Atomic Scale Processing Mini-Symposium
Room 206 A W - Session AP+PS+TF-ThA

Emerging Applications for Atomic Scale Processing (ALD/ALE) including Precursors and Surface Reactions

Moderator: Robert Bruce, IBM Research, T. J. Watson Research Center

2:15pm **AP+PS+TF-ThA-1 ALD Thin Films for Protecting Limestone Cultural Heritage**, ***Gillian Boyce***, *Suveena Sreenilayam,* University of Maryland, College Park*; Eleonora Balliana, Elisabetta Zendri,* Università Ca' Foscari Venezia, Italy*; Raymond Phaneuf,* University of Maryland, College Park

From natural erosion to pollution-accelerated decay, stone cultural heritage deteriorates constantly through interactions with the environment. Common protective treatments such as acrylic polymers are generally prone to degradation and loss of performance, and they are often limited in their ability to achieve uniform and conformal coverage across a stone's topographical features. In this work, we report on the results of investigations of atomic layer deposited (ALD) amorphous alumina thin films for the protection of calcium carbonate substrates of a wide range of porosity against acid-based dissolution. The protective effects of the ALD coatings were investigated by aqueous acid immersion. The solution pH was tracked over time for a constant volume of acetic acid solution with an initial pH of 4 with the stone samples immersed. We find the protective effect of ALD alumina coatings is extremely promising, with 90 nm thick coatings slowing the average rate of pH evolution significantly, by between one and two orders of magnitude, depending on the porosity of the substrate. The eventual failure of the ALD coatings during immersion was also investigated, with the development of pits on the substrates, whose area fraction correlates to the changing pH of the acid solution during immersion. The variation of the protective action of the films with thickness is consistent with kinetics which are limited by diffusion within the pits, rather than through the films. Our findings point to the dominant role of defects in the thin films in their eventual failure

2:30pm **AP+PS+TF-ThA-2 Atomic Layer Depositionon Ceramic NanopowdersforPrecisely Engineered Microstructure of Sintered Ceramics**, ***Eric Bissell***, *Alexandros Kostogiannes, Steve Lass, Anna Zachariou, Brian Butkus, Luis Tomar, Terrick Mcnealy-James, Ayelen Mora, Blaine Mauri-Newell,* University of Central Florida*; Nicholas Rudawski,* University of Florida, Gainesville*; Romain Gaume, Parag Banerjee,* University of Central Florida

In this work, we have utilized the conformal nature and monolayer control of growth of ALD films to develop ≤ 10 nm, ultrathin diffusion barriers on the surfaces of ceramic nanoparticles. The barrier layer restricts grain growth during sintering leading to formation of bulk, nanocrystalline ceramics which demonstrate unique properties such as superior hardness and optical transparency, otherwise not achievable using traditional powder preparation and sintering steps.

Zinc oxide (ZnO) nanoparticles of 60 nm nominal diameter were coated with 1 or 10 nm of Al2O3in a custom-built, rotary ALD powder reactor. In situ mass spectrometry was used to end point the half-reaction pulse times. The powder was subsequently mixed at a 1:1 mass ratio with uncoated ZnO nanoparticles where the uncoated ZnO served as the 'control' sample undergoing the exact thermal and pressure cycling as the coated regions. The powder mixtures were subsequently compacted and hot pressed at 850 ^{o}C under uniaxial loading of 150 MPa. The sintered ceramics reveal that the 1nm and 10nm 'shell' Al2O3 layers effectively restrict grain size of the ZnO to 89 ± 23 nm and 55 ± 7 nm respectively, whereas the uncoated regions grow large polycrystalline grains of 601 ± 104 nm and 717 ± 80 nm respectively. The crystal structure analysis reveals ZnO in its thermodynamically stable wurtzite phase with no evidence of secondary phase formation. This study demonstrates the broad applicability of ALD based coating technology to the field of ceramics for fine microstructural control and precise tunability of bulk properties.

