

Wednesday Afternoon, December 10, 2014

Energy Harvesting & Storage

Room: Lehua - Session EH-WeE

Characterization of Materials for Energy Applications II

Moderator: Jim McQuillan, University of Otago, New Zealand

6:20pm **EH-WeE3 Nano Structured Thin Films for Hydrogen Permeation Barrier**, *Motonori Tamura*, The University of Electro-Communications, Japan

A considerable increase in scientific exploration concerning hydrogen production and storage has occurred within the last ten years. Numerous technologies including blast furnace production, biomass production, high temperature electrolysis, thermochemical cycles, advanced gaseous storage tanks, chemical hydrides, and advanced metal hydrides are being developed to provide competitive alternatives to fossil fuel energy technologies. One issue for successful commercial implementation of these technologies is the ability of structural materials for process vessels and piping, storage containers, and engineered components to resist embrittlement from hydrogen.

Hydrogen embrittlement, hydrogen induced cracking, and hydrogen corrosion cracking have long been studied for a wide variety of materials and operating conditions. Major structural component materials for hydrogen service applications are austenitic stainless steels such as Type 304, 316L, etc. These austenitic stainless steels have been previously shown to have a mild susceptibility to hydrogen embrittlement. However, this susceptibility can vary with changing environmental conditions. And as such these materials are often coated with permeation barriers to minimize the potential impact from hydrogen exposure. Some permeation barrier materials such as Al or Al₂O₃ have been evaluated. These materials have shown permeation reductions that range from 10 to 10000 times. This variation is due to several factors such as inherent permeation resistance and microstructure or nanostructure of thin films. Previous study showed that fine-grained dense films obtained by physical vapor deposition performed low hydrogen permeability. In this study, effect of nanostructure of thin films on hydrogen permeation is evaluated.

The hydrogen permeation behavior of thin films coated Type 316L stainless steel was investigated. Thin films of TiN, TiC, Al₂O₃ were deposited by ion plating. Coated samples were examined using optical microscopy and scanning electron microscopy (SEM). The coating chemistry was determined using Energy Electron Probe Micro Analysis (EPMA) and the crystallography was analyzed by X-ray diffraction (XRD). Hydrogen permeation test of samples, 35 mm diameter and 0.1 mm thick, was conducted at 773K. The fine-grained and (111) oriented TiN film whose grain size was under 100 nm reduced hydrogen permeation by three orders of magnitude compared to untreated stainless steel. Grain interface was thought to be effective hydrogen trap sites.

6:40pm **EH-WeE4 Laser Processing and Photoacoustic Characterization of Nanomaterials and Thin Films**, *Mayo Villagrán-Muniz*, *CSA. Sánchez-Aké*, *F.T. Tenopala*, *M.A.V.A. Valverde-Alva*, *A.C. Canales*, *J.M.DL. Martínez-De León*, *B. de la Mora*, *C.G.S. García-Segundo*, Universidad Nacional Autónoma de México, *T.G.F. García-Fernández*, Universidad Autónoma de la Ciudad de México, México, *F.A.C.M. Alvarez-DelCastillo-Manzanos*, Universidad Nacional Autónoma de México

INVITED

The synthesis of metallic nanoparticles (NPs) either covered or embedded in transparent dielectric thin films has recently received great attention for its possible applications as plasmonic structures. There are several methods to synthesize and incorporate metal NPs such as chemical synthesis, photoreduction, thermal and laser annealing^[1]. The annealing methods have the advantage of being free of chemical wastes. The formation of NPs by thermal annealing of thin films inside ovens is the result of the minimization of surface energy, and thus the disaggregation of the film into particles. For the case of laser annealing, nanoparticles of few tens of nm are produced irradiating metal thin films with nanosecond laser pulses^[2]. The physical mechanisms behind the annealing of metallic thin films have been widely studied^[3]. These studies mainly focus on the resulting final nanostructure as a function of the involved experimental parameters, without studying the evolution of the process in time; notwithstanding the formation of NPs is a time-dependent process. For example, the shape and size of the NPs depends on the number of pulses in the case of laser annealing^[4]. For the case of thermal annealing, the NPs size strongly depends on the interval of time in which the sample is inside the oven^[5]. In this work we study the formation of gold NPs by thermal and laser

