from 75 µm to ~10 nm. In conclusion, the concept of ALNE and SR has realized the inhibitor-free AS-ALD with high selectivity, which is substantially beneficial to further extension of Moore's Law.

9:30am **AS1-TuM-7 Dopant-selective Choreography of Metal Deposition for Bottom-up Nanoelectronics***, **Nishant Deshmukh**, D. Aziz, A. Brummer, S. Kurup,* Georgia Institute of Technology, USA*; M. Filler,* Georgia Institute of Technology

The entirely bottom-up fabrication of nanoelectronic devices promises an unprecedented combination of performance and scalability. While current bottom-up methods can create suitable semiconductor structures, creating semiconductor-metal contacts or the gate stack of a transistor still require top-down processes. For example, contacting Si nanowire pn diodes grown with the vapor-liquid-solid (VLS) mechanism usually employs e-beam lithography, deposition, and lift-off. Here, we report a fully bottom-up approach that combines dopant-modulated surfaces, dopant-selective attachment of a self-assembled monolayer (SAM), and area-selective atomic layer deposition (AS-ALD) to direct the deposition of Pt contacts on Si. Briefly, a bifunctional undecylenic acid SAM is first blanket attached to the Si surface. Exposure to KOH removes it from heavily-doped (~10^{20} cm^{-3}) Si surfaces while it remains on lightly-doped (~10^{14} cm^{-3}) Si surfaces. Subsequent Pt ALD yields deposition primarily on the heavily-doped Si, with selectivity ratios as high as 100. X-ray photoelectron spectroscopy (XPS) studies of undecylenic acid and its monofunctional derivatives show that undecylenic acid attaches primarily through the alkene on lightly-doped Si surface. In situ oxidation of the heavily-doped Si surfaces leads undecylenic acid to bond via the carboxylic acid. This difference in attachment allows facile undecylenic acid removal from the heavily-doped surface but not the lightly-doped surface upon exposure to aqueous KOH. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) studies as a function of ALD cycle number reveal Pt film morphologies consistent with classic Pt nucleation and growth. The contact resistance of the resulting Pt contacts will also be presented. This work shows a method for the dopant-selective deposition of metal contacts on semiconductors, with potential use in the fully bottom-up fabrication of semiconductor devices such as diodes and transistors for hyper-scalable nanoelectronics.

9:45am **AS1-TuM-8 Effect of Surface Pretreatment to reduce the Incubation Period of Iridium Thin Film grown by ALD on the Oxide Surface***, **Myung-Jin Jung**, J. Baek, S. Lee, S. Kwon,* Pusan National University, Republic of Korea

Iridium (Ir) has low figure of merit ($\rho_0\lambda$) and high melting temperature properties, so it has been recently spotlighted as a very important copper (Cu) alternative interconnect material in next-generation semiconductor devices. In particular, in the case of depositing a thin film using atomic layer deposition (ALD) technology, it can be expected to deposit extremely thin film with conformal, uniform and excellent step coverage characteristics even in a very complex structure or a trench structure of several nm dimension due to the inherent self-limiting characteristic of ALD. In this regard, ALD-Ir is considered as one of the most suitable metallization process for the application of advanced semiconductor interconnects. Therefore, considerable efforts have been conducted to develop a reliable ALD-Ir process having improved film qualities. And, ALD-Ir process with excellent thin film properties such as low electrical resistivity and negligible oxygen impurities was recently reported using Tricarbonyl (1,2,3-η)-1,2,3-tri(tert-butyl)-cyclopropenyl iridium ($C_{18}H_{27}IrO_3$, TICP) precursor and oxygen [1]. However, in the case of this TICP precursor, it was difficult to deposit extremely thin and continuous Ir films on the hydroxyl-terminated oxide layer due to its long incubation delay.

Therefore, in this study, a method for depositing a very thin, uniform and continuous ALD-Ir thin film with low resistivity even on oxide materials was explored by reducing the incubation period and promoting nucleation using various surface pretreatment conditions. In addition, the nucleation behavior as well as film properties of ALD-Ir on the oxide material were systemically compared and analyzed according to the surface pretreatment conditions, and finally, ALD-Ir thin film with excellent properties on the oxide surface was obtained.

References

1. Park, Na-Yeon, et al. Chemistry of Materials 34.4 (2022): 1533-1543.

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