ALD for Manufacturing
Room On Demand - Session AM4
ALD on Particles

AM4-1 Improvement of Mechanical Properties of Nanoparticles-Based Thin Films by Using Atomic Layer Deposition*, **Fatma Trabelsi**, M. Fivel ,* Univ. Grenoble Alpes, CNRS, Grenoble INP, SIMaP, France*; R. Salhi,* Laboratory of Advanced Materials, National School of Engineers of Sfax, University of Sfax, Tunisia*; F. Mercier, E. Blanquet ,* Univ. Grenoble Alpes, CNRS, Grenoble INP, SIMaP, France

Nanoparticle-based thin films are gaining interest in recent decades for catalysis, electronic or optical applications. However, their poor mechanical reliability and durability limit their industrial and commercial applications.

In this work, we report on a low temperature hybrid synthesis approach to insure the durability and encapsulation of photonic conversion films for its further integration in silicon solar cells. The proposed hybrid approach consists first on the synthesis of rare earths (Erbium and Ytterbium) codoped TiO_2 nanoparticles (size ~ 11 nm) fabricated by hydrothermal-assisted sol-gel method. Then, the nanoparticles are dispersed at the surface of silicon substrates using a spin-coating process (film thickness 750-900 nm). Finally, Er^{3+}-Yb^{3+}codoped TiO_2 upconversion nanoparticles in the powder phase are coated with an amorphous Al_2O_3 layer using atomic layer deposition technique (ALD) as a unique approach to reinforce mechanical properties of various photoluminescent nanoparticle porous thin films at a relatively low temperature without drastically changing their original structure.

The impact of different ALD-Al_2O_3 thicknesses and forming gas annealing step on the structural, compositional and mechanical properties ofEr^{3+}-Yb^{3+} codoped TiO_2 nanoparticles assembled on n-type Si (100) substrate are investigated. For that purpose, various analysis approaches involving automated crystal phase and orientation mapping in TEM (ACOM-TEM), scanning transmission electron microscopy–energy-dispersive spectroscopy (STEM-EDS), scratch test and nanoindentation are performed to understand the links between the structural properties and the mechanical properties.

The results indicate a clear increase in the adhesion of nanoparticle thin films to the Si substrate with increasing ALD-Al_2O_3 thickness followed by forming gas annealing treatment. This behavior is a consequence of the infiltration of Al_2O_3 layer within the porous matrix, as a result, effective interparticle bonding and filling of the pores are accomplished.

AM4-2 Three-Dimensional Conformal Coating of Particles *Resting* on a Surface by Vapor-Phase Infiltration*, **Chang-Yong Nam**,* Brookhaven National Laboratory

Three-dimensional (3D) encapsulation of micro- and nanoparticles by atomic layer deposition (ALD) can have broad applications but remains a technical challenge. Current ALD techniques for coating particles employ physical agitation to expose all surfaces of particles to precursors during the deposition process, requiring specialized chambers, such as fluidized bed reactors and rotary chambers and, therefore, only applicable to bulk powders in large volume and quantities. Achieving 3D encapsulation by directly applying conventional ALD on particles resting on a substrate without agitation would allow much smaller volumes and smaller sizes of particles to be used, but the conventional ALD on a particle stationary on a flat substrate yields a coating only on exposed surfaces, not on the bottom side directly in contact with the substrate. Here, we report a novel 3D conformal coating technique for individual particles on all sides while they are resting on an inert polystyrene (PS) film to enable the growth of inorganic films not only on the particle's exposed surfaces, but also on the bottom side that is in contact with the polystyrene [Liapis et al., *Adv. Mater. Interfaces***7**, 2001323 (2020)]. This technique repurposes vapor-phase infiltration (VPI), an organic-inorganic hybridization technique derived from ALD in which vapor-phase inorganic precursors perfuse into a polymer matrix and react with functional groups within it to form organic–inorganic hybrids. We exploit the inert nature of PS to use it as a substrate 'transparent' to vapor-phase ALD precursors. We demonstrate that the conformal coatings of alumina realized by this technique improve the stability in aqueous environments for two optically relevant particles: compound semiconductor laser microdiscs and lead halide perovskite nanocrystals, which have important optical tagging applications for *in vivo* and *in vitro* biomedical imaging.

AM4-5 Atomic Layer Deposition (ALD) of Ultra-Thin Diffusion Barriers on ZnSe Microparticles for Phase Stability in Chalcogenide Glasses for Mid-Infrared Optics*, **Jaynlynn Sosa**,* Nanoscience Technology Center, University of Central Florida*; M. Chazot ,* CREOL, College of Optics and Photonics, University of Central Florida*; C. Feit ,* Department of Materials Science & Engineering, University of Central Florida*; A. Kostogiannes,* Department of Chemistry, University of Central Florida, Orlando, FL 32816, USA*; M. Kang, C. Blanco , K. Richardson,* CREOL, College of Optics and Photonics, University of Central Florida*; P. Banerjee,* Department of Materials Science & Engineering, University of Central Florida

ZnSe embedded chalcogenide glass (ChG) composites are optically active in the mid-infrared (IR) and are ideal for niche applications in medical diagnosis, military missile heat-sensing, and chemical identification. The embedded ZnSe crystals play a critical role in providing lasing activity while the ChG - $As_2S_{3-x}S_{ex}$ matrix, acts as a host that can be drawn into fiber and provides the necessary mid-IR transparency. However, during synthesis, the ZnSe particles are prone to dissolution in the $As_2S_{3-x}S_{ex}$ matrix due to a high temperature (650 C) melting and homogenization process. Here we demonstrate that a thin amorphous barrier layer of Al_2O_3 deposited using atomic layer deposition (ALD) on ZnSe microparticles 5-10 µm in average diameter is successful to prevent ZnSe dissolution in the $As_2S_{3-x}S_{ex}$ matrix even after extended melting and homogenization at 650 C for 8 hours. This talk will highlight some of the key process innovations required to overcome challenges of ALD on powdered components for functionalizing and enhancing performance of multiphasic glasses for optical applications.

Amorphous aluminum oxide (Al_2O_3) was deposited using alternate pulses of trimethyl aluminum and H_2O on 1 gm batch size ZnSe using a customized rotary barrel reactor inside a viscous-flow ALD furnace attached to a quadrupole mass spectrometer (QMS). The temperature of deposition was kept at 180 C and the number of cycles were varied from 100 to 300 cycles. The ZnSe particles were sieved to an average size of 5-10 µm and a maximum size ≤ 20 µm. The coated particles were characterized by x-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). The crystallinity of the ZnSe-$As_2S_{3-x}S_{ex}$ glasses were evaluated using x-ray diffraction (XRD) and their composition stability spatially mapped across individual ZnSe particles embedded in $As_2S_{3-x}S_{ex}$ matrix using Raman microspectroscopy.

Whereas 100 ALD cycles provide partial protection to dissolution for the ZnSe in $As_2S_{3-x}S_{ex}$, a 300 cycle ALD Al_2O_3 on ZnSe particles is sufficient to provide phase and composition stability to the ZnSe embedded $As_2S_{3-x}S_{ex}$ glass. Through our investigation, we exemplify the efficacy and potential of ALD of ZnSe powder in improving the stability of optical materials while still achieving optimal mid-IR lasing and transparency.

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