Atomic Scale Processing Mini-Symposium
Room 116 - Session AP2+EM+PS+TF-WeM

New Advances in Atomic Layer Deposition

Moderators: Ashley Bielinski, Argonne National Laboratory, USA, **John F. Conley, Jr.**, Oregon State University

11:15am AP2+EM+PS+TF-WeM-14 Direct Atomic Layer Processing (Dalp™): Revolutionizing Precision Coatings for Emerging Device Technologies, *S. Santucci, M. Akbari, B. Borie,* **Mira Baraket**, *I. Kundrata, M. Plakhotnyuk,* ATLANT 3D Nanosystems, Denmark

As the microelectronics sector advances towards further miniaturization, precision in thin film deposition becomes crucial. Traditional Atomic Layer Deposition (ALD) techniques, vital for semiconductor manufacturing, often require extensive surface preparation, limiting throughput. ATLANT 3D's μDALP™ technology adapts ALD using microreactor technology for localized thin film deposition with accuracy down to a few hundred microns, maintaining all conventional ALD benefits. This approach uses micronozzles for precise delivery of precursors, allowing rapid film formation on targeted substrate areas under atmospheric conditions. The μDALP™ achieves a vertical resolution of 0.2 nm, offering exceptional precision.

This technology enhances conventional ALD's capabilities in selective patterning for microfluidic channels, optical gratings, and nanostructured surfaces, improving its use in next-generation device fabrication. This presentation will discuss how μDALP™ retains ALD's core advantages while enhancing scalability, processing speed, and cost-efficiency. We will highlight the transformative impact of μDALP™ on thin-film manufacturing across optics, photonics, MEMS, and advanced electronics, underscoring its potential to propel future innovations in energy storage and conversion, quantum computing, and advanced packaging solutions.

Keywords:Atomic Layer Deposition, μDALP™, Nanotechnology, Thin Film, Microelectronics.

Fig. 1. (a)Top view of aligned Si trenches (aligned horizontally) coated with a perpendicular line of TiO2(low magnification SEM). (b) Microfluidic precursor delivery concept: Schematic view of the delivery nozzle in frontal view (top) and in cross-section (lower panel).

References

(1)Parsons, G. N.; Clark, R. D.,2020, 32(12), 4920–4953.

(3)Kundrata, I.; Barr, M. K. S.; Tymek, S.; Döhler, D.; Hudec, B.; Brüner, P.; Vanko, G.; Precner, M.; Yokosawa, T.; Spiecker, E.,Small Methods2022, 6(5), 2101546.

11:30am AP2+EM+PS+TF-WeM-15 Electrical and Optical Properties of Macroscopic Nanocomposites Fabricated by ALD Infiltration and Pressure-Assisted Sintering of Nanoparticle Compacts, *Benjamin Greenberg, K. Anderson, A. Jacobs,* U.S. Naval Research Laboratory; *A. Cendejas,* American Society for Engineering Education; *E. Patterson, J. Freitas, J. Wollmershauser, B. Feigelson,* U.S. Naval Research Laboratory

Over the past 20+ years, a wide variety of nanocomposite thin films with unique property combinations have been produced by atomic layer deposition (ALD) infiltration of nanoparticle (NP) films. Examples include electrochromic WO_{3-x} NP films with photochemical stability enhanced by Ta_2O_5 ALD[1] and superhydrophilic and antireflective TiO_2/SiO_2 NP films with elastic modulus and hardness enhanced by Al_2O_3 ALD.[2] Applications of such nanocomposite films, however, are limited by their small thickness (typically a few μm or thinner), reliance on substrates, and/or residual porosity that can remain after ALD infiltration.

In this work, we explore fabrication of macroscopic, freestanding, dense nanocomposites—pucks with ~1 mm thickness, ~10 mm diameter, and solid volume fraction that can exceed 99%—via ALD infiltration of NP compacts followed by pressure-assisted sintering. For a prototype, we use monodisperse 100 nm SiO_2 NPs and an ALD coating of Al-doped ZnO to form electrically conductive ceramic nanocomposites with electrical and optical properties dependent on the coating thickness. Infiltration of the ultra-high-aspect-ratio (>10,000) SiO_2 NP compacts with ZnO:Al is accomplished via a recently developed cyclical-temperature ALD process.[3] The ZnO:Al-coated SiO_2 compacts are then densified via environmentally controlled pressure-assisted sintering (EC-PAS), wherein NPs are cleaned and kept in an inert atmosphere to maintain high surface energy, which enables low-temperature densification with minimal grain growth.[4] An EC-PAS process with a maximum pressure of ~2 GPa and a maximum

temperature of 450 °C yields dense SiO_2/ZnO:Al nanocomposites that contain nanocrystalline ZnO:Al networks and exhibit low electrical resistivity, ρ. At nominal ZnO:Al coating thicknesses, t, of ~3 nm and ~6 nm, ρ is on the order of 1 and 0.1 Ω-cm, respectively, at 300 K. Moreover, at $t \approx$ 6 nm, the Hall mobility approaches 1 $cm^2V^{-1}s^{-1}$ at 300 K, and ρ increases by less than a factor of 3 upon cooling to 10 K, suggesting proximity to the metallic/band-like charge transport regime. Interestingly, the nanocomposites are blue in color with transparency and hue apparently dependent on t. Characterization techniques employed in our investigation into these electrical and optical properties include X-ray diffractometry, scanning electron microscopy, Hall and Seebeck effect measurements, absorption/transmission/reflection spectroscopy, and photoluminescence spectroscopy and imaging.