2:45pm **AP+PS+TF-ThA-3 Hot-Wire-Assisted Atomic Layer Deposition of Transition Metals**, ***Kyeongmin Min***, *Han-Bo-Ram Lee,* Incheon National University, Republic of Korea

To replace conventional Cu interconnects, atomic layer deposition (ALD) of low figure-of-merit (FOM) materials such as cobalt (Co) and nickel (Ni) is crucial. While noble metals have been extensively studied as alternative interconnect materials due to their excellent performance, the high cost necessitates the development of low cost materials with superior properties. However, existing Co and Ni ALD processes inevitably require plasma to achieve high purity, leading to inherent limitations such as poor step coverage due to radical recombination and unavoidable damage to 3D structures caused by energetic ions and photons. In this study, we studied transition metal ALD processes using a hot-wire-activated counter reactant, enabling the deposition of high-purity films without generating energetic ions or photons. NH_x radicals were generated by exposing NH_3 counter reactant gas to a filament heated over 1300 °C. Due to the high thermal energy of the filament, NH_3 gas molecules dissociated into high energy radicals, which played a crucial role as reactants in the transition metal ALD processes. The concentration of NH_x radicals was studied as a function of the hot wire temperatures and correlated with the physical properties of films. The purity of transition metal films was analyzed using X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). Based on the results of this study, we believe that the hot-wire-assisted ALD process can be widely utilized in various applications where overcoming the limitations of conventional plasma ALD is essential.

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3:00pm **AP+PS+TF-ThA-4 Ni Thin Film Deposition Using Hot Wire ALD and Non-Halogen Precursor**, ***Mruthunjaya Uddi***, *Mike Denchy, Prawal Agarwal, Josh Kintzer, Patryk Radyjowski,* Advanced Cooling Technologies Inc.

Scale up of pure phase nickel (Ni) thin film deposition process for various applications of catalysis, microelectronics, chemical sensors, and MEMS, especially, using environmentally friendly non-halogen precursors is challenging. ALD is a variation of Chemical Vapor Deposition (CVD), with the complete metal deposition reaction broken into two half steps. Since each half-step saturates at a single atomic layer, a very precise control over deposition can be achieved. Although slower than CVD deposition rates, ALD can enable precise, uniform, conformal coating of Ni thin films. Recently, we assembled an automated Hot Wire Atomic Layer Deposition (HW-ALD) reactor and demonstrated Ni thin film deposition using a non-halogen precursor nickelocene and NH_3. The hot wire implementation enabled the non-halogen chemistry pathway. The details of reactor design, operation parameters and characterization of the Ni thin film deposited will be presented. Future experiments will involve large area (> 15 cm diameter) substrate coating with Ni thin films and the uniformity of distribution will be studied.

3:15pm **AP+PS+TF-ThA-5 Pyroelectric Calorimetry for ALD**, ***Ashley Bielinski***, Argonne National Laboratory

A deeper understanding of the self-limiting surface reactions that make up and ALD processes is vital for the development of many emerging applications such as area and site selective ALD processes that rely on chemical differentiation between a range of surface sites. Natural variation and defects in real surfaces necessitate in situ measurements of these surface reactions in order to develop a complete picture of the process. These in situ measurements can be combined with computational results on simplified model surfaces to help understand not only the single most favorable reaction pathways but also changes in the reactions as surfaces dynamically approach saturation and reactions on a realistic range of surface conditions.

Pyroelectric calorimetry can be used to quantitatively measure the heat evolved during an ALD surface reaction with high time resolution within a single saturating precursor reaction. This approach has been used to measure the reaction enthalpy of various ALD precursor reactions during the deposition of Al_2O_3, ZrO_2, and MgO. Analysis of the heat generation rate profiles of these processes in combination with techniques such as in situ spectroscopic ellipsometry and quartz crystal microgravimetry have provided insight into properties including multi-step reaction mechanisms and the driving role of entropy in certain reaction mechanisms. Recent hardware developments further enable measurements of precursor delivery and reaction kinetics. Knowledge of the mechanisms, thermodynamics, and kinetics of these reactions will guide the development of future ALD processes and provide the necessary parameters for the development of more complex and accurate computational models.

