ALD Applications

Room Grand Ballroom A-C - Session AA1-WeA

Emerging Applications II

Moderators: Arrelaine Dameron, Forge Nano, Se-Hun Kwon, Pusan National University

1:30pm **AA1-WeA-1 Atomic Layer Deposited Nano-Coatings to Protect $SrAl_2O_4$ Based Long-Life Phosphors from Environmental Degradation**, ***Erkul Karacaoglu***, Georgia Institute of Technology; *E Ozturk,* Karamanoglu Mehmetbey University, Turkey; *M Uyaner,* Necmettin Erbakan University, Turkey; *M Losego,* Georgia Institute of Technology

Strontium aluminate ($SrAl_2O_4$) phosphors activated with Eu^{2+} and co-doped with RE^{3+} elements (RE: Nd, Dy, etc) are long-life phosphors (>12 hrs of persistent luminescence) of significant commercial relevance. These phosphors have been widely used as luminescent additives in many commercial products including plastics and textiles. Today, these phosphors are of interest for zero-energy safety lighting both in residential markets and on roadways. However, these phosphors are prone to degradation in moist or humid conditions. This talk will discuss our work to use ALD to protect these phosphors from degradation in aggressive aqueous environments. We specifically study degradation of $SrAl_2O_4$ powders co-doped with Eu_2O_3 and Dy_2O_3 and then coated with Al_2O_3 or TiO_2 by atomic layer deposition (ALD). ALD coatings of about 10 to 250 nm in thickness are investigated. Uncoated phosphor powders dispersed directly in water show rapid hydroxylation as tracked with increasing water basicity from pH 7 to 13. XRD analysis, FT-IR spectroscopy, and optical microscopy all confirm post-mortem that these uncoated powders readily decompose to SrO, $Al(OH)_3$, and Al_2O_3 within 3 hours of water exposure and fully degrade to $Sr_3Al_2O_6$ and $Al_2O_3{\cdot}H_2O$ after 48 hrs of water exposure. This degradation results in a severe loss of phosphorescence. Powders that are ALD coated with even 5 nm of Al_2O_3 or TiO_2 show minimal change in aqueous pH and no change in morphological appearance after 48 hours of direct water exposure. 10 nm coatings are found to protect the phosphor powders for up to 2 weeks in direct water exposure. XRD confirms no emergence of secondary phases and photoluminescence properties are retained. Achieving good conformality over all powder surfaces appears to be an important requirement. Interestingly, the photoluminescence intensity of the raw powders also appears to increase with Al_2O_3 ALD coating thickness. This photoemission increase continues even up to a 250 nm coating thickness which shows a 1.5x increase in phosphorescence. This enhancement of emission intensities for ALD coated samples could be attributed to increased radiation absorption caused by surface defects or surface strain introduced by the coatings. Prior work on other luminescent materials has shown similar effects, and our current understanding of these photophysics phenomena will be discussed.

1:45pm **AA1-WeA-2 Enhanced Interfacial Fracture Toughness of Polymer-Epoxy Interfaces using ALD Surface Treatments**, ***Yuxin Chen***, *N Ginga, W LePage, E Kazyak, A Gayle, J Wang, M Thouless, N Dasgupta,* University of Michigan

Polymer interfaces play a critical role in a variety of applications, including consumer products, structural components, biomedical devices, and flexible electronics. In many cases, polymers need to be bonded with adhesives to create structural joints or multi-layer structures. For adhesives to efficiently wet and bond to a substrate, the surface free energy of the substrate must be equal to or higher than the surface free energy of the adhesive. However, the surface energy of most polymers is low, which makes adhesion difficult. Thus, there often is a need to increase the surface energy of a polymer without changing the bulk mechanical and chemical properties.

In this work, we demonstrate that atomic layer deposition (ALD) can be applied on poly(methyl methacrylate) (PMMA) and fluorinated ethylene propylene (FEP) to increase their surface energies and, hence, to increase the interfacial fracture toughness when bonded to an epoxy adhesive.

ALD alumina films were deposited on each type of polymer to modify the surfaces towards high energy surfaces of metal oxide. Transmission-electron microscopy (TEM) and atomic-force microscopy (AFM) were used to study the film morphology on the polymers. These indicated that the ALD treatment increased the surface roughness and changed the sub-surface chemistry by vapor-phase infiltration (VPI). The increase in surface energy after ALD was measured by the sessile-drop test with water, ethylene glycol and glycerol.

