

Energy Harvesting & Storage

Room: Lehua - Session EH-MoM

Nano-based Approaches for Photovoltaics

Moderator: Jason Baxter, Drexel University, USA

8:40am **EH-MoM1 Thin Film Solar Cells from Colloidal Nanoparticle Dispersions**, *Eray Aydil, B. Chernomordik, N. Trejo*, University of Minnesota **INVITED**

The global installed capacity to generate electricity using solar cells has doubled every 2.5 years since 1975, an exponential growth similar to the Moore's law which states that the number of transistors on a computer chip doubles every 2 years.¹ Maintaining this aggressive Moore-like growth requires sustainable, high-throughput low-cost production of thin film solar cells. Copper zinc tin sulfide (Cu₂ZnSnS₄ or CZTS), copper zinc tin selenide (Cu₂ZnSnSe₄ or CZTSe) and their alloys (Cu₂ZnSn(S_xSe_{1-x})₄ or CZTSSe) are emerging as promising solar absorber materials for thin-film solar cells because they are comprised of earth abundant elements and can potentially help increase the solar electricity production to terawatt levels without the concerns associated with the toxicity and low abundance of the elements in the current commercial thin-film solar cells. A potentially high-throughput and low-cost approach to making thin polycrystalline CZTSSe films is through annealing of coatings cast from colloidal dispersions (inks) of CZTS nanocrystals in sulfur and/or selenium vapor. In this way, the nanocrystal coatings are transformed into polycrystalline films with micrometer size grains, a suitable morphology for making solar cells. The transformation of the nanocrystal coating to a polycrystalline coating is driven by the high surface area of the nanocrystals and, consequently, the high total surface energy of the nanocrystal coating. This approach is well suited for high throughput low-cost roll-to-roll manufacturing. However, many scientific and technical challenges remain. In this talk we will review the advances made towards this end and the remaining challenges. Specifically, we will describe our most recent findings on the effects of sulfidation/selenization time, temperature, sulfur and selenium vapor pressures, presence of alkali and carbon impurities on the microstructure of CZTSSe films.

¹ D. J. Norris and E. S. Aydil, "Getting Moore from Solar Cells," *Science* **338**, 625-626 (2012).

9:20am **EH-MoM3 XPS Analysis of Solution-Based Thin Films of Nano Structured Chalcogenides for Solar Cells Applications**, *F. Servando Aguirre-Tostado, R. Garza-Hernández*, CIMAV, Mexico **INVITED**

The employment of solution based methods for the deposition of semiconductor materials for solar cells applications comes with promise of enabling large area applications at the same time of driving down costs. The optimization of thin film semiconductors such as CuZnSnS requires the understanding of the structure and chemical reactions taking place during deposition of thin films and post-deposition thermal treatments. In this respect, X-ray photoelectron spectroscopy (XPS) is uniquely suited for tracking down chemical reactions occurring at the surface and interface of nanometric layers. The chemical analysis and thermal stability for surface and interface reactions of binary chalcogenide semiconductors is presented. CuS, ZnS, and SnS₂ thin films were deposited on top of CdS by the successive ionic layer absorption and reaction method (SILAR) in a glove-box attached to the XPS load-lock chamber for in-situ analyses. Step by step XPS analysis of the SILAR process reveals an incubation period that depends on temperature and ion concentrations. Multilayer structure stability is discussed in terms of chemical reactivity and diffusion of cations. Finally, a demonstration of how the obtained results can help to engineer a more stable structures is presented.

10:20am **EH-MoM6 Nanoscale Characterization of Defects and Interfaces in Thin Film Solar Cells**, *Mowafak Al-Jassim*, NREL

Thin-film solar cells based on polycrystalline CdTe, Cu(In,Ga)Se₂ (CIGS), and Cu₂ZnSnSe₄ (CZTSe) have demonstrated high solar-to-electricity conversion efficiencies. Typically, polycrystalline thin-film solar cells are expected to exhibit poor performance compared to their single-crystalline counterparts, due to the existence of unavoidable structural defects such as dislocations and grain boundaries (GBs). It is surprising, therefore, that CdTe-, CIGS-, and CZTSe-based polycrystalline thin-film solar cells have achieved higher efficiencies than their single-crystalline counterparts.

Here, we present our results on the study of the atomic structure and electronic properties of structural defects including stacking faults, twins, dislocations, and GBs in CdTe, CIGS, and CZTSe using a combination of

aberration-corrected scanning transmission electron microscopy (STEM) and first-principles density-functional theory calculation. Polycrystalline CdTe thin films were grown by closed-space sublimation, whereas CIGS and CZTSe thin films were deposited by co-evaporation. Atomic resolution scanning transmission electron microscopy (STEM) images were acquired with Nion UltraSTEM 100 and 200 microscopes. We found that intrinsic GBs in CdTe, CIGS, and CZTSe create deep levels mainly due to the anion-anion "wrong" bonding. However, these deep levels can be removed through extrinsic and/or intrinsic passivation. In addition to high resolution structural and chemical characterization, we will present data on the electrical and optoelectronic properties of defects obtained by a correlative approach that involves STEM, cryogenic cathodoluminescence defect spectroscopy and electron beam induced current imaging.

10:40am **EH-MoM7 Two-Step Thermal Annealing Improves the Morphology of Spin-Coated Films for Highly Efficient Perovskite Hybrid Photovoltaics**, *ChihPing Chen*, Ming Chi University of Technology, Taiwan, Republic of China

We describe the relationships between the morphologies and the power conversion efficiencies (PCE) of perovskite photovoltaics having a conventional p-i-n heterojunction structure, indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS)/CH₃NH₃PbI_{3-x}Cl_x/PC₆₁BM/Al. The PCE of such a device is highly dependent on the morphology of the perovskite film, which is governed by the concentrations of its precursors and the annealing conditions. A two-step annealing process allowed sufficient crystallization of the perovskite material, with a high coverage at a high precursor concentration. Relative to the device prepared using a one-step process (90 °C for 30 min), we observed a 60% increase in PCE for this optimized device. We observed a PCE of 10% of our optimized cells. Corresponding devices exhibited extremely high stability after long-term storage (>1368 h) in the dark in a N₂-filled glove box, with consistently high PCEs (AM 1.5G, 100 mW cm⁻²).

11:00am **EH-MoM8 Charge Transport in PbS Quantum Dot Arrays for Photovoltaic Applications**, *Miquel B. Salmeron*, Lawrence Berkeley Lab, USA **INVITED**

New forms of matter can be designed by combining nanoscale building blocks to create artificial solids with novel functionalities for device applications, such as field effect transistors, solar cells, photodetectors, and light emitting diodes. Artificial atoms or quantum dots (QDs) are ideal elements for this purpose since their electronic properties can be tuned through control of their size, shape and composition, while charge transport through QD assemblies can be engineered by controlling the hopping barrier between neighboring dots. However, fabrication of the QDs comprised of hundreds to thousands of atoms is inevitably imperfect and defects and impurities are always present. The nature of the defect states is unknown and the microscopic mechanisms of charge transport are far from being understood. In this presentation we show, by means of nanoscale imaging, spectroscopy, and density functional theory (DFT), that charge transport takes place in PbS QD arrays following percolation pathways that are spatially different for electrons and holes, electrons via in-gap states (IGS) instead of conduction band states, and holes via valence band states. This novel and exotic transport phenomenon is explained by the measured electronic structure and energy level alignment of the individual QDs. In contrast with previous hypothesis that surface stoichiometry and ligands are responsible for IGS, we found that the IGS are induced by adsorbed oxygen molecules whose p* states hybridize with QD valence band states, thus enabling inter-particle coupling and electron transport. We demonstrate that chemical treatments can be used for surface impurity engineering to achieve tunable electronic structure and transport properties.