annealing of thin films. Simultaneously we use pulsed- photoacoustic and laser scattering techniques to analyze in situ the synthesis of NPs during the annealing process. The influence of the initial film thickness on the size and size distribution of the resulting NPs was studied. The cumulative effect of the laser pulses and the temperature and annealing time were also analyzed. The changes in the photoacoustic signal and in the scattered intensity of the laser were compared with the SEM images of the samples. The current results suggest that both techniques are suitable for real time monitoring of the changes produced by the annealing. [1] M.J. Beliaty, S.J. Henley, S. Han, K. Gandhi, A.A.D.T. Adikaari, E. Stratakis, E. Kymakis, S.R.P. Silva, Phys. Chem. Chem. Phys., 15, 8237, 2013. [2] S. Imamovaa, N. Nedyalkov, A. Dikovska, P. Atanasov, M. Sawczak, R. Jendrzewski, G. Sliwinski, M. Obara, Appl. Surf. Sci., 257, 1075-1079, 2010. [3] C.V. Thompson, Annu. Rev. Mater. Res., 42, 399-434, 2012. [4] H. Krishna, N. Shirato, C. Favazza, R. Kalyanaraman, J. Mater. Res., 26(2), 154-169, 2011. [5] C. Worsch, M. Kracker, W. Wisniewski, C. Russel, Thin solid films 520, 4941-4946, 2012.

7:40pm **EH-WeE7 Mapping the Propagation of Excitons through Organic and Inorganic Light Harvesting Nano Composites**, *Alexander Weber-Bargioni*, *S.Y. Leblebici*, *J. Lee*, *M. Melli*, *W. Bao*, *K. Munechika*, *S. Barja*, *S. Aloni*, Lawrence Berkeley Lab, USA, *F. Intonti*, European Laboratory for Non Linear Spectroscopy, *D.F. Ogletree*, Lawrence Berkeley Lab, USA

Here we present unprecedented insight into the local exciton transport through organic and inorganic semiconducting nano building block assemblies using state of the art near field optics, hyperspectral mapping, and Field Effect Transistors to control the exciton transport electronically.

Controlling individual excitons and their deliberate movement through a material will provide the access to a new parameter space for the development of next generation light harvesting materials. Nano materials have in principle the potential to realize this vision due to their tuneability. However, the lack of spatial resolution has so far prevented the insight needed to control the transport of optically excited electronic states at their native length scale.

To study the local exciton transport we use optical antennae to locally excite our sample optically and map spatially independent the energy flow by detecting either the local photo luminescence or the local photo current. We use this approach to study exciton transport through three model systems: Inorganic nano wires, 2-D assemblies of inorganic nano crystals, and through organic PV materials.

In InP nanowire system we demonstrate that the transport is mediated by locally enhanced exciton recombination velocity due to charge puddles on nanowire surfaces. CdSe Quantum Dot assemblies are another excellent absorber material system for light harvesting purposes. We determined exciton transport length through well ordered 2-D films of CdSe Nano Crystals of 80 nm and 120 nm for the 1-D case, mediated by Foerster Resonance Energy Transfer (FRET). To develop a better understanding of FRET between quantum dots (which is still not really understood) we used a graphene Field Effect Transistor to study FRET between individual quantum dots and graphene. In this device we can systematically tune with high precision the distance between graphene and quantum dot and the electronic structure of the exciton adsorber (graphene), while building the currently smallest light switch in the world.

Exciton diffusion is also a key hurdle for the systematic development of Organic Photo Voltaic. We used our techniques to directly measure the exciton diffusion length in polymer (P3HT) and small molecule (rubrene) organic photo voltaic materials and show a crystallinity dependent exciton diffusion length that correlates to the OPV device power conversion efficiency. Furthermore we have evidence that local electric field gradient can modify the exciton diffusion length in organic semiconductors, where the exciton binding energy is large (1 eV) and the transport is mainly mediated by tunneling processes.

8:00pm **EH-WeE8 Probing Exciton Diffusion in Thin Film Organic Photovoltaics with Femtosecond Stimulated Raman Spectroscopy**, *P. Hoffman*, *Y. Leblebici*, *A. Mathies*, University of California Berkeley, *Adam Schwartzberg*, Lawrence Berkeley Lab, USA

The nature of the organic photovoltaic (OPV) bulk heterojunction interface, and how charge carriers diffuse through the individual components of this system, is of critical importance to understanding how these devices function, and how they can best be optimized. Using femtosecond stimulated Raman spectroscopy (FSRS), we have observed that in the MDMO-PPV/PCBM system there is a 150 fs time window during which excitons may propagate to the interfacial donor/acceptor region, despite the fact that the excitons persist for as much as 170 ps, greatly limiting the

mobility of exciton mobility and device performance. In addition, we have found that the charge transfer region where carriers efficiently pass from donor to acceptor is approximately one monolayer wide, significantly narrower than was previously believed. This understanding is possible through the examination of electron density and chemical modifications in the molecular species which we observe using the FSRS technique in thin film samples for the first time.

8:20pm **EH-WeE9 Correlating Local Morphology and Local Opto-Electronic Properties of Hybrid Organic-Inorganic Perovskite Solar Cell Materials**, *Sibel Leblebici, Y. Li, F.M. Toma, M. Melli, I. Shlesinger, I.D. Sharp, A. Weber-Bargioni*, Lawrence Berkeley Lab, USA

We demonstrate an in-depth characterization of local opto-electronic properties in hybrid organic-inorganic perovskite materials for solar cells using complementary scanning probe techniques.