The interfacial fracture toughness of each polymer-epoxy interface was measured using a customized motor-controlled wedge tester. After ALD film growth, the interfacial fracture toughness of the PMMA-epoxy and FEP-epoxy interfaces increased by factors of up to 7 and 60, respectively. The two ALD samples and two control samples were tested at the same level of humidity. Furthermore, we observed stress-corrosion cracking of the ALD-polymer interfaces. By conducting wedge tests in different levels of humidity, we found that although ALD increased equilibrium interfacial fracture toughness at all humidity, the effect decreased as humidity increased. Scanning-electron microscopy (SEM) of samples after testing provided additional evidence for stress-corrosion cracking of the ALD-polymer interface. These results suggest a new application of ALD for engineering the mechanical properties of chemically inert surfaces.

2:00pm **AA1-WeA-3 Atomic Layer Deposition of Pd on ZnO Nanorods for High Performance Photocatalysts**, ***Jong Seon Park***, *B Kim, G Han, K Park, E Kang, H Park, J Shim,* Korea University, Republic of Korea

The metal oxide-metal heterostructure is reported to be effective for improving the performance of photocatalysts. Zinc oxide (ZnO) is widely used as a photocatalyst due to its proper band gap (3.3 eV) that enables outstanding semiconducting characteristics. Also, ZnO has been fabricated in variety of forms including thin film, particles or nanowires, that are useful for catalysis with high surface area. Palladium (Pd) is considered as a well-matching metal with ZnO to synergistically improve photocatalytic performance with an appropriate Fermi level. Recombination of generated charges are prohibited since Pd catches excited charges from ZnO leading to highly improved photocatalytic efficiency.

In this study, ZnO nanorods coated with Pd nanoparticles is evaluated as photocatalysts. The ZnO nanorods are prepared by hydrothermal growth on silicon wafers. The Pd nanoparticles are fabricated by atomic layer deposition (ALD). ALD Pd is conducted using Pd(II) hexafluoroacetylacetonate (Pd(hfac)-$_2$) precursor with formalin in a customized ALD chamber (ICOT Inc.). The growth temperature is 90ºC. To evaluate the photocatalytic performance, the degradation rate of methylene blue is measured under the ultraviolet radiating condition. As a result, it is confirmed that the degradation rates are accelerated with the ZnO-ALD Pd catalysts compared to bare ZnO nanorods. This result will be discussed in more details at the presentation.

2:15pm **AA1-WeA-4 Accelerating Light Beam (ALB) Generation through Dielectric Optical Device Fabricated by Low Temperature Atomic Layer Deposition (ALD)**, *W Zhu, C Zhang, A Agrawal, H Lezec,* National Institute of Standards and Technology; ***Huazhi Li***, Arradiance LLC

Accelerating light beam (ALB) or bended light along an arbitrary curvature enables many intriguing applications such as particle manipulation, optical illusion and cloaking[1]. To date, one common method to generate ALBs is based on spatial light modulators (SLMs)[2], which are large and lack spatial resolution due to the large pixel size of the SLMs. Acceleration control of Airy beams (one representative form of ALB) in a photorefractive crystal by applying ultrahigh voltages have been recently reported[3]. However, the scheme usually only operates at a specific wavelength, or imposes a stringent requirement on the ALB generation process. Furthermore, the ALB is generated inside the crystal, not in free-space.

In this presentation we successfully demonstrated a novel scheme to generate ALBs through an ultrathin all- dielectric optical metasurface consisting of nano-posts with cylindrical cross-sections. By properly configuring the lateral dimensions of the nano-post (major axis length and short axis length), as well as its orientation angle, arbitrary phase modulations of an incident beam can be created, thus providing an efficient approach to generate ALBs. The dielectric metasurfaces are fabricated by first creating the reverse patterns in an electron beam (E-beam) resist, followed by low-temperature atomic layer deposition (ALD) of TiO_2, which fills the openings in the exposure E-beam resist in a conformal manner without causing any degradation of the resist (enabled by low temperature ALD).

The proof-of-concept devices demonstrated include: 1) Generation and switch between two arbitrary ALBs that follow different caustic trajectories in free-space (schematically represented in the following figure); 2) simultaneously achieving efficient and broadband generation and dynamic control of ALBs across the visible region. Our study opens up the possibility of creating ultra-compact, fine-spatial-resolution, and flat-profile nanophotonic platforms for efficient generation and dynamical control of structured light beams.