11:40am **EH-MoM10 The Effect of n and p Delta Doping on InAs/GaAs Quantum Dot Solar Cell**, *W.J. Choi, HoSung Kim, S.H. Kim, J.D. Song*, Korea Institute of Science and Technology, Republic of Korea, *J.H. Park*, Korea University, Republic of Korea

The efficiency of single junction solar cells (SJSCs) is limited by Shockley-Queisser limit and intermediate band solar cell (IBSC) concept has been introduced in order to overcome the efficiency limit of conventional SJSC. For IBSC model, low dimensional semiconductor structures such as quantum wells and quantum dots (QDs) have been applied to the SJSC. Especially, self-assembled InAs QDs have been frequently applied to GaAs/AlGaAs SJSCs because QDs provide quantum confined states that lower the average band gap of the SJSCs to absorb longer wavelength light beyond GaAs band edge of 870 nm. Theoretical studies of QDSCs have suggested a maximum efficiency of 45 % under 1 sun and 63 % under 1000X concentration. Contrary to their expectations,

actual QDSC devices suffer from photocurrent loss due to inhomogeneous distribution in QD sizes and high carrier confinement of QDs. In order to solve these problems, n delta doping techniques on QDs have been investigated. Here, we introduce the result of QDSCs with n and p delta doping on QDs.

For this study, two types of SC samples were grown on N-GaAs substrate and P-GaAs substrate respectively by molecular beam epitaxy. The undoped and delta-doped QDSCs with doping density of $1 \times 10^{12} \text{ cm}^{-2}$ were prepared and every SC samples has spacer layer with thickness of 20 nm between InAs QD layer and delta doping layer. SC samples grown on N-GaAs and P-GaAs substrate were delta doped with Si and Be respectively. The InAs QDs were grown by modified Stranki-Krastanov growth method. With this growth technique, the QD size and density can be controlled by using the repetition period of a cycle.

The efficiency of QDSCs with and without Si delta doping are 13.6 % and 11.4 % respectively. The enhancement of the efficiency of QDSCs with Si delta doping is due to the increase of J_{sc} . This increase of J_{sc} is due to the n-delta doping and this enhances electron transitions in QDs and increase the carrier lifetime in QDs. The efficiency of QDSCs with and without Be delta doping are 8.45 % and 10.9 % respectively. Compare to the result of QDSCs grown on N-GaAs substrate, the efficiency of QDSCs with Be delta doping has been decreased. This could be attributed to the P delta doping. The Be delta doping induces suppression of the photocarrier generation in the radiative QDs because intentionally doped holes are strongly localized in the radiative QDs. We will present the result of the time-resolved photoluminescence of the QDSCs with Si and Be delta doping.

Tuesday Morning, December 9, 2014

Energy Harvesting & Storage

Room: Lehua - Session EH-TuM

Solar Cells

Moderator: Eray Aydil, University of Minnesota

8:40am **EH-TuM3 Understanding and Improving Solar Energy Conversion through Interface Engineering**, *Stacey Bent*, Stanford University, USA **INVITED**

Meeting the world's growing energy needs in a sustainable fashion is one of the most pressing problems of our time. The most abundant source of renewable energy is the sun, which can be converted directly to useful forms of energy such as electricity and fuels by photovoltaics and photoelectrocatalysts, respectively. In this talk, we will discuss the use of nanoscale materials in solar energy conversion, and in particular the role of interface engineering in improving conversion efficiencies. Quantum dots (QDs), which are nanoscale materials typically based on low-band-gap metal chalcogenides, have been widely explored for next generation solar absorbers due to their tunable band gap and high absorption coefficient. Colloidal quantum dot (CQD) solar cells made from lead sulfide (PbS) QDs have achieved a power efficiency of ~ 8%. In these devices, it is important to control the band gap as well the band position of the QDs to efficiently inject electrons and holes into their respective electrodes. We will describe experimental and theoretical studies of the effects of interface engineering through surface ligand modification on the band gap and relative band positions in lead chalcogenide (PbSe_xSi_{1-x}) QDs. Multilayer CQD solar cells were fabricated to investigate the effect on carrier collection of QD layers with different relative band positions. We will show that interface engineering can be applied to lead chalcogenide QDs in order to create a favorable band diagram and achieve enhanced photogenerated carrier collection in multilayer CQD devices.

9:20am **EH-TuM5 Understanding Carrier Dynamics in Cu₂ZnSn(S,Se)₄ Using Time-Resolved Terahertz Spectroscopy**, *G.W. Guglietta*, Drexel University, USA, *K. Roy Choudhury*, *J.V. Caspar*, DuPont Central Research and Development, USA, *Jason Baxter*, Drexel University, USA

We have used time-resolved terahertz spectroscopy (TRTS) to measure lifetimes and determine recombination mechanisms in Cu₂ZnSn(S,Se)₄ (CZTSSe) thin films fabricated from nanocrystal inks. TRTS probes photoconductivity on femtosecond to nanosecond time scales that are relevant for recombination in thin film photovoltaics. Terahertz frequencies (0.2-2.5 THz) correspond to typical scattering rates in semiconductors, enabling determination of carrier density and mobility. Ultrafast time resolution permits tracking the evolution of carrier density to determine recombination mechanisms. By manipulating the photoexcitation wavelength and fluence, we can tailor the generation profile of photoexcited carriers to distinguish between surface, Shockley-Read-Hall (SRH), and Auger recombination mechanisms and determine rate constants.

TRTS experiments and modeling were used to understand the role of recombination mechanisms and their contribution to CZTSSe photovoltaic performance. TRTS photoconductivity shows an instrument-limited onset within 1 ps of an ultrafast pump pulse, followed by a slow decay over nanoseconds. Photoconductivity decay kinetics were fit with a bi-exponential model with two time constants and a weight fraction. The short time constant is typically ~200 ps and roughly corresponds to diffusion to and recombination at the surface. The long time constant is typically ~2 ns and is attributed to SRH recombination. Assignment of these mechanisms is supported by the dependence of kinetics upon excitation fluence and wavelength. Normalized kinetics are independent of fluence over a range of 40x, indicating that no Auger recombination is occurring. Without Auger recombination, we can distinguish between surface and SRH rates by tuning the pump wavelength. As the excitation wavelength is shifted towards the blue, carriers are generated nearer to the front surface and the photoconductivity kinetics are sensitive to the surface recombination velocity. With blue excitation, we see that a larger fraction, ~0.5, of carriers recombine with a short time constant. With redder excitation wavelengths, the carriers are generated more evenly throughout the film and the kinetics are dominated by SRH recombination with the long time constant having a majority of the weight fraction, ~0.8. TRTS provides a pathway to determine performance-limiting recombination mechanisms and measure key parameters like SRH lifetime and surface recombination velocity, helping to direct the design of efficient thin film photovoltaics.

9:40am **EH-TuM6 The CdS/CdTe Solar Cell with the Back Contact Protected by ITO/Mo**, *Juan Peña*, *V. Rejón*, Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional, Mexico, *M. Riech*, Universidad Autónoma de Yucatán, Mexico, *N. Hernández-Rodríguez*, Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional, Mexico

Today CdS/CdTe heterojunction is an important photovoltaic system for conversion of solar energy. Due to the simple techniques used for thin films deposition, it has been brought from laboratory to industrial scale. Although the thin films are deposited by using techniques such as sputtering and CSS, the back contact layers are a challenge in both: the formation of an ohmic contact and that endures a long time. There are several prospects for back contacts using Mo as can be seen in [1]. The solar cell with Cu/Mo as a back contact deposited by using rf-sputtering is reported in [2]. There are few researches that studied how Mo film can be protected against oxidation without adding series resistance. The bilayer Mo/ITO has been used in microelectronics devices [3].