Perovskite solar cells have the potential to combine high efficiency and low-cost fabrication compared to other third-generation solar technologies; Since 2009, power conversion efficiency of perovskite solar cells has rapidly increased from 3.8% to almost 20%. However, one of the main challenges to systematically increase power conversion efficiency and to develop cost efficient fabrication techniques is the lack of understanding of the exact operating mechanism in perovskite solar cells. In particular, the relationship between morphology, chemical composition, and optoelectronic processes and their impact on overall performance in these materials is hardly understood.

We have studied two promising solution processed hybrid organic-inorganic perovskite materials, $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$, using scanning probe techniques to determine local photocurrent generation, topography, and the local electronic structure. Depending on composition and fabrication approach, we observed substantial differences in local morphology, crystallinity, photocurrent generation, and photoluminescence. Specifically, we have measured a significant heterogeneity in the local photocurrent generation that does not correlate with topography but rather with the local electronic structure.

8:40pm **EH-WeE10 Oxide Heterojunction Electrodes for Sunlight Conversion and Storage**, *S. Kim, Hyunwoong Park*, Kyungpook National University, Korea

TiO_2 and WO_3 heterojunction electrodes are studied for their bifunctionality on harvesting light and storing energy. Both semiconductors are fabricated either 'single' (mixed) electrodes or two different electrodes galvanically coupled in a mixed electrolyte of 0.1 M sodium formate and 0.1 M sodium chloride. Irradiation of AM 1.5-light shifts the open circuit potentials (OCPs) of the mixed and coupled electrodes from around $-0.1\text{V}_{\text{SCE}}$ (dark OCPs) to a potential range between -0.8 and $-0.5\text{V}_{\text{SCE}}$, which slowly return to their respective dark OCPs over a period of around 14 hours. Such discharging periods are significantly influenced by the irradiation (photocharging) time and weight or area ratios of TiO_2 and WO_3 . When the TiO_2 and WO_3 mixed electrodes are galvanically coupled to stainless steel electrodes for application to anticorrosion, the mixed potentials of the couple are maintained at ca. $-0.4\text{V}_{\text{SCE}}$ over 10 hours even after light off. The measured galvanic currents verify that the photogenerated electrons of TiO_2 flow to WO_3 (charging) and even overflow to the steel (cathodic protection) during the irradiation, while the stored electrons at WO_3 flow to the galvanically coupled steel electrodes directly or through the TiO_2 upon light off. This research was financially supported by the Basic Science Research Program (NRF-2012R1A2A2A01004517) and Frame-work of International Cooperation Program (NRF-2013K2A1A2052901).

Authors Index

Bold page numbers indicate the presenter

— A —

Aloni, S.: EH-WeE7, 1
Alvarez-DelCastillo-Manzanos, F.A.C.M.: EH-WeE4, 1

— B —

Bao, W.: EH-WeE7, 1
Barja, S.: EH-WeE7, 1

— C —

Canales, A.C.: EH-WeE4, 1

— D —

de la Mora, B.: EH-WeE4, 1

— G —

García-Fernández, T.G.F.: EH-WeE4, 1
García-Segundo, C.G.S.: EH-WeE4, 1

— H —

Hoffman, P.: EH-WeE8, 1

— I —

Intonti, F.: EH-WeE7, 1

— K —

Kim, S.: EH-WeE10, 2

— L —

Leblebici, S.Y.: EH-WeE7, 1; EH-WeE9, 2
Leblebici, Y.: EH-WeE8, 1
Lee, J.: EH-WeE7, 1
Li, Y.: EH-WeE9, 2

— M —

Martínez-De León, J.M.DL.: EH-WeE4, 1
Mathies, A.: EH-WeE8, 1
Melli, M.: EH-WeE7, 1; EH-WeE9, 2
Munehika, K.: EH-WeE7, 1

— O —

Ogletree, D.F.: EH-WeE7, 1

— P —

Park, H.: EH-WeE10, 2

— S —

Sánchez-Aké, CSA.: EH-WeE4, 1
Schwartzberg, M.: EH-WeE8, 1
Sharp, I.D.: EH-WeE9, 2
Shlesinger, I.: EH-WeE9, 2

— T —

Tamura, M.: EH-WeE3, 1
Tenopala, F.T.: EH-WeE4, 1
Toma, F.M.: EH-WeE9, 2

— V —

Valverde-Alva, M.A.V.A.: EH-WeE4, 1
Villagrán-Muniz, MVM.: EH-WeE4, 1

— W —

Weber-Bargioni, A.: EH-WeE7, 1; EH-WeE9, 2