Fundamentals and Technology of Multifunctional Materials and Devices
Room Pacific Salon 3 - Session C3+C2+C1-ThM

Thin Films for Energy-related Applications II/Novel Oxide Films for Active Devices/Optical Metrology in Design, Optimization, and Production of Multifunctional Materials

Moderators: Per Eklund, Linköpings Universitet, **Tushar Shimpi**, Colorado State University, USA

8:40am **C3+C2+C1-ThM-3 Nanoflaky Titanium Dioxide Grown on Titanium Foil for Capacitive Deionization Purpose***, **Jung-Ta Huang**, P Hsieh, J He,* Feng Chia University, Taiwan

Capacitive deionization (CDI) is considered to be one of the most promising technologies for many water treatment and purification applications. To meet the demand for pursuing high efficiency of desalination, the key component, CDI electrode, requires high chemical stability, high specific surface area, high water wetting ability, and suitable porous structure for ion electrosorption. In this study, a facile approach involving alkali treatment followed by post-annealing was utilized to develop nanoflaky titanium dioxide (TiO_2) structure on titanium (Ti) foil. Furthermore, the feasibility of using nanoflaky TiO_2 grown Ti as electrode for CDI application was evaluated.

The results showed that the grown TiO_2 possessed a porous nanoflaky structure with a mixed-phase of anatase and rutile; in addition, the porous size is in the range of 30 ~ 100 nm. Such microstructure characteristics implies a high specific surface area. Superhydrophilic surface property was also obtained for this nanoflaky TiO_2 structure. According to the cyclic voltammetry results, the nanoflaky TiO_2 grown Ti electrode exhibited electrosorption/electrodesorption ability in 1 M sodium chloride solution, indicating the stability and regeneration. Finally, the deionization performance of flow-through CDI device using nanoflaky TiO_2 grown Ti electrode was demonstrated.

9:00am **C3+C2+C1-ThM-4 Mixed-oxide Coated Ni Foam for High Performance Supercapacitor***, **Kuang-Cheng Lin**,* National Cheng Kung University, Taiwan

Supercapacitors have become a popular energy storage device in the past ten years, owing to its excellent properties in many aspects, like electrical conductivity, cycle stability, and higher power density than lithium battery. However, the biggest challenge for supercapacitors to compete with the Li battery is energy density, i.e., its discharging time is still insufficient to satisfy for many desired applications. Therefore, we have studied a novel supercapacitor electrode made out of a mixed transition metal oxide grown on Ni foam to combat this problem. The mixed transition metal oxide is MnCo2O4 was synthesized using a one-pot synthesis involving hydrothermal treatment. We show that simply varying the precursor concentration would lead to the formation of MnCo2O4 nanostructures having different morphologies. The resulting MnCo2O4 provides more oxidation states that can participate in the electron transfer than monoxide. Several material characterizations and electrochemical tests were performed. Moreover, we demonstrate that the novel electrode gives very excellent specific capacitance of 1,740 F/g and stability after 5,000 cycles. Effect of the material characteristics on the electrochemical performance is discussed.

9:20am **C3+C2+C1-ThM-5 Wavefront Shaping: A New Tool in Optics***, **Moussa N'Gom**,* University of Michigan, USA **INVITED**

The newly emerging field of optical wavefront shaping involves the ability to manipulate light fields both spatially and temporally. It has largely been enabled by the availability of spatial light modulators (SLM). SLMs are used to create arbitrarily complex light fields that are now powerful elements of the optics toolbox. An SLM provides means to manipulate the fundamental constituents of classical light or single photons, which obey the laws of quantum physics. These new tools open up novel ways to address topics where conventional optical techniques are hard to apply, such as the control of light propagation in biological tissues, complex photonic structures, plasmonic systems, and multimode fibers. In this talk, I outline how I exploit the versatility of wavefront shaping to focus through and beyond highly scattering media. I will show its potential to manipulate entangled structured light fields to address coherence degradation in optical communication transmission channels and to address challenges in biomedical imaging.

10:00am **C3+C2+C1-ThM-7 Optical Optimisation of Semi-transparent a-Si:H Solar Cells for Photobioreactor Application***, **Agathe Brodu**, C Ducros,* Univ. Grenoble Alpes, CEA, France*; C Dublanche-Tixier,* Univ. Limoges, France*; C Seydoux, G Finazzi,* Univ. Grenoble Alpes, CNRS, CEA, France

One of the main limitations of microalgae culture in a photobioreactor is the low efficiency of sunlight conversion. To improve the overall photoconversion efficiency and provide energy support, a photobioreactor (PBR) and photovoltaic technology (PV) coupled system can be developed.