In this work, the CdS/CdTe solar cells that uses Cu/Mo as back contact is investigated. It is shown that the formation of MoO_x at surface of Mo thin film influences the series resistance. The oxide is formed when the solar cell is used at outdoor conditions without any encapsulation. Here some indoor experiments were made. First, we show how the Mo/Glass film is oxidized when it is annealed at 400 °C in air. Second, how the Mo is degraded at same conditions when it is used on CdTe/CdS cell and annealed at same conditions. Third, how ITO works when it is deposited over of Mo on the solar cell. Preliminary results indicates that the ITO avoids the formation of MoO_x and mechanical scratching, preserves its electrical properties and the solar cell shows good stability after an annealing at 400 °C.

The films Cu, Mo and ITO were deposited by rf-sputtering. We show evidences that the p-n junction remains working properly and the oxidation of Mo is the main cause of the cell efficiency degradation. By using the thin film of ITO on Mo layer all solar cell characteristics are preserved. The CdTe film was grown by conventional CSS technique. The cells were activated by using CHClF₂-argon-oxygen gases. DRX spectra and HR-SEM were made for Mo/Glass and ITO/Mo/CdTe structure before and after annealing at 400 °C in air.

Acknowledgement

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References

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- [3] H. Piao, et al. *Surface and Interface Analysis*, vol. 39, pp. 493-500, 2007.

10:20am **EH-TuM8 Study of Energy Level Alignment at Electrode Interfaces in Organic Solar Cells**, *Takeaki Sakurai*, *S. Wang*, *T. Miyazawa*, *H. Xia*, *W. Fu*, *K. Akimoto*, University of Tsukuba, Japan **INVITED**

Control of electrical properties at organic semiconductor/metal electrode interfaces is one of the significant issues for improving performances of the organic solar cells since it has an influence on carrier extraction and exciton quenching. In small molecule based organic solar cells, bathocuproine (BCP) is used well as a buffer layer between C₆₀ and metal cathode to improve the device efficiency. Lifetime and the stability of the device with BCP buffer layer, however, are not good for the practical application. To obtain the strategies for the development of the effective buffer layer, we have investigated the electronic structures at the interfaces between C₆₀ and a large variety of organic semiconductors by means of synchrotron based in-situ ultraviolet photoelectron spectroscopy. The C₆₀/buffer/Ag heterostructures were formed by depositing buffer materials on Ag and subsequently depositing C₆₀ onto buffer/Ag stack layer in a step-by-step way in a vacuum deposition chamber. A series of perylene derivatives (PTCDA, PTCDI and PTCBI), TCNQ derivatives (TCNQ and F4TCNQ) and pyridine based acceptor molecules (BCP, TPBi and TAZ) were applied as buffer layers. For all buffer/Ag stack structures, the LUMO level of buffer layers almost accords with Fermi level of Ag, that is, electron is easily transferred from the Ag electrode to the buffer layers due to the disappearance of the electron injection barrier. In contrast, the electron injection barrier height between LUMO of C₆₀ and LUMO of buffer materials correlates with the work function of the buffer/Ag stack structures

(Φ_{buff}). We conclude that to select a buffer/Ag heterostructure with low work function is important in order to maintain good electric contact near Ag cathode. The detailed physical mechanism about the energy level alignment will be discussed using charge transfer model.

11:00am **EH-TuM10 n-type Thin Film WSe₂ for use in Homojunction WSe₂ Solar Cells**, *A. Sarkar, Natale Ianno, R.J. Soukup*, University of Nebraska-Lincoln

Previously we have shown that as-grown p-type thin film WSe₂ is an excellent candidate for an earth abundant photovoltaic absorber.¹ The vast majority of thin solar cells are heterojunction devices with a wide band gap n-type window layer. Many of the device issues are centered on the heterojunction interface, making a homojunction more desirable. The problem here is growing n-type material in thin film systems. In this work we present the structural, optical, and electrical properties of n-type thin film WSe₂ grown via the selenization of sputter deposited copper doped tungsten films. We will show that highly textured films with an optical band gap in range of 1.45 eV, and absorption coefficients greater than 10⁵/cm across the visible spectrum can be easily achieved. In addition we will present Hall Effect and carrier density measurements as a measure of film quality. We employ these results to numerically simulate homojunction solar cells based on this material, where we will show efficiencies greater than 20% are possible.

1. Q. Ma, H. Kyureghian, J. D. Banninga and N. J. Ianno, MRS Proceedings , Volume 1670 , 2014. DOI: <http://dx.doi.org/10.1557/opl.2014.477>

11:20am **EH-TuM11 Samarium Sulfide-Cerium Sulfide, A Potential Band Gap Variable Alloy System for Use in Spectrum Splitting Photovoltaic Systems**, *Rodney Soukup, N.J. Ianno, F. Urias-Cordero, C. Berger, A. Sarkar, M. Hilfiker*, University of Nebraska-Lincoln

A new research thrust to obtaining high efficiency photovoltaic systems is spectrum splitting, where the input solar radiation is physically separated via input optics and channeled to a planar array of individual cells, each with a band gap tuned to absorb a specific band width of radiation. This approach allows for simpler device fabrication and a wider breadth of band gaps than the common multi-junction design, in exchange for a complex optics structure to separate the incoming light. Both these approaches require high efficiency cells over a broad range of band gaps. Currently this is met by III-V alloy single crystal cells and while significant advances have been made in reducing the fabrication cost, recent best estimates place their cost at 1-5x single crystal silicon cells. In addition many of these materials contain indium, whose supply may be limited.

In order for the multi-junction and split spectrum designs to fully realize their potential, it is necessary to explore other classes of semiconducting materials with tunable band gap, better crustal abundance and lower production costs. The Sm_{2-x}Ce_xS₃ alloy system with its potentially broad band gap range (0.8-1.9 eV), as grown p-type majority carrier, potentially excellent optoelectronic properties in polycrystalline form and abundance is an excellent candidate. We will present preliminary data on the growth, optical and electrical properties of thin film Sm₂S₃, and Ce₂S₃ as an initial study of the alloy formation.

Energy Harvesting & Storage

Room: Mauka - Session EH-TuP

Energy Harvesting & Storage Poster Session

EH-TuP4 Synthesis and Hydrogen Properties of Beryllium Intermetallic Compound, Jae-Hwan Kim, Japan Atomic Energy Agency, Japan, *H. Iwakiri*, University of the Ryukyus, Japan, *M. Nakamichi*, Japan Atomic Energy Agency

Beryllium intermetallic compounds have shown a variety of excellent properties, such as neutron multiplier, refractory function, hydrogen storage, superconductivity and so on. Be_{12}M compounds ($\text{M}=\text{Ti}, \text{V}$ and Zr) have been investigated as neutron multiplier in fields of fusion reactor while Be_{17}M_2 compounds have been focused on refractory materials. In addition, Be_2M have been known as a Laves phase which is characterized by an A_2B type compound performing higher H_2 gas storage potential. Although great interest on hydrogen properties of Be_2M owing to its lower density has been aroused from viewpoints of reactivity with H_2O , trap site of hydrogen and amount of H_2 gas in this compound, few studies on the Be_2M found and its data base is still unsatisfactory.

In this study, we report on preliminary synthesis of Be_2Ti compound and its properties, such as hydrogen generation due to reaction with H_2O and hydrogen storage. Additionally, first principles calculation of hydrogen trap site in this compound was carried out in order to compare to empirical data.

