## ALD Applications
## Room Tamna Hall A - Session AA3-WeA
## Emerging Applications

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4:00pm **AA3-WeA-11 Atomic Layer Deposition for Self-Healing Stone Cultural Heritage Preservation***, Ancy Mini Vibin Lal Nayakom Mini, Gabriele Botta, Mato Knez, **Aranzazu Sierra Fernández**,* CIC nanoGUNE, Spain

The preservation of stone cultural heritage (CH) materials faces growing challenges due to environmental stressors exacerbated by climate change. Fluctuating humidity, temperature variations, and air pollutants accelerate ageing and erosion, compromising the structural integrity of historical materials. To address these issues, we develop advanced self-healing coatings designed to repair microdamage and enhance the durability of stone substrates. Inspired by the autonomous repair mechanisms observed in ancient Roman concrete, our research seeks to translate this phenomenon into protective coatings. Using Atomic Layer Deposition (ALD), we create structured nanofilms capable of mimicking self-healing properties, significantly improving the long-term preservation of stone substrates.

A key aspect of this research is the functionalization of the stone surface to optimize coating deposition, ensure homogeneity, and improve chemical adhesion. Refining pre-treatment methodologies enhances the chemical affinity and uniformity of the coatings, maximizing their stability and self-healing efficiency. The ALD process provides nanoscale metal oxide films, which, upon exposure to environmental humidity and atmospheric $CO_2$, initiate mineral nucleation and growth. This controlled mineralization autonomously seals microcracks before they propagate, reinforcing the mechanical stability and durability of treated stone substrates.

To assess self-healing performance, we employ nano- and microindentation techniques to monitor changes in hardness and elastic modulus across different scales, providing quantitative insights into mechanical recovery. Additionally, high-resolution Focused Ion Beam Scanning Electron Microscopy (FIB-SEM) and Transmission Electron Microscopy (TEM) characterize the mineral phases responsible for self-healing, offering a detailed understanding of the microstructural evolution within damaged regions. These findings highlight the potential of self-healing coatings to preserve the mechanical integrity of stone substrates, offering a promising solution for sustainable CH conservation.

By emulating historical self-repair mechanisms, our coating system establishes a foundation for resilient and proactive heritage protection strategies. This research not only advances CH preservation technology but also contributes to innovative materials that extend the lifespan of cultural heritage assets.

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4:15pm **AA3-WeA-12 Surface Modification of Additive Manufacturing Feedstocks***, Chris Gump, Brandon Castro, Joeseph Gauspohl,* Forge Nano*; Anthony Manerbino, Jeremy Iten,* Elementum3D*; Guillermo Rojas, Casey Christopher, Markus Groner, Dane Lindblad, Brandon Woo, **Arrelaine Dameron**,* Forge Nano

Additive Manufacturing (AM), also called 3D printing, constructs objects from a digital model, typically by depositing and solidifying material layer by layer. AM processes that utilize powder feedstocks include laser powder bed fusion and binder jetting. AM can manufacture objects with intricate internal structures and/or small features that cannot be easily or economically fabricated by top-down machining methods or when these machining tools are not available. However, the number of alloys that can be printed successfully with superior mechanical properties by AM is limited. Possible reasons include 1) the crystal structure/internal stresses of the as-printed part leads to adverse mechanical properties, 2) the feedstock powders do not flow well and are difficult to print uniformly leading to part defects, or 3) high reflectivity of the feedstock preventing effective absorption of input energy, 4) the powder is sensitive to ambient air and has a limited shelf life or powder degradation leads to chemical inclusions and defects. These material deficiencies can be mitigated by nanoscale surface coatings that are chemically precise and uniformly distributed. We demonstrate ALD $Al_2O_3$, $SiO_2$ and $Y_2O_3$ coatings on AlSi10Mg, Ti64, and SiC powders at gram and kg scale. ICP, LECO, and STEM imaging and elemental mapping demonstrated successful surface modification. These coatings increased feedstock oxidation resistance by acting as a moisture and oxygen barriers, and increased powder flowability, demonstrated by a reduction in Hall Flow time. 3D printed cubes and bars from each material were tested ‘as printed’ and after hot isostatic pressing. Parts using the ALD-coated material had the highest density, yield stress, and UTS, while also having the lowest surface roughness.

4:30pm **AA3-WeA-13 Energy Storage Performance of Field-Induced Ferroelectric $Al_2O_3$-Inserted $Hf_{0.5}Zr_{0.5}O_2$ Thin Films for Electrostatic Supercapacitors***, **Jonghoon Shin**, Dong Hoon Shin, Haengha Seo, Kyung Do Kim, Seungheon Choi, Tae Kyun Kim, Heewon Paik, Haewon Song, Seungyong Byun, In Soo Lee, Cheol Seong Hwang,* Seoul National University, South Korea

The growing global energy demand requires the development of efficient and reliable energy storage systems.[1] Electrostatic dielectric supercapacitors have attracted significant attention due to their high power density, fast charge/discharge speeds, high operating voltages, and excellent cycling and thermal stability.[1] Identifying ferroelectric (FE) materials that maximize both energy storage density (ESD) and efficiency by achieving high saturated polarization ($P_S$), low remnant polarization ($P_r$), large breakdown field ($E_{BD}$), and slim hysteresis loop is crucial.[2] Achieving fast charging and discharging speeds is also essential for rapid energy storage and release.

$Hf_{1-x}Zr_xO_2$ thin films are promising candidates due to their well-established atomic layer deposition (ALD) processes, lower leakage current (bandgap: ~5.5 eV), and low crystallization temperatures (400-550 °C). Field-induced ferroelectric (FFE) materials are particularly promising for energy storage applications due to their reversible field-induced phase transition between the non-polar tetragonal phase (t-phase, space group: $P4_2/nmc$) and polar orthorhombic phase (PO-phase, space group: $Pca2_1$), enabling significant energy to be charged and discharged.[3] Consequently, FFE thin films display antiferroelectric-like double hysteresis loops in the polarization-electric field measurements, characterized by high $P_s$ and low $P_r$.[3] Hence, enhancing energy storage performance requires maximizing the t-phase.

This study investigated the impact of $Al_2O_3$ doping on the structural and chemical characteristics, and the energy storage performance of atomic layer deposited $Hf_{0.5}Zr_{0.5}O_2$ (HZO) thin films. By adjusting the number of $Al_2O_3$ dopant cycles and layer insertion positions, optimized $Al_2O_3$-inserted HZO films achieved a record-high ESD of ~138 J $cm^{-3}$ among $(Hf,Zr)O_2$-based thin films, with a high efficiency of ~80%. (Figure 1) The films maintained stable energy storage performance over $10^9$ cycles at 6.0 MV $cm^{-1}$ without electrical breakdown. (Figure 2) A single $Al_2O_3$ cycle (~0.12 nm), uniformly diffused at multiple locations within the HZO matrix, suppressed the monoclinic phase (m-phase, space group: $P2_1/c$) and stabilized the t-phase. This structure enhanced the FFE switching, decreased the hysteresis loop area, and increased the breakdown field (above ~8.0 MV $cm^{-1}$). In contrast, thicker $Al_2O_3$ layers (~0.24-0.36 nm) formed continuous, non-diffusive layers that hindered FFE t-phase stabilization. These findings highlight the critical role of precise $Al_2O_3$ insertion in maximizing the energy storage capabilities of HZO thin films.

4:45pm **AA3-WeA-14 Closing Remarks and Awards***,*

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