Semi-transparent thin film solar cells based on hydrogenated amorphous silicon technology could be directly placed on the PBR's surface. PV cells absorb a part of the incident light to produce electricity while being transparent in the specific photosynthesis wavelength range. To reach this objective, very thin solar cells must be produced. Decreasing the active layer thickness (intrinsic a-Si:H layer) of solar cells induces a better transparency but also a lower efficiency. As a consequence, we worked on the compensation of efficiency losses of thin solar cells by improving optical properties of substrate surfaces. Texturing process using reactive ion etching was applied on glass substrate to obtain a light scattering property on its back side and an antireflective property on the upper side. We studied the influence of those both textured surfaces on a-Si:H solar cells properties.

First, by texturing the back side of the substrate, the influence of light scattering was investigated. That should improve the light absorption in PV solar cells. The best result shows a raise of the short circuit current (Jsc) of the thin solar cells from 8.5 to 10 mA/cm^2, while the other parameters (the open circuit voltage (Voc) and the fill factor (FF)) remained the same. Thus the efficiency increased from 3.7 to 4.5 %.

In a second step, the influence of an antireflective texture of the substrate upper side was studied. The antireflection texture with light scattering effect gives the best results on PV cells. Short circuit current of this thin solar cell goes to 11.2 mA/cm^2 and its efficiency increased to 5.2 %.

The influence of these solar cells, used as optical filter, on the microalgae production rate was investigated. The photosynthesis peaks of microalgae correspond to wavelengths [400 - 500 nm] and [550 – 700 nm]. The first peak of photosynthesis is absorbed by the solar cell. Furthermore, an important diffusion of light in the solar cells also induces losses of transmitted light to microalgae for the second peak of photosynthesis. Finally growing test of *Phaeodactylum Tricornutum* shows that PV optical filtering does not have influence on growth rate. Optical modifications of substrate applied to very thin solar cells allowed to keep a high PV efficiency while maintaining the growing rate of microalgae.

10:20am **C3+C2+C1-ThM-8 Properties of Highly Transparent AlN/SiOx Multilayer Systems***, **Chelsea Appleget**, A Sáenz-Trevizo, A Hodge,* University of Southern California, USA

The new generation of engineered materials is required to perform under extreme conditions of stress, temperature and irradiation, among others. Nano multilayer (NM) materials have been shown to be promising candidates to overcome current structural and functional limitations. To date, most of the studied NM systems are comprised of metal/metal layers, where the optical properties do not represent an area of interest. Therefore, in this work we extended the structural potential of metal/metal NM configurations to ceramic/ceramic NMs which display a broad range of properties but in particular, they offer the possibility to modulate the optical properties depending on their morphology, grain size, layer thickness, and composition. Three different systems composed of alternated layers of AlN and SiO_xwere studied. For each sample, the number of layers and the individual thicknesses were varied until a total thickness of 1 µm was reached. The optical properties of the multilayers were determined using UV-Vis-NIR spectroscopy, revealing the formation of uniform and smooth interfaces with an average optical transparency above 80% that extends through the entire region. Furthermore, the microstructure and plastic behavior were also studied and correlated with the multilayer configuration of the synthesized systems.

10:40am **C3+C2+C1-ThM-9 Tailoring the Optical Properties of Highly Porous Superlattice-type Si-Au Slanted Columnar Heterostructure Thin Films***, U Kilic,* University of Nebraska-Lincoln, USA*; A Mock,* Linköping University, Sweden*; R Feder,* The Fraunhofer Institute for Microstructure of Materials and Systems (IMWS), Germany*; D Sekora, M Hilfiker, R Korlacki, **Eva Schubert**, C Argyropoulos, M Schubert,* University of Nebraska Lincoln, USA

The subwavelength scale periodic arrangement of nanostructures, so-called artificially engineered nano-structures exhibit distinct optical, mechanical, and magnetic properties when they are compared with their bulk counterparts which has recently gained a growing interest due to its potential applications in various optical and optoelectronic systems such as lenses, solar cells, photodetectors, and sensors [1-3]. Tailoring aforementioned inherent properties cannot merely possible with the material choices (ie. elemental composition), but also the size and shape of these artificial structures play a significant role. Unraveling the mechanisms that influence and control the optical properties of highly-porous, periodic, and three dimensional arrangements of nanoplasmonic structures can offer new approaches for the development of next generation sensors. Particularly, both glancing angle deposition and atomic layer deposition can be used to create periodic nanostructures with multiple constituent materials, so-called heterostructured metamaterials.[4]

In this study, we employ a two-source (ie. Au and Si) electron-beam-evaporated, ultra-high-vacuum glancing angle deposition which allows for the fabrication of highly-ordered and spatially-coherent super-lattice type Au-Si slanted columnar heterostructured thin films. We perform a combinatorial spectroscopic generalized ellipsometry and finite-element method calculation analysis to determine anisotropic optical properties. We observe the occurrence of a strong locally enhanced dark quadrupole plasmonic resonance mode (bow-tie mode) in the vicinity of the gold junctions, with a tunable and geometry dependent frequency in the near-infrared spectral range. In addition, inter-band transition-like modes are observed in the visible to ultra-violet spectral regions. Using finite element method, we demonstrate that changes in the index of refraction due to the concentration variation of a chemical substance environment (gaseous or liquid) within a porous nanoplasmonic structure can be detected by transmitted intensity alterations down to 1 ppm sensitivity.