X-ray diffraction profiles and electron probe micro-analysis results clarify that the preliminary synthesis of Be_2Ti was successful by homogenization treatment and plasma sintering. Hydrogen generation rate of the Be_2Ti by a reaction with 1 % H_2O increased as test temperature increased. High temperature exposure with H_2O leads to formation of TiO_2 on the surface. In addition, hydrogen storage result of Be_2Ti evaluated by pressure-concentration-temperature curve depicts that Be_2Ti indicated H_2 gas storage concentration with 1.6 w.t. % at 323 K when the H_2 pressure increases up to 10 MPa. According to the first principle calculation, there were two hydrogen trap sites, tetrahedron and center of triangle with solidus energies of -0.52 and -0.05 eV, respectively, indicating maximum trap site with 5.4 w.t. %.

EH-TuP5 Characterization of Real Cyclic Performance of Air Electrode for Li-Air Batteries, DaeHo Yoon, Y.J. Park, Kyonggi University, Republic of Korea

In this study, we characterized the cyclic performance of an air electrode employing a carbon nanotube (CNT)/ Co_3O_4 nanocomposite. The lithium anode and electrolyte were replaced every 50 cycles in order to exclude the effect of a corrupted anode and electrolyte and to determine the "real" cyclic performance of the electrode. The overpotential of the cells increased during the first 50 cycles; however, it almost vanished when the lithium anode and electrolyte were replaced. This result indicates that the increased overpotential of the cells during cycling is highly attributed to the corrupted lithium anode and electrolyte [1, 2]. The cycle life of the cell also significantly increased upon replacement of the lithium anode and electrolyte. This confirms that air electrodes have the ability to maintain their designated capacity (such as $1000 \text{ mAh} \cdot \text{g}_{\text{electrode}}^{-1}$) for much longer cycles if the lithium anode and electrolyte can be made more stable. A polydopamine-coated electrode and a LiI-containing electrolyte were introduced and characterized in order to obtain enhanced cyclic performance of the air electrode.

References

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EH-TuP6 Nano-Sized $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.16}\text{Mn}_{0.56}\text{Co}_{0.08}]\text{O}_2$ /Carbon Composite for Improving Electrochemistry Performance, S.B. Lim, Kyonggi University, *YongJoon Park*, Kyonggi University, Republic of Korea

Since the commercialization of lithium ion battery, development of cathode materials with high capacity has been one of the important factors for enhancing the performance of that. Lithium rich compounds are promising cathode materials due to their high capacity for satisfying demand of high-capacity batteries. However, they have several disadvantages to overcome for commercialization such as poor rate capability, low cyclic performance, and low stability. In this study, we prepared nano-sized $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.16}\text{Mn}_{0.56}\text{Co}_{0.08}]\text{O}_2$ /carbon composite for enhanced electrochemical performance such as rate capability. A general method to improve the surface electronic conductivity and enhance the rate capability of cathode is

carbon coating. The carbon coating by in-situ carbonization from organic precursors has been successfully applied to LiFePO_4 . However, it is difficult to apply to Li-rich compounds because they will lose oxygen during carbonization. That is why we introduced composite between cathode and carbon, instead of carbon coating. In this work, super P, a commercial carbon, was composed with nano-sized $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.16}\text{Mn}_{0.56}\text{Co}_{0.08}]\text{O}_2$. Nano-sized powders were synthesized by combustion method using surfactants (HPC and Gelatin) to disperse the granule particles [1-3]. The polydopamine pre-coating layer was used as a binding agent between cathode powder and super P [4-8]. Nano-sized $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.16}\text{Mn}_{0.56}\text{Co}_{0.08}]\text{O}_2$ /Super P composite is expected to exhibit improved rate capability because of dispersed nano-sized lithium rich particles and good electronic conductivity attributed to Super P.

References

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EH-TuP8 Fabrication of Structured Organic Solar Cell with Patterned ITO Electrode and Study of Their Effect on Power Conversion Efficiency, Jin-Hyo Boo, J.S. Lee, Sungkyunkwan University, Korea

In organic photovoltaics (OPVs), there is a competition between the reduction of absorber thickness and the improvement of the probability of carrier collection. To overcome the competition a highly structured interface is highly desirable. However, a solution-based soft-lithography processing resulted in non-uniform structured surfaces. In this report, we proposed and demonstrated a silica-templated soft-lithographical approach for structuring well-defined and controllable transparent ITO layer for enhancing power conversion efficiency (PCE). Also, we focused on the morphological effects of the patterned ITO on optical properties and PCE.

The brief experimental scheme is as follow. First, close-packed PS nanospheres were formed on a cleaned ITO glass substrate by using gas-liquid-solid interfacial self-assembly method and drying for 3days in vacuum desiccator. After that, PS covered ITO glass was etched at 65°C with TIN etching solution. Finally, PEDOT:PSS, P3HT:PCBM, and Al electrode were gradually deposited.

The morphology, optical, electric, and cell properties are investigated by FE-SEM, AFM, UV-VIS spectrophotometer, Haze measurement, and solar simulator.

EH-TuP9 Supercapacitive Properties of 2D-arrayed Inverse-Opal Nanostructure of Manganese Oxide, Ilhwan Ryu, D. Park, G. Kim, S. Yim, Kookmin University, Republic of Korea

Supercapacitor has attracted growing attention as an important energy conversion and storage device which basically consists of current collector, electrolyte and active materials. Manganese oxide (MnO_2) is one of the most promising active materials due to its environmentally friendly characteristic and low price. Fabrication of nanostructured active materials has also been widely studied since it can provide large surface area and short diffusion path for ions and electrons, and hence improve the capacitive properties of the supercapacitors. In this work, we fabricated well-ordered MnO_2 inverse-opal nanostructures using two-dimensionally arrayed polystyrene nanospheres. We also investigated their optical, morphological and electrochemical properties, and compared them with the properties of the device based on the planar MnO_2 films.

EH-TuP10 Inorganic-organic Core-Shell Nanowire Solar Cells with Excellent Light-Trapping Properties, Keisuke Sato, Tokyo Denki University, Japan, *M. Dutta, N. Fukata*, National Institute for Materials Science, Japan

Development of solar cells using one-dimensional architecture, such as semiconductor nanowires (NWs), have been proceeding rapidly in recent years. The main advantage of such NWs-based solar cells is that they cause greater light absorption (minimal reflectivity) due to incident light-trapping within the NW arrays. This phenomenon is most glaringly apparent in silicon nanowires (SiNWs)-based solar cells, leading to higher absorbance per unit thickness than achieved by commercial crystalline Si solar cells. Thus, the introduction of the SiNW arrays with high light-trapping properties enable lower-cost cell production due to the massive reduction of the consumption of Si materials needed for cell fabrication. We have developed inorganic-organic core-shell NW solar cells in which the vertically-aligned SiNWs were surrounded by organic poly(3,4-

ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) layer in order to further facilitate the cell fabrication. We report herein on the cell performances of Si-PEDOT:PSS core-shell NW solar cells with excellent light-trapping properties. To investigate the light-trapping capability, the lengths of the core-shell NWs were varied within the range from 2 to 8 μm . In the core-shell NWs with shorter length of 2 μm , the reflectance were suppressed to below 8%, which is extremely lower than the crystalline Si with value of 31%, over a wide spectrum range between 300 and 1000 nm. This suppression is far more effective for longer NW length, resulting in a reflectance of below 4.6% for the core-shell NWs with longer length of 8 μm . These results demonstrate that the longer core-shell NW arrays can extend the broadband anti-reflection effect due to enhanced light-trapping in NW arrays. However, the cell performances of such core-shell NW solar cells closely were intimately related to the NW length-dependent carrier transport efficiency rather than the light-trapping effects. The core-shell NW solar cells with shorter length of 2 μm exhibited the best cell performance with a power conversion efficiency (PCE) of approximately 7%, exceeding those with longer length of 8 μm (PCE of 3.7%). The depression of cell performance with the increase in the NW length was caused by inefficient carrier collection at electrodes due to the enhancement of the carrier recombination, because the transportation distances to electrodes were increased with NW length. Therefore, we suggest that it is important to simultaneously tune the NW length and light-trapping properties to be able to fabricate efficient inorganic-organic core-shell NW solar cells.