1. Y. Wang *et al.*, *Chem. Mater.* **28**, 7198 (2016)
2. M. I. Dafinone *et al.*, *ACS Nano* **5**, 5078 (2011)
3. B. L. Greenberg *et al.*, *J. Vac. Sci. Technol. A* **42**, 012402 (2024)
4. H. Ryou *et al.*, *ACS Nano* **12**, 3083 (2018)

11:45am AP2+EM+PS+TF-WeM-16 Tunable Growth of Layered Double Hydroxide Nanosheets through Hydrothermal Conversion of ALD Seed Layers, *Daniel Delgado Cornejo, A. Ortiz-Ortiz, K. Fuelling,* University of Michigan, Ann Arbor; *A. Bielinski,* Argonne National Laboratory, USA; *T. Ma, N. Dasgupta,* University of Michigan, Ann Arbor

Nano-architected materials have seen a rise in recent years and have produced advancements in a variety of fields including biomedicine, energy storage, and catalysis. As such, there is great motivation to develop novel synthesis and processing methods designed to improve the degree of fine control over the material's geometric parameters. In this study, we explore a method known as surface-directed assembly which makes use of the synergy between atomic layer deposition (ALD) and hydrothermal synthesis to grow layered-double hydroxide (LDH) nanosheets. The formation of the LDH product stems from the interaction between the deposited ALD Al_2O_3 film and an aqueous zinc solution. Unlike other reported seeded hydrothermal syntheses, which rely on epitaxial growth from a seed layer, this interaction results in the consumption and conversion of the initial ALD film into the LDH product, where aluminum from the ALD film serves as a limiting reagent in the kinetic processes of nucleation and growth. Geometric parameters such as the nanosheet inter-spacing and length can be tuned by varying the thickness of the ALD film with sub-nanometer precision. A non-linear trend in nanosheet length is observed and characterized within three regimes: (I) depletion limited, (II) length independent, and (III) steric hindrance. In addition, we observe an inverse relationship between the nanosheet inter-spacing and the ALD film thickness. Finally, this process enables the formation of hierarchical nanostructured surfaces onto three-dimensional substrates including microposts, paper fibers, and porous ceramic supports. By leveraging the tunability and conformality of the ALD process, this work enables the programmable control of nano-architected material geometries for a variety of applications, including for energy and medical devices.

12:00pm AP2+EM+PS+TF-WeM-17 Passivation Strategies for Far-Ultraviolet Al Mirrors Using Plasma-Based AlF_3 Processing, *Maria Gabriela Sales, D. Boris,* U.S. Naval Research Laboratory; *L. Rodriguez de Marcos,* NASA Goddard Space Flight Center; *J. Hart, A. Lang, B. Albright, T. Kessler,* U.S. Naval Research Laboratory; *E. Wollack, M. Quijada,* NASA Goddard Space Flight Center; *S. Walton, V. Wheeler,* U.S. Naval Research Laboratory

Far-ultraviolet (FUV) astronomy (λ = 100-200 nm) relies on efficient Al mirrors because Al has a very high theoretical reflectance in this region. However, since Al readily oxidizes in air, the strongly absorbing native oxide layer appreciably degrades its FUV performance. A novel surface passivation technique for Al mirrors was previously demonstrated using an electron beam (e-beam) generated SF_6/Ar plasma, which proceeds via a combined etching of the native oxide and simultaneous fluorination of the Al surface [1].

In our present work, this novel e-beam plasma technique is integrated into a plasma-enhanced atomic layer deposition (PEALD) system. We use a Veeco Fiji G2 reactor, equipped with substrate biasing, that has been uniquely modified to include an on-axis e-beam generated plasma source. Trimethylaluminum (TMA) and SF_6/Ar plasma, produced with an inductively coupled plasma (ICP) source, were used as our precursor and reactant for the ALD AlF_3 process. Optimization of the ALD parameters was performed, and our best ALD AlF_3 films (F/Al ≈ 3, ~1% oxygen content, and roughness < 1 nm) were attained using 100 W ICP power and total plasma gas flows > 30 sccm. Our ALD AlF_3 films provide improved FUV reflectivity compared to oxidized bare Al, however, these optical properties are still limited by Al

oxide at the AlF_3/Al interface. To overcome this, we utilize our in-situ e-beam plasma, produced in a gas mixture of SF_6/Ar, to minimize the native oxide layer prior to ALD.

In this talk, we discuss the processing parameters of the in-situ e-beam plasma (SF_6/Ar ratio and flow, sample bias) and how they affect the AlF_3 growth rate, film/interface chemistry, and surface roughness. These material properties are related to optical performance, which compares favorably to state-of-the-art coatings ($\approx$90% at 121 nm). We then discuss hybrid AlF_3 films, in which the growth is initiated by e-beam plasma, and then continued using an optimized ALD AlF_3 recipe. For the initial step, pre-treatments using the in-situ e-beam plasma and the previously developed ex-situ e-beam plasma [1] are compared. We show that both in-situ and ex-situ hybrid techniques significantly reduce the interfacial oxygen compared to ALD AlF_3 alone (no pre-treatment), which enhances the FUV reflectivity. This work highlights the importance of the interface quality of passivated Al mirrors on their optical performance in the FUV range.

[1] Rodriguez de Marcos, et al., Opt. Mater. Express 11, 740-756 (2021)

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