Literature:

1. Cai, W.; Chettiar, U. K.; Kildishev, A. V.; Shalaev, V. M. *Nat. Photonics* 2007, 1, 224−227; Valentine, J.; Li, J.; Zentgraf, T.; Bartal, G.; Zhang, X. *Nat. Mater*. 2009, 8, 568−571.

2. Siviloglou, G. A.; Broky, J.; Dogariu, A.; Christodoulides, D. N. *Phys. Rev. Lett.* 2007, 99, 213901.

3. Ye, Z.; Liu, S.; Lou, C.; Zhang, P.; Hu, Y.; Song, D.; Zhao, J.; Chen, Z. *Opt. Lett.* 2011, 36, 3230−3232.

2:30pm **AA1-WeA-5 Tunable Plasmonic Colours Preserved and Modified by Atomic Layer Deposition of Alumina***, J Guay, A Lesina, G Killaire,* University of Ottawa, Canada*; **Peter Gordon**,* Carleton University, Canada*; C Hahn,* University of Ottawa, Canada*; S Barry,* Carleton University, Canada*; L Ramunno, P Berini, A Weck,* University of Ottawa, Canada

Decorative colouring of pure silver and gold surfaces is an important application for jewelry and coinage, particularly collector's coins. In order to preserve the purity of these substrates, colours created by adding materials like inks or patinas should be avoided. A novel colouring method that uses careful laser treatment to create a surface with nanoscale, plasmonic features has been developed but the bare surface features undergo dynamic coalescence that dulls and shifts the available colour palette. This work demonstrates that colours generated by nanostructured plasmonic silver surfaces can be preserved and tuned by overcoating with alumina films by ALD. These colours were observed to shift with increasing alumina film thickness.

Two types of laser treatment were used to create surface features on silver that gave rise to colours in the visible spectrum: burst and nonburst. For burst surfaces, the colours first degrade with increasing alumina film thickness but recover at larger thicknesses with an expanded colour range. For nonburst surfaces the colours degraded with increasing thickness without any recovery. Underlying periodic structures specific to the burst method are responsible for this behavior. FDTD modeling of representative surfaces, including the conformal alumina layer, helps explain these colour changes. For alumina thicknesses smaller than the nanoparticle gaps, the changes in the perceived colours are due to the perturbation of plasmonic resonances. For alumina thicknesses larger than the nanoparticle gap, the change in colours originates primarily from the complex reflectance response of the alumina coated structures and modification of the refractive index of the resulting complex surface.

The coloured surfaces were evaluated for applications in colourimetric and radiometric sensing showing large sensitivities of up to 3.06/nm and 3.19 nm/nm, respectively. The colourimetric and radiometric sensitivities are observed to be colour dependent.

2:45pm **AA1-WeA-6 TFE of OLED Displays by Time-Space-Divided (TSD) PE-ALD and PE-CVD Hybrid System***, **Bongsik Kim**,* JUSUNG Engineering, Republic of Korea

In this paper we introduce a time space divided (TSD) plasma assisted deposition equipment available to in-situ atomic layer deposition (ALD) and chemical vapor deposition (CVD) process and a thin film encapsulation (TFE) of organic light emitting diodes (OLEDs) deposited by the above mentioned equipment, TSD hybrid system. Figure 1 represents a structure of the TSD hybrid system. The 1st electrode, included protruding rod-like metal bars, is composed of two types of gas injection systems and the protruded parts are inserted into holes of the 2nd electrode. Each electrode is rigorously designed considering the hollow cathode effect (HCE), the plasma sheaths and the surface area for optimizing RF power efficiency. The remote plasma source cleaning (RPSC) system enables an in-situ cleaning to etch away the film residue in the chamber.

Figure 2 show cross-sectional views of two kinds of TFEs in particle environments. Figure 2-1 represents seam defect of general SiO film, deposited by using the hexamethyldisiloxane (HMDSO), and figure 2-2 represents the cross-sectional view of the coated particle by flowable SiO, named pp-HMDSO. Because deposited films generally growth to the direction from which the gas is flowing, almost films which are deposited by the general CVD process cannot avoid to growth of the defect from the blind spot. So, we, by controlling process conditions, fabricated the TFE which includes flowable SiO film in order to fill the blind spot and hardened the film to reinforce the adhesion to neighbored layers.