EH-TuP11 Characterization of Zn(O,S) Buffer Layers for Cu(In,Ga)Se₂ Solar Cells. *JiHyun Choi, S.M. Hwang, A. Garay Dixon, C.W. Chung, Inha University*

In photovoltaic solar cell, CdS thin films are mostly used buffer layer due to their wide direct band gap (~2.42 eV). The CdS buffer layers which form a p-n junction with absorber layer are deposited by using a variety of deposition methods such as chemical bath deposition (CBD), spray pyrolysis, vacuum-evaporation and sputtering. Among these techniques, chemical bath deposition is widely used method due to its advantage such as easy and inexpensive process. However, CBD technique also has some disadvantages including production of toxic liquid waste containing Cd and ammonia and difficulty in application to mass production scale. In addition, CBD method should be done in liquid phase, so that it can oxidize the absorber layer.

To overcome these disadvantages of CBD method and to apply for large scale deposition, sputtering of Zn(O,S) thin films was proposed. Sputtering method of Zn(O,S) films can reduce the liquid wastes and save the deposition time for fast deposition. It enables all processes for solar cells to be carried out by vacuum processes without exposure to air. In addition, Zn(O,S) thin films can replace the CdS which contains a toxic Cd. Generally, Zn(O,S) thin films can be deposited by sputtering with pure ZnS target by adding oxygen or by co-sputtering using ZnO and ZnS targets. ZnS itself has very high band gap about 3.6 eV, so that oxygen should be added to control the band gap. Currently, their electrical and optical properties of the sputtered Zn(O,S) films have not been fully studied yet.

In this study, Zn(O,S) thin films are deposited on Cu(In,Ga)Se₂ layer and glass substrate by RF sputtering in O₂/Ar atmosphere using pure ZnS target. By varying the deposition parameters including O₂ concentration in O₂/Ar, deposition pressure and RF power, the electrical, optical properties and the morphology of the sputtered Zn(O,S) films were investigated. From this research, the optimal condition for Zn(O,S) buffer layer using sputter method will be obtained.

EH-TuP12 Formation of CuInSe₂ from Cu-Se and In-Se binary compounds by wet process for solar cell application. *Hyungmin Lee, D.-S. Jeong, C. Park, Yeungnam University, Republic of Korea*

CIS was synthesized from binary compound of CuCl, InCl and selenium powder using alcohols as solvent. CIS thin film was prepared by mixing powders of Cu-Se and In-Se binary phase and heat treatment. The binary precursors such as CuSe, InSe and In₂Se₃ were synthesized using facile chemical route from suitable resources at different stoichiometric ratios. And then, high-quality CIS absorption layer was formed by using three binary compounds. The properties of CIS films were studied and characterized, systematically. The structural and optical properties of CIS films were studied by using X-ray Diffraction, photoluminescence (PL), and UV-Vis. The surface morphological property of the films was also recorded by Scanning Electron Microscope (SEM). The CIS solar cells having the structure of Soda lime glass (SLG) / Mo / CIS / CdS / i-ZnO / Al-doped ZnO (AZO) / Al metal grid was then fabricated. The solar cells' current density-voltage (J-V) characteristics were investigated both in the dark and under AM1.5G illumination by a solar simulator (Keithley 69911).
Keywords: CuInSe₂, Binary compound, Solar cell, Wet process, Photoluminescence
Acknowledgment This work was supported by the New & Renewable Energy Core Technology Program of the Korea Institute of

Energy Technology Evaluation (No. 20133030011330) and the Human Resources Development Program (No. 20104010100580) Planning (KETEP), granted financial resource from the Ministry of Trade, Industry & Energy, Republic of Korea.

EH-TuP13 In-situ Investigation of phase Evolution during Cu₂ZnSnSe₄ Thin Film Photovoltaic Absorber Formation from Various Stacked Cu-Zn-Sn Precursors. *Hyeonwook Park, J. Han, W.K. Kim, Yeungnam University, Republic of Korea*

For several decades, chalcopyrite Cu(InGa)Se₂ (CIGS) thin films were considered as a potential candidate for use as light absorbers in high-efficiency thin film photovoltaic cells. Recently, a cell efficiency of 20.9% (Solar Frontier, 2014), which is a little bit higher than multi-crystalline Si cells (20.4%), has been reported. Over the last decade, great attention has been moved to kesterite Cu₂ZnSn(S,Se)₄ (CZTSSe) as a promising low-cost alternative to chalcopyrite CIGS. In this paper, temperatur-dependent reaction pathways to kesterite Cu₂ZnSnSe₄ (CZTSe) thin film photovoltaic absorber formation by selenization of various stacked precursor structures including (Cu+Sn)/Zn and (Cu+Zn)/Sn were systematically investigated using in-situ high-temperature X-ray diffraction system, consisting of a PANalytical X'pert Pro MPD diffractometer and an Anton Paar HTK 1200 N furnace. A custom-designed graphite dome was utilized in order to create Se vapor at the elevated temperatures and minimize the loss of vaporized Se. Furthermore, CZTSe films formed by selenization of stacked Cu-Zn-Sn/Se precursors were characterized by X-ray diffraction and raman spectroscopy. The results revealed that the formation temperature of CZTSe and detailed phase evolution would be affected by stacked structure of Cu-Zn-Sn. Furthermore, precursor structure with co-sputtered Cu and Sn (e.g., (Cu+Sn)/Zn and Zn/(Cu+Sn)) could reduce Sn loss effectively during the formation of CZTSe than that with single-layered Sn (e.g., (Cu+Zn)/Sn and Sn/(Cu+Zn))

EH-TuP14 Feasibility Study on Graphene as Back Contact for Cu(InGa)Se₂ Thin Film Solar Cells. *Hee-San Ryu, K. Moon, Yeungnam University, Republic of Korea, Y. Jun, J. Kim, Korea University, Republic of Korea, W.K. Kim, Yeungnam University, Republic of Korea*

Chalcopyrite Cu(InGa)Se₂ (CIGS) solar cells have been considered as the most promising thin film solar cell, holding a record cell efficiency of 20.9% (Solar Frontier, 2014), which is slightly higher than that of multi-crystalline Si solar cells (20.4%). Molybdenum (Mo) is the most common material used as a back contact electrode for CIGS solar cells due to its low cost and electrical suitability with CIGS layer. In this paper, mono- or multi-layer graphene has been explored as an alternative back contact electrode to replace Mo layer. As a back contact electrode, graphene has many attractive properties such as high flexibility, excellent optical transmittance, low resistance, and high mechanical and chemical stabilities. In particular, transparent back contact like a graphene is essential to bifacial photovoltaic cells that can absorb lights from the front and back sides. In this study, the graphene films produced by chemical vapor deposition process on Cu foil were transferred onto soda-lime glass substrate using a simple wet-based transfer process. Graphene-coated glass was analyzed by tape test, four point probe measurement and UV visible spectroscopy to evaluate adhesion strength, resistance and transparency, respectively. CIGS absorbers were then deposited onto graphene-coated glass by using 3-stage co-evaporation process in a vacuum evaporator. A series of characterizations including X-ray diffraction, scanning electron microscopy and raman spectroscopy were performed to investigate the effect of number of graphene layers (e.g., 1, 2 and 4 layers) on the formation of chalcopyrite CIGS structure, and compare the characteristics of CIGS absorbers on different back contacts, graphene vs. Mo layers.