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3:30pm **AP+PS+TF-ThA-6 Fabrication of Atomically-Precise Nanoimprint Masks by STM Lithography***, **James Owen**[1], Ehud Fuchs, John Randall,* Zyvex Labs

The Semiconductor industry is struggling to continue to follow Moore's Law. For both technical and economic reasons, it is likely that the ASML High-NA Extreme Ultraviolet Lithography (EUV) tools will be the last photolithography technology to push to higher resolutions. Simultaneously, E-Beam Lithography (EBL) mask writers, while improving throughput by going highly parallel, are also very near the end of resolution improvements. The industry does not appear to expect any significant downscaling of devices beyond what will be possible with the ASML High-NA EUV tool which has a resolution of 8 nm.

The DOE Advanced Materials and Manufacturing Technologies Office (AMMTO) sponsored Semiconductor Industry Energy Efficiency Scaling (EES2) roadmap has identified EUV as a significant contributor to the energy budget of advanced digital electronics. Strikingly, EUV is so inefficient that only about 0.04% of the beam energy actually affects the resist. The EES2 roadmap proposes that replacing EUV with Nanoimprint lithography (NIL) would be a way to improve the energy efficiency of semiconductor manufacturing. NIL offers equal and better resolution and precision than EUV, with up to 90% lower energy costs, resulting in lower costs of production. However, NIL uses a mold of the pattern to be printed on the wafer as a mask and the best resolution of the current EBL mask writers is 15nm. Therefore, a mask writing technology with better resolution than EBL is required; it must provide resolution at least as good as the High NA EUV tool's 8nm to be widely adopted.

We describe a pathway towards unprecedented resolution in nanoimprint mask fabrication. Ultrahigh-precision NIL templates are made by writing sub-nm-precision patterns on Si(001) using Scanning Tunnelling Microscope(STM) lithography followed by selective growth via atomic layer deposition of a hard mask such as TiO_2, which is then used as an etch mask for Reactive Ion Etching to form a Si template, replicating the STM pattern. This template would then be transferred into a quartz template using existing step and flash NIL processes which will then be used to pattern devices on the die or wafer scale. We show that sub-10 nm feature sizes and full-pitch gratings with feature radius of curvature down to 1.5 nm in the lateral dimension are achievable, although the throughput is currently much too slow to be industrially feasible at the moment. This process therefore addresses the EES2 goal of improving the energy efficiency during manufacturing of digital electronics.

3:45pm **AP+PS+TF-ThA-7 Three-In-One Isolation New Integration Solution for Monolithic CFET***, Junjie Li, Longrui Xia,* Institute of Microelectronics of the Chinese Academy of Sciences, China*; **Mingmei Wang**,* Lam Research Corporation

Introduction: Monolithic complementary transistors (CFET) will replace gate all around field-effect transistor (GAA FET) in technology nodes below 1nm [1].CFET stacks N-type transistors on top of P-type transistors to reduce footprint and increase transistor density. Therefore, it is important to isolate the gate and source drain, as well as the gate of the upper and lower transistors. The current publicly available solution is to isolate the gate and source drain of the outer wall and inner wall, and isolate the gate of the upper and lower transistors with an intermediate isolation layer (MDI). This is achieved through three process steps, requiring at least three atomic layer deposition and atomic layer etching[2] (figure 1 of supplemental material). In order to simplify the process and reduce its difficulty, this article proposes a new process integration scheme that combines the above three steps into one deposition step and one etching step to achieve.

Results and Discussion :

Conclusion:We conducted a detailed comparison between the publicly available CFET process flow and the new process flow proposed in this article, as shown in Figure 2 f supplemental material, and ultimately successfully implemented a new three-in-one integrated solution of inner and outer side spacers and MDI. And demonstrated the results of key intermediate steps such as concave dummy gate and CH_x dummy gate self-aligned etching source drain.

Reference:

【1】 C. Cavalcante, VLSI, (2025).

【2】 T.Lill, VLSI (2025).