References

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[2] Schmidt, Daniel, and Mathias Schubert. Journal of Applied Physics 114.8 (2013): 083510.

[3] Frölich, Andreas, and Martin Wegener. Optical Materials Express 1.5 (2011): 883-889.

[4] Sekora, Derek, et al. Applied Surface Science 421 (2017): 783-787.

11:00am **C3+C2+C1-ThM-10 Microstructures and Optoelectronic Properties of Cu_3N Thin Films and its Diode Rectification Characteristics***,* ***Yin-Hung Chen****, S Chen, S Sakalley, S Huang, A Paliwal,* Ming Chi University of Technology, Taiwan*; M Liao,* National Taiwan University, Taiwan*; H Sun,* Shandong University at Weihai, China*; S Biring,* Ming Chi University of Technology, Taiwan

Rapidly growing applications of p-type Copper nitride (Cu_3N) films in optical storage media, photovoltaics etc. has motivated us to study Cu_3N thin films which were deposited on glass and silicon substrates by reactive magnetron sputtering at 150˚C from a metallic copper target. Until now, few researchers have studied the p-type conductivity of Cu_3N films which is low compared to the result obtained in our experiment. In this work, we discuss the effects of working pressure on the microstructures, electrical, and optical properties of the Cu_3N films. The working pressures were varied from 5 mtorr to 23 mtorr while gas flow rate was kept constant at $N_2/(Ar+N_2)$%=40%. When the working pressure increases, the Cu_3N (111) peak intensity decreases as evident from XRD studies. Meanwhile, conduction type changes from n-type to p-type. When working pressure is increased to 15 mtorr, the resistivity is 1.575 Ω•cm and the sample shows p-type conduction. This is possibly due to the formation of many copper vacancies (i.e. vacancies at Cu cation sites) in the films. When the working pressure is 5 mtorr, a Cu (111) pattern was observed from selected area electron diffraction (SAED) by TEM analysis. It disappears upon increasing the working pressure to 15 mtorr. It was also found that the ratio of Cu^{2+}/Cu^{+} increases from 0.39 to 0.93 when the working pressure is raised from 5 mtorr to 20 mtorr. More substitution of Cu^{2+} for Cu^{+} results in the formation of more Cu vacancies, which leads to the transition in conduction from n-type to p-type. Finally, n-type Cu_3N/p-type Cu_3N homojunctions and n-type ZnO/p-type Cu_3N heterojunctions diodes were fabricated. It was found that homojunction devices Al/n-type Cu_3N/p-type Cu_3N do not show significant rectification effects. As we observed, at ±3Volts, the I_{on}/I_{off} was only 0.24. Whereas, in heterojunction devices Al/n-type ZnO/p-type Cu_3N, a higher I_{on}/I_{off} of 3118 can be achieved. Heterojunction devices outperform the homojunction devices instead of interfacial issues indicating the superior electrical properties which are explained considering the mismatch in the built-in potentials of the p-n junctions.

11:20am **C3+C2+C1-ThM-11 Effects of the Frequency of Pulsed DC Sputtering Power on Amorphous Carbon Film used for Metallic Bipolar Plates in Proton Exchange Membrane Fuel Cells***,* ***Xiaobo Li****, P Yi, L Peng, X Lai,* Shanghai Jiaotong University, China

Amorphous carbon (a-C) film is a promising material serving as a protective film for metallic bipolar plates in proton exchange member fuel cells (PEMFCs) due to its high electrical conductivity and corrosion resistance. However, the performance of a-C needs to be further improved to meet the commercial requirements of PEMFCs. During the process of preparing a-C film by magnetron sputtering, the sputtering power supply has significant influences on the structure and performance of the film. In this paper, the influence of the frequency of pulsed DC sputtering power supply are investigated to further improve the performance of a-C. The corrosion and interfacial contact resistance (ICR) test results show that the film prepared at 200 kHz exhibits excellent performance. The compactness of the films can be enhanced by the bombardment of high-energy sputtering particles produced by pulsed DC sputtering power. In addition, the proper frequency is beneficial to the formation of graphite nanocrytalline, which is embedded into a-C and improve the sp2 fraction of the film and decrease the ICR synchronously. Furthermore, the a-C containing graphite nanocrytalline exhibits better stability in simulated acid environment of PEMFCs. This study provides a new direction for further improving the performance of a-C films on bipolar plates in PEMFCs.