EH-TuP15 SnO₂ Hollow Spheres with Core-Shell Nanostructures of TiO₂ Nanosheets for Dye-Sensitized Solar Cells. *J.Y. Lim, S.H. Ahn, C.H. Park, Jong Hak Kim, Yonsei University, Korea*

In this study, SnO₂ hollow spheres were synthesized using sulfonated polystyrene (PS) as template. After sintering at 450oC for removing PS, SnO₂ hollow spheres were dispersed in isopropyl alcohol with amounts of titanium isopropoxide and diethyltrilamine followed by transferring to Teflon-lined autoclave. The mixture was heated to 200 oC and maintained for 24 hour, centrifuged, and calcined to obtain a highly crystalline phase. These preformed SnO₂ hollow spheres with core-shell nanostructures of TiO₂ nanosheets were mixed with sol-gel solution of graft copolymer PVC-g-POEM for preparing photoanode of DSSC. The solution was deposited on FTO glasses by doctor-blade method. These core-shell nanostructures were uniformly distributed in the TiO₂ film with large pores, high porosity, and good inter-connectivity due to its relatively low density resulting from high porosity and empty voids inside the shell. Nanostructures of SnO₂ hollow spheres with core-shell nanostructures of TiO₂ nanosheets provide good pore-filling for solid polymer electrolytes, faster electron transfer, and enhanced light scattering, as confirmed by reflectance spectroscopy,

incident photon-to-electron conversion efficiency (IPCE), and intensity-modulated photocurrent spectroscopy (IMPS) / intensity-modulated photo voltage spectroscopy (IMVS). DSSC with this material shows a high-energy conversion efficiency of 8.2% at 100 mWcm⁻². This is one of highest values for N719-based, solid-state, dye-sensitized solar cells.

EH-TuP16 Effect of MoN Diffusion Barrier on High Temperature Selenization of Cu(In,Ga). *Min-Su Kwon, H.-G. Kim, S.-H. Kim, C.-W. Jeon,* Yeungnam University, Republic of Korea

In commercial manufacturing of CIGS photovoltaic module, the absorber films are usually produced by sputtering and selenization/sulfurization process. During high temperature selenization above 450 °C, the surface of Mo back contact is easily transformed to MoSe₂, which is beneficial for ohmic contact formation in Mo/CIGS interface.[1] Although MoSe₂ has a high resistance, because it is a semiconductor of having bandgap energy of 1.35~1.41 eV, the thin layer of 100nm or less does not adversely affect the characteristics of solar cell.[2] However, since MoSe₂ may provide a current blocking capability when thicker than 200nm, it is necessary to control the thickness of the MoSe₂. In this study, Mo/MoxN/Mo multi-layer back contact was selenized to evaluate capability of diffusion barrier of MoxN layer to prevent the excessive MoSe₂ formation. The CIGS absorber films were obtained by solid state selenization, where a sputtered CuInGa alloy film on Mo/MoxN/Mo/glass was subsequently selenized at 460~560 °C for 10 minutes by using Se vapor. Behavior of generated MoSe₂ was analyzed by using XRD, SEM. The conducting compound of MoxN as a diffusion barrier against Se was deposited by a reactive sputtering. The thickness and N content of MoxN was found to be linearly proportional to N₂ gas flow rate, which suggests that MoxN could be easily adjusted by a simple modification of Mo formation process. As a result of selenization, because of the formation of MoSe₂, thickness of Mo mono-layer precursor was abruptly increased. But the thickness of multi-layered back contact with MoxN was not changed significantly. Therefore, as a diffusion barrier, MoxN was confirmed to be excellent diffusion barrier that is suited for a high temperature selenization process. The effect of MoxN layer on solar cell performance will be discussed. Acknowledgements This research was financially supported by the Ministry of Knowledge Economy(MKE), Korea Institute for Advancement of Technology(KIAT) and Dae-Gyeong Leading Industry Office through the Leading Industry Development for Economic Region). References [1] P.J. Rostan*, J.Mattheis, G.Bilger, U. Rau, J.H. Werner, Thin Solid Films Volume 480-481, Pages 67-70(2005). [2] SeJin Ahn, Ki hyun Kim, Jae Ho Yun, and Kyung Hoon Yoon, Journal of Applied Physics 105, 113533(2009)

EH-TuP17 Nano-patterned Pt Counter electrode Enhancing Light harvesting for Dye-Sensitized Solar Cells, *Won Seok Chi, D.J. Kim, J.P. Jung, J.H. Kim,* Yonsei University, Korea

Nano-patterning is one of the most simple and effective techniques for efficiently light trapping to boost the energy conversion efficiency. By imprinting with poly(dimethyl siloxane) (PDMS) nanostamp cross-rotate two steps onto thin layered commercial TiO₂ paste, a mesh-shaped (200 nm × 200nm) TiO₂ scaffold electrode with a large area was fabricated. Platinum (Pt) nanoparticles deposited onto TiO₂ pattern by diverse method such as sputtering, thermal deposition and UV-radiation deposition. The Pt nanoparticles distribution as mesh-shaped structure onto counter electrode was characterized by a field emission scanning electron microscope (FE-SEM) and an atomic force microscope (AFM). Moreover, the light trapping ability was measured reflectance by comparison of mesh-shaped patterned and non-patterned counter electrode as a function of angle. For the four cases : 1) patterned Pt counter electrode by sputtering, 2) non-patterned Pt counter electrode by sputtering, 3) non-patterned Pt counter electrode by thermal deposition and 4) patterned counter electrode by UV-radiation deposition were fabricated for all-solid-state dye-sensitized solar cells (ssDSSCs). Among them, patterned Pt counter electrode by sputtering assembled solar cell showed highest solar energy conversion efficiency up to 7.0%. This remarkable result, observed for N719 dye based DSSC, was due to enhanced light harvesting and superior surface area confirmed by incident photon-to current efficiency (IPCE), electrochemical impedance spectroscopy (EIS), and cyclic voltammetry (CV) measurements. More importantly, we believe this approach is universally applicable to a variety of electrochemical cells requiring Pt catalysts such as fuel cells and catalytic chemical reactors. Furthermore, this process could include nano- and micro-sized patterns and can be extended to metal nanoparticles other than Pt.

Tuesday Afternoon, December 9, 2014

Energy Harvesting & Storage

Room: Lehua - Session EH-TuE

Batteries, Capacitors & Storage Materials

Moderator: Stacey Bent, Stanford University, USA

5:40pm **EH-TuE1 Electrochemical Deposition of Organic-inorganic Composites for Supercapacitors**, *M. Bai, Xiaoxia Liu*, Northeastern University, China

Electrochemical Deposition of Organic-inorganic Composites for Supercapacitors

Ming-Hua Bai, [Xiaoxia Liu*](#)

Department of Chemistry, Northeastern University, Shenyang, 110819, China

Electrochemical capacitors (supercapacitors) are widely recognized as an important class of energy storage devices. Development of high performance supercapacitors is highly desirable to meet the increasing demand for energy storage devices. Conducting polymers, including polyaniline (PANI) and polypyrrole (PPy) have promising applications in a variety of technological fields, including supercapacitor. One-dimensional (1D) growth control of conducting polymer, directing to polymer nanofibers, has aroused great interest because an ordered arrangement of the polymer chains favours higher conductivity and better performance in charge storage. The growth of nanofibers is known to be intrinsic to PANI, however heterogeneous nucleation on the initially-formed PANI nanofibers would result in irregularly-shaped PANI particles. The suppression of this overgrowth on the surface active sites of initially-formed PANI nanofibers has been achieved by some chemical polymerization methods, including aqueous/organic interfacial polymerization, rapidly-mixed reactions, which led to the formation of nanofibrous PANI. However, only nonfibrillar, granular powder PPy can be yielded by these methods since fibrillar structure is not intrinsic for PPy and so it is very hard for PPy to grow one dimensionally. Electrochemical deposition is very attractive due to the ability to anchor the product onto substrate materials in the desired quantity, shape and size in one single step, enabling the final application to be performed easier.

