

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

Moderators: Robert Bruce, IBM Research, T. J. Watson Research Center, John F. Conley, Jr., Oregon State University

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 Deposition on Ceramic Nanopowders for Precisely 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 Al₂O₃ in 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 °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 NH₃ counter reactant gas to a filament heated over 1300 °C. Due to the high thermal energy of the filament, NH₃ 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, Praval 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 NH₃. 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 Al₂O₃, ZrO₂, 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, Ehud Fuchs, John Randall*, Zyvox 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 Tunneling Microscope (STM) lithography followed by selective growth via atomic layer deposition of a hard mask such as TiO₂, 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 Chemistry of a 2D Material Fe₃GaTe₂ for Atomically-Precise Processing: Etching and ALD, *Marissa D. Piña, Andrew V. Teplyakov*, University of Delaware

Fe₃GaTe₂ is a 2D van der Waals material that displays intrinsic ferromagnetism above room temperature along with strong perpendicular anisotropy, making it a possible candidate for spintronics and magnonics applications. Recent computational studies have shown that the Fe₃GaTe₂ Curie temperature becomes elevated and its magnetic properties are tunable at the monolayer, demonstrating the importance of obtaining ordered and defect-free thin film and monolayer structures of this material by using atomically-precise treatments.

To determine whether Fe₃GaTe₂ can be etched controllably in nearly atomic layer etching regime, we performed a chlorine gas dose followed by an acetylacetone dose on Fe₃GaTe₂ flakes exfoliated onto a silicon substrate. AFM and XPS after the chlorine dose at elevated temperature show a partially etched but rougher surface. The consequent acetylacetone dose at the same temperature shows further etching. We aim at exploring atomic layer etching of Fe₃GaTe₂ under further optimized and controlled conditions. We are also exploring the etching mechanism to determine why the chlorine dose causes the initial change.

To explore the role of surface structure and chemistry of Fe₃GaTe₂ in ALD reactivity and also to determine whether ALD is feasible on Fe₃GaTe₂ flakes, we followed the ALD of Al₂O₃ on unmodified Fe₃GaTe₂ flakes. We observed alumina growth from TMA/water deposition cycles on Fe₃GaTe₂ after 10 and 30 cycles in a similar amount compared to what was grown on the reactive silicon substrate, as confirmed by ToF-SIMS depth profiling. We are

currently evaluating the changes in Al₂O₃ growth after chemical surface modification of Fe₃GaTe₂ with small organic molecules.

4:00pm AP+PS+TF-ThA-8 Optimizing Semiconductor Wafer Manufacturing with Proper Thermal Management, *Margaret Brennan*, Swagelok Company

This presentation by Margaret Brennan, Applications Solution Principal Engineering Lead, addresses the critical role of thermal management in semiconductor wafer manufacturing, with a specific focus on the thermal loop system. The thermal loop provides essential cooling to semiconductor wafers and requires precise temperature control to maintain optimal manufacturing conditions. The presentation highlights three key reasons for properly insulating the thermal loop: improving chiller efficiency, maintaining thermal stability for higher yields, and preserving uptime by preventing condensation issues.

Various insulation options are compared, ranging from basic covered hoses to high-performance vacuum jacketed solutions, with each offering different temperature ranges and performance characteristics. The presentation emphasizes that proper installation is equally important as product selection, with considerations for spacing, bending, air flow, and environmental conditions all affecting performance. As semiconductor manufacturing trends toward increasingly lower temperatures (projected to reach -120°C by 2027), advanced insulation technologies like vacuum barriers are becoming essential to eliminate convection heat transfer.

The presentation concludes by emphasizing the value of effective thermal management solutions that can reduce downtime, increase yields, and improve overall efficiency in semiconductor manufacturing operations.

About the speaker:

Margaret Brennan began her career as a mechanical design engineer responsible for developing blueprints for various construction projects across the higher education, healthcare, and medical research industries. She joined Swagelok Company in 2023 as a semiconductor application solutions engineer, where she supports the Swagelok sales and service network by developing solutions to address customer needs the semiconductor market.

Swagelok is a worldwide leader in industrial fluid systems—founded in 1947 on the merits of its revolutionary, leak-tight tube fitting. Swagelok has been servicing the semiconductor industry since the 1950s and provides fluid system products, assemblies, services, and training worldwide. With over 50 years of semiconductor innovation, the company introduced VCR fitting technology in 1968, expanded high-purity manufacturing capacity, continues to grow its workforce to adapt to business cycles, and employs knowledgeable specialists globally to support customer needs. Discover more at [swagelok.com](http://www.swagelok.com/) [<http://www.swagelok.com/>]

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