4:00pm **AP+PS+TF-ThA-8 New Silicon-containing Precursors for Metal Silicide Films***, **Sean Barry**, Dexter Dimova,* Carleton University, Canada

Group 3 metals, particularly scandium and yttrium, offer tunable electropositivity when incorporated in thin films. They are attractive for next-generation microelectronic applications, including silicide and germanide thin films in gate-all-around FET architectures. However, suitable precursors for vapor phase deposition of lanthanide films remain scarce. In this work, we explore a new family of geminal diamidosilane (gDAS) ligands, designed for both homoleptic and heteroleptic coordination to Group 3 centers. These ligands provide modular steric control and enhanced volatility, allowing for the design of thermally stable precursors.

We report the synthesis and characterization of several Sc and Y complexes with methyl- and tert-butyl-substituted gDAS ligands. Thermogravimetric and isothermal analyses reveal decomposition pathways involving γ-hydride elimination, which is critical for understanding volatility and thermal stability in thin film deposition. Notably, $Y(gDAS)_3$ precursors exhibit promising volatility, while extended thermolysis suggests silicide incorporation may be feasible under atomic layer deposition conditions. We also demonstrate preliminary hydrogenation and dehydrocoupling strategies to prepare silicon-containing intermediates compatible with gDAS ligand frameworks. This presentation will show the groundwork for tailored ligand design strategies that enable selective, low-temperature deposition of lanthanide-silicon films.

4:15pm **AP+PS+TF-ThA-9 Conversion-free Atomic Layer Etching of ZnO Using Hydrofluoric Acid and Trimethylgallium for Reduced Residues***, **Taewook Nam**,* Sejong University, Republic of Korea*; Steven George,* University of Colorado Boulder

Thermal atomic layer etching (ALE) is a crucial technique for advanced semiconductor manufacturing, offering precise material removal with sub-nanometer control. While various etching mechanisms exist, including the widely used fluorination-ligand exchange reaction, some materials are etched via a "conversion" mechanism where the original material is converted into a different compound before being removed. This conversion-based ALE, as seen in zinc oxide (ZnO) etching with hydrofluoric acid (HF) and trimethylaluminum (TMA), can leave undesirable residues of the converted material, Al_2O_3, on the surface, which is detrimental for fabricating high-performance, sub-nanometer scale devices.

In this study, we present a novel, conversion-free thermal ALE process for ZnO using HF and trimethylgallium (TMG) as precursors. This alternative chemistry was investigated using a suite of characterization techniques, including quartz crystal microbalance (QCM) and quadrupole mass spectrometry (QMS). ZnO films were initially grown via atomic layer deposition (ALD) using diethylzinc (DEZ) and water at 100°C. QCM measurements during the ALE process showed self-limiting mass gain during HF exposure and mass loss during TMG exposure, confirming the characteristic digital nature of the process. The etch rate was found to increase with temperature, reaching 3.82 Å/cycle at 300°C.

A significant advantage of the HF-TMG process is its ability to etch at temperatures as low as 30 °C, which is dramatically lower than the ≥ 240 °C required for the conventional HF-TMA process. This difference in temperature is attributed to the distinct reaction mechanisms of the metal precursors. While TMA exposure converts ZnO to Al_2O_3, enabling the subsequent unwanted deposition of AlF_3 during HF exposure, TMG exposure results in mass gain from precursor adsorption without conversion. The absence of this competing ALD reaction allows for effective, low-temperature ALE with HF-TMG. QMS analysis further supports this, showing no evidence of conversion and confirming a fluorination-ligand exchange mechanism.

The conversion-free nature of the HF-TMG process also leads to a notable reduction in residual contamination on the etched surface. X-ray photoelectron spectroscopy (XPS) confirms that the HF-TMA process leaves significant concentrations of both F (8.6 at.%) and Al (8.9 at.%) on the surface after ALE. In contrast, the HF-TMG process results in much lower residual concentrations of both F (1.1 at.%) and Ga (2.4 at.%).

[1] **JVST Highlighted Talk**

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