In this work, we will present the one-dimensional growth of conducting polymer through electrochemical co-deposition with inorganic oxide. Pseudocapacitive properties of the obtained composite films are studied as well. The local environment at the electrode surface for polymerization was tried to be controlled by the electrodeposition of inorganic oxide from their precursors like VO^{2+} , in which process proton may be released and some of the anodic charges may be consumed. Composites with improved electrochemical performance were obtained through 1D growth control of the conducting polymer, leading to increased surface area and organic-inorganic synergistic effect.

Acknowledgements

We gratefully acknowledge financial supports from National Natural Science Foundation of China (project number: 21273029) and Research Foundation for Doctoral Program of Higher Education of China (project number: 20120042110024).

6:20pm **EH-TuE3 Soft X-ray Operando Spectroscopy for Polymer Electrolyte Fuel Cells and Li Ion Batteries**, *Masaharu Oshima*, The University of Tokyo, Japan **INVITED**

In order to meet strong demands for electronic structure analysis of green devices, namely 1) power generation devices such as polymer electrolyte fuel cells (PEFC), 2) power efficient devices such as graphene FET and Resistive RAM, and 3) energy storage devices such as Li ion battery (LIB), we have developed two soft X-ray nano-spectroscopy systems at the Spring-8 University-of-Tokyo (UT) outstation. One is *operando* soft-X-ray emission spectroscopy (XES)¹⁾ for PEFC cathode catalysts and Li ion battery, and the other is scanning photoelectron microscopy with 70 nm spatial resolution²⁾, which has been used to analyze graphene FET and organic FET *in operando*.

First, we analyzed electronic structures of carbon-related catalysts alternative to Pt for PEFC in order to elucidate the oxygen reduction reaction (ORR) mechanism. We prepared metal phthalocyanine-based carbon catalysts with 1-2% nitrogen and less than 1 % of Fe for PEFC. Photoelectron spectroscopy and first principles calculation revealed that zigzag edge carbons with neighboring graphite-like nitrogen are ORR active sites. Based on these analyses, we fabricated fuel cell stack for PEFC which showed comparable performance to Pt catalysts. Furthermore, we

have taken *operando* XES spectra of Fe 2p-3d transition during power generation, revealing that Fe impurity may act as an ORR catalyst³⁾.

Next, we analyzed the change of Fe 3d states accompanied with the Li intercalation/ deintercalation process by resonant photoemission spectroscopy. Since the battery voltage should reflect the energy difference between Li 2s and Fe 3d down-spin state, we measured the change in Fe 3d down-spin states for LiFePO_4 (3.4V) and $\text{Li}_2\text{FeP}_2\text{O}_7$ (3.6V) and found that 0.2 eV shift from PO_4 to P_2O_7 poly-anions directly reflects battery voltage. Furthermore, the *operando* XES method was applied to cathode materials LiMn_2O_4 in Li ion battery to reveal the electronic structure change of Mn with changing OCV (open circuit voltage). It was demonstrated that the Mn^{3+} and Mn^{4+} states are successfully distinguished using high-energy-resolution resonant XES⁴⁾. Multiplet calculations⁵⁾ have been performed to determine the electronic structures in comparison with *operando* XES spectra for both Fe and Mn chemical states in FC and LIB, respectively.

This work has been done in collaboration mainly with Y. Harada, H. Niwa, T. Aoki, Y. Nabae, Y. Nanba and D. Asakura.

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7:40pm **EH-TuE7 Water as Promoter and Catalyst in Di-Oxygen Reactions at Aqueous and Organic Electrified Interfaces**, *Nenad Markovic*, Materials Science Division, Argonne National Laboratory, Argonne, IL 60439, USA

Understanding the role of water in di-oxygen electrochemistry at atomic and molecular levels is the key to driving technological innovations that are urgently needed to deliver reliable, affordable and environmentally friendly energy [1-4]. Surprisingly, all previous studies have treated the water molecule as reactants needed to satisfy the stoichiometry of the reaction, rather than as vital hydrogen-donor molecules that can promote the rates of transformation of oxygen intermediates to final products. It is the impact of water on di-oxygen electrochemistry that constitutes the focus of our paper. First, we introduce a universal model that is capable of rationalizing, and ultimately understanding, electrocatalysis of the oxygen reaction in aqueous media, as well as in Li-O_2 electrochemistry in organic environments. The model is based on the formation of $\text{HO}_{ad}\cdots\text{H}_2\text{O}$ (alkaline) and $\text{LiO}_2\cdots\text{H}_2\text{O}$ (organic solvents) complexes that place water in a configurationally favorable position for proton transfer to O_2^- and HO_2^- intermediates that are formed on neighboring active sites. We propose that monometallic electrodes modified by omnipresent oxygenated spectators such as OH_{ad} and LiO_2 are, in fact, bifunctional catalysts capable of facilitating different parts of the overall multi-electron process: providing adsorption sites for the formation of complexes as well as bare metal sites to facilitate the electron transfer to O_2 , O_2^- and HO_2^- .

Moreover, we demonstrate that water plays a dual role in Li-O_2 electrochemistry, acting simultaneously as a promoter in the production of Li_2O_2 and also as a *catalyst*, regenerating itself through a sequence of steps that include the recombination of H^+ and OH^- back to water. Water acting as a catalyst has not, to the best of our knowledge, previously been reported for any electrochemical reaction.

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8:20pm **EH-TuE9 Electrochemical Reduction of CO2 as a Way to Store Energy from Intermittent Sources**, *Paul Kenis*, University of Illinois at Urbana-Champaign

The desire to increase the utilization of sustainable energy sources such as solar and wind is hampered by their intermittent nature. Large scale energy storage capacity is needed to maximize utilization of these sources,

specifically to avoid large amounts of renewable energy being wasted when their supply exceeds demand.

Over the last years we have studied the electrochemical reduction of CO₂ to various value-added chemicals such as carbon monoxide (CO), formic acid, and methane. When coupled to renewable energy sources such as wind and solar, this process can produce carbon-neutral fuels or commodity chemicals, possibly providing a method for storage of otherwise wasted excess energy from intermittent renewable sources [1].

For this process to become economically feasible, more active and stable catalysts as well as better electrodes are necessary such that CO₂ electrolyzers can be operated at sufficient conversion (current density >250 mA/cm²), reasonable energetic efficiency (>60%), and sufficient product selectivity (Faradaic efficiency >90%). For CO production, a key reactant in the Fischer-Tropsch process, the best performance reported to date is current densities on the order of 90 mA/cm² and energy efficiencies up to 45%, when operating at ambient conditions [2]. This presentation will focus on new catalyst systems for efficient conversion of CO₂ to CO: (i) Ag nanoparticles supported on TiO₂ [3]; (ii) Au nanoparticles supported on multiwall nanotubes; and (iii) metal-free N-doped carbons. These catalysts have been characterized in a 3-electrode cell and in an electrolyzer. Current densities of between 100 and 250 mA/cm² as well as energy efficiencies of up to 70% were obtained. The electrodes in all these cases are prepared using automated airbrushing [2], which reduced catalyst loadings to 0.75 mg/cm² for Ag and 0.17 mg/cm² for Au. These performance levels, together with the lower cost due to low precious metal loading (due to the use of catalyst supports), or even the elimination of precious metals altogether (N-doped carbons), brings electrochemical reduction of CO₂ to CO closer to economic feasibility.

We also performed an economic / life-cycle analysis of this process, to determine whether this technology can become, economically viable for large scale application in the storage of energy from renewable sources, and/or in the reduction of greenhouse gas emissions.