Figure 3 show measured characteristics of the TFE structure of the figure 2-2, deposited by the TSD hybrid system at low substrate temperature (<100℃). In order to suppress film defects, induced by particles, first, we coated particles with the pp-HMDSO and then, the ALD SiO layer is deposited as a second barrier and a buffer layer between the SiO and the SiN. Even if the film coats conformally without any defect, the permeation of water and oxygen through the film bulk direction would be occurred. So, finally, we coated with the CVD SiN layer for an ultra-low water vapor transmission rate (WVTR). As shown in figure 3, the WVTR of $<5\times10^{-5}$g/m^{2}day at 40 ℃ /100%RH conditions is measured by MOCON Aquatran2 and also we get the optical transmittance (>95%) and the low film stress (<100MPa) data.

The TSD hybrid system can make various kinds of thin films, such as CVD SiN, SiON, SiO, ALD SiO, SiN, etc, by in-situ ALD or CVD process and also can control characteristics of thin films widely by changing the process conditions. By TSD hybrid system, manufactured by JUSUNG engineering, we expecting to contribute the OLED industry development.

3:00pm **AA1-WeA-7 Tailoring the Ferroelectricity of ZrO_2 Thin Films using Ultrathin Interfacial Layers Prepared by Plasma-Enhanced Atomic Layer Deposition***, **Sheng-Han Yi**, B Lin, T Hsu, J Shieh, M Chen,* National Taiwan University, Republic of China

In recent years, HfO_2/ZrO_2-based ferroelectric thin films have been recognized as promising candidates for memory devices and negative-capacitance field-effect-transistors to achieve a further improvement of device performance. The ferroelectric(FE) and antiferroelectric(AFE) properties of these CMOS-compatible oxides have been confirmed to originate from the polar orthorhombic phase and non-polar tetragonal phase, respectively. In this work, we report the significant impact of ALD-deposited interfacial layers on the microstructures and FE/AFE properties of ZrO_2 thin films. Sub-nanometer interfacial layers deposited by plasma-enhanced atomic layer deposition are intentionally introduced between the ZrO_2 thin film and the electrodes of metal-insulator-metal structures to tailor the crystalline phase and ferroelectricity of the ZrO_2. The interfacial layers boost the formation of orthorhombic ZrO_2, leading to significant enhancement of the ferroelectricity with a significant increment of the remanent polarization. On the other hand, another interfacial layers contribute to the formation of tetragonal ZrO_2, giving rise to the dramatic transformation of ZrO_2 from ferroelectricity to antiferroelectricity. The findings indicate that interface engineering by ALD is an effective and advantageous approach to tailor the FE/AFE characteristics of materials.

3:15pm **AA1-WeA-8 Spin-Hall-Active Platinum Thin Films Grown Via Atomic Layer Deposition***, **Michaela Lammel**,* IFW Dresden, Germany*; R Schlitz,* Technische Universität Dresden, Germany*; A Amusan,* IFW Dresden, Germany*; S Schlicht,* FAU Erlangen, Germany*; T Tynell,* IFW Dresden, Germany*; J Bachmann,* FAU Erlangen, Germany*; G Woltersdorf,* Martin-Luther-Universität Halle-Wittenberg, Germany*; K Nielsch,* IFW Dresden, Germany*; S Goennenwein,* Technische Universität Dresden, Germany*; A Thomas,* IFW Dresden, Germany

Due to its strong spin orbit coupling platinum (Pt) is often used as a spin injector/detector in spintronics. We used atomic layer deposition (ALD) to fabricate platinum thin films on a substrate consisting of liquid phase epitaxy grown yttrium iron garnet ($Y_3Fe_5O_{12}$, YIG) on gadolinium gallium garnet ($Gd_3Ga_5O_{12}$). Magnetotransport experiments were performed on the YIG/Pt heterostructures in three mutually orthogonal rotation planes, revealing the fingerprint of spin Hall magnetoresistance. Samples with different platinum thicknesses were used to estimate the spin transport parameters of the Pt thin films. Comparing the values for the spin Hall angle as well as the spin diffusion length with literature we found the spin diffusion length in the ALD Pt thin films agrees well with results reported for high-quality sputtered platinum. The spin Hall magnetoresistance however is smaller by approximatley a factor of 20. Clearly, further experiments will be required to optimize the interface quality in such ALD-based heterostructures. Nevertheless, our results show that spin Hall active Pt thin films can be fabricated by ALD featuring an appropriate quality for spin transport. The reported results build the framework for establishing conformal coatings for non-planar surface geometries with spin Hall active metals via ALD which in the future can provide the basis for developing 3D spintronic devices [1].

[1] Schlitz et al., Appl. Phys. Lett. **112**, 242403 (2018)

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