11:40am **C3+C2+C1-ThM-12 On the Mechanisms of Halloysite Nanotubes Incorporation in the Surface Layer of Forsterite Grown by Plasma Electrolytic Oxidation***, B Mingo, Y Guo, A Němcova, A Gholinia, A Matthews,* ***Aleksey Yerokhin****,* The University of Manchester, UK

Increasing demand for high-performance lightweight metallic materials underlies the interest to Plasma Electrolytic Oxidation (PEO) as one of the most promising techniques for surface engineering of Mg alloys. In order to enable smart and multifunctional performance, it can be beneficial to incorporate into ceramic PEO coatings nanocontainers to carry appropriate active and functionalising agents. In situ incorporation of nanocontainers is challenging since their integrity may be compromised by plasma discharge assisting coating formation. We studied incorporation of halloysite nanotubes (HNTs) as potential nanocontainers into forsterite, Mg_2SiO_4, formed during PEO processing of AM50 Mg alloy. Detailed analysis of the coating microstructure, chemical and phase composition carried out by Scanning Electron Microscopy/Energy Dispersive X-ray Spectroscopy, Transmission Kikuchi Diffraction and X-ray Diffraction enabled evaluation of a pattern of surface temperature evolution during current pulses underpinning the PEO process. Consequent thermal transient analysis revealed that at pulses longer than 10^{-4} s, the surface heating becomes affected by the metal substrate acting as a heat sink. As the pulse duration approaches 10^{-3} s, raising surface temperature and increasing thermal gradients across the coating cause crystallisation of forsterite and grain growth towards the surface; this triggers thermally induced degradation and decomposition of HNTs adsorbed on the surface. In contrast, at short pulse durations (2´ 10^{-5} s), the energy released is insufficient to induce forsterite crystallisation and incorporated HNTs are retained in their original tubular structure. Due to the fine porosity and good structural integrity, such coatings show the highest corrosion resistance in saline solution. Strong correlations between surface thermodynamic conditions and evolution of coating microstructure disambiguate the fundamental mechanisms underlying incorporation of nanoparticles into growing PEO coatings, thus creating the basis for efficient design of PEO processes and development of novel smart and multifunctional coatings with potential applications in many industrial sectors.

12:00pm **C3+C2+C1-ThM-13 Inorganic-Organic Perovskites: Handle with Care, Properties May Depend on It***,* ***Nikolas Podraza****, B Subedi, M Junda, K Ghimire,* University of Toledo, USA

Inorganic-organic lead halide based perovskites (ABX3) have been applied as the absorbing, current-generating layer in thin film photovoltaics over the last decade. In that time, device efficiency has increased from virtually nothing to 22.7% at the time of writing this abstract (that number is likely now higher at the time you are reading it). In spite of the ability to manipulate band gap to absorb different parts of the solar irradiance spectrum, the low deficit between the open circuit voltage and band gap, and the overall high electronic quality of the material based on fill factor and device efficiency, these perovskites still pose challenges—namely related to instability in atmosphere and under external heat, moisture, and electric field driven stimuli. Some instability is mitigated when layers are within solar cell devices, as the perovskites are over-coated with other layers and do not share an interface with the ambient. The susceptibility of thin films to atmosphere leads to a disconnect between measured properties for films and what those properties of similarly prepared materials are in the final device structure. Spectroscopic ellipsometry over the near infrared to ultraviolet is applied for perovskite (A: MA, FA, Cs; B: Pb, Sn; X: I, Br, Cl) thin films and layers in solar cells to deduce structure in the form of thickness and surface roughness as well as complex optical response in the form of the complex index of refraction and complex dielectric function spectra. Photothermal deflection spectroscopy probes the optical response in the vicinity of the band gap for improved sensitivity to low values of the absorption coefficient resulting from Urbach tails and other sub-band gap absorption. For both techniques, measurements are performed for films with no exposure to atmospheric ambient and those exposed for controlled amounts of time. From these comparisons, changes appear in the complex optical response both above and below the band gap, including higher energy electronic transitions, Urbach energies, and other sub-gap absorption features. Understanding the origin of differences due to sample handling allows for more realistic comparison of samples and results in literature. Expectedly, upon continued atmospheric exposure Urbach energies increase and very prominent sub-gap absorption features develop. Samples characterized without atmospheric exposure have comparable properties to layers of the same composition in device structures, and correlations between Urbach energies and photovoltaic device performance parameters are identified.

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