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Wednesday Morning, December 10, 2014

Energy Harvesting & Storage

Room: Lehua - Session EH-WeM

Characterization of Materials for Energy Applications I

Moderator: Mayo Villagran

8:00am **EH-WeM1** **Hindering Effect of Surface Point-Defects for Photoreactivity on TiO₂(110)**, *Igor Lyubinsky*, Pacific Northwest National Laboratory

Hindering Effect of Surface Point-Defects for Photoreactivity on TiO₂(110)

I. Lyubinsky*

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While surface point-defects are expected to act as charge trapping and/or recombination centers in photoinduced processes, their direct impact of surface defects on photoreactivity is not well explored. We present the first observation of a suppressing effect of oxygen vacancy (V_O) defects on photoreactivity of TiO₂(110). Direct scanning tunneling microscopy imaging reveal a pronounced site-selectivity in the hole-mediated photooxidation of trimethyl acetate (TMA) on TiO₂(110) upon ultra-violet light irradiation, wherein the reaction readily occurs at regular Ti sites but is completely inhibited at V_O defects. Utilizing electron energy loss spectroscopy and density functional theory, we show that the lack of reactivity of TMA groups adsorbed at V_O 's cannot be attributed to either a less active adsorption conformation or electron transfer from the V_O defect. Instead, we propose that the excess unpaired electrons associated with the V_O promptly recombine with photoexcited holes approaching the surface, effectively 'screening' TMA species at V_O site. We also show that this screening effect is spatially short-ranged, being predominately localized at the V_O , and only mildly affecting TMA's at adjacent Ti sites. The direct impact of O vacancies on TMA photoreactivity over TiO₂(110) is expected to have similar implications for other hole-mediated (e.g., photooxidation) reactions in which adsorption at or near electronic point-defects is possible. Furthermore, the localized influence of these defects on hole-mediated chemistry offers opportunities for additional study of site-selective photocatalysis on TiO₂.

* In collaboration with Z.-T. Wang and M.A. Henderson, PNNL and N.A. Deskins, Worcester Polytechnic Institute. We acknowledge support from the US DOE BES, Division of Chemical Sciences, Geosciences & Biosciences. A portion of this research was funded by the Chemical Imaging Initiative LDRD at PNNL.

8:20am **EH-WeM2** **Atomic Structure and Intrinsic Electronic States of the In₂O₃(111) surface**, *Holger Eisele Eisele, R. Zielinski, A. Lenz*, Technische Universität Berlin, Germany, *Z. Galazka*, Leibniz Institute for Crystal Growth, Germany, *M. Dähne*, Technische Universität Berlin, Germany

Indium oxide as transparent semiconductor is one of the most promising materials for contact layers in photovoltaic applications. Nevertheless, due to the delicate fabrication process for single crystals only a few intrinsic properties are known about In₂O₃, yet. Especially the storage under air conditions may influence the surface properties. Hence it is hard to decide, which properties are intrinsic and which ones are influenced by physisorbed and/or chemisorbed atoms and molecules from the ambient air.

In this contribution for the first time we studied high quality single crystals at their freshly UHV-cleaved (111) surfaces by scanning tunneling microscopy (STM) and spectroscopy (STS). From these investigations we achieve knowledge about the atomic configuration at the surface. This configuration fits well with recent density functional theory calculations, and indicate a local charge enhancement within the surface unit cell. Furthermore, STS reveals intrinsic electronic surface states within the fundamental band gap. The Fermi level is also energetically located within the fundamental bulk band gap, which leads to the assumption that previously reported electron accumulation at this surface is not an intrinsic property, but related to extrinsic effects, such as e.g., non-stoichiometric material reorganization. After oxidation of the In₂O₃(111) surfaces outside the UHV their structural as well as their electronic properties look quite different: astonishingly both show much more metallic behaviour as the freshly cleaved ones kept under UHV-conditions. The processes leading to such an behaviour are still under discussions, but the data fits much better to previous observations.

8:40am **EH-WeM3** **Laser-Excited Scanning Tunneling Spectroscopy of Materials for Solar Cell Application**, *Verena Portz, M. Schnedler, R.E. Dunin-Borkowski, P. Ebert*, Forschungszentrum Jülich GmbH, Germany

Materials for solar cell and optoelectronic applications are critically affected by defects. The defects can give rise to deep gap states, which can lead to non-radiative carrier recombination centers. These are detrimental to both the electron-light and light-electron conversion efficiencies in optoelectronic and solar cell devices, respectively. In order to understand the physical processes involved at the atomic scale, the materials used in the device structures need to be investigated under illumination with atomic resolution.

Therefore, we investigated the prototype group III-V semiconductor GaAs as a model system by light-excited scanning tunneling microscopy and spectroscopy. We used GaAs(110) cleavage surfaces, which are free of intrinsic surface states in the band gap, and hence the surface potential is governed by the underlying bulk doping. The effect of the laser irradiation on the scanning tunneling spectra was determined on the clean defect-free surface, at dopant sites, and close to defects, using a newly developed measurement methodology, whose advantages will be discussed. The atomically-resolved spectra show distinct changes of the local potential at the different sites, which can be related to the local distribution of the illumination-induced carrier concentration. In order to analyze the spectra in detail, we developed a simulation program, which allows us for the first time to calculate quantitatively the effect of laser irradiation on the tunnel current. The physical models used for the simulation will be discussed. Fits of the simulated spectra to the measured ones allow the determination of the local redistribution of light-excited carriers and the identification of atomic scale carrier recombination centers

9:00am **EH-WeM4** **TEM Observation of Nano Porous Gold in Reaction Environment**, *Takeshi Fujita*, Tohoku University, Japan
INVITED

Nanoporous gold (NPG) produced by dealloying possesses a self-organized, self-supporting three-dimensional (3D) nano-architecture, which gains increased attentions as a multifunctional material for a wide range of applications. Similar to small gold nanoparticles, NPG has been demonstrated to be catalytically active for a number of important chemical/electrochemical reactions, but at a much larger characteristic size (>20 nm) for both gold ligaments and nanopores. While many factors have been suggested to explain the nano-size chemical effect of gold nanoparticles, such as quantum size effects, charge transfer between gold nanoparticles and oxide supporters, and enhanced concentration of low-coordination atoms, on the other hand the self-supported NPG indicates that the unique morphological characteristics alone is responsible for the catalytic activity of NPG.

We characterized the microstructure of NPG using spherical-aberration-corrected transmission electron microscopy (Cs-corrected TEM). The atomic structure of the internal surfaces of NPG, responsible for the catalytic activity, was imaged by scanning transmission electron microscopy (STEM) using a high-angle annual dark-field (HAADF) detector. The arrangement of near-surface atoms was also measured accurately by Cs-corrected high-resolution TEM (HRTEM), which provides phase-contrast images with high displacement sensitivity. On the basis of extensive HRTEM and STEM characterization, the high catalytic performance of NPG was suggested to originate from surface strains and a high concentration of low-coordination atoms stabilized by the complex geometry of bicontinuous nanoporosity of NPG. In addition to the static observation in inert vacuum environment, we also characterized the surface atomic structure evolution during CO oxidation in a reactive atmosphere using a newly dedicated environmental HRTEM [1].

Our key observation also provided the first direct atomic observations of the coarsening process of the porous catalyst, which shows completely different mechanisms of catalytic degeneration when compared to conventional nanoparticulate catalysts. More importantly, the atomic observation provides compelling evidence that planar defects such as twins can effectively prevent structure coarsening, suggesting a new strategy for developing chemically active and structurally sound catalysts. The effect of planar defects on catalysis has been highlighted recently and our observation offers the first direct experimental evidence of this important phenomenon [2].

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9:40am **EH-WeM6 Characterizing Automotive Fuel Cell Materials by Soft X-Ray Scanning Transmission X-Ray Microscopy (STXM)**, *Adam Hitchcock, V. Lee*, McMaster University, Canada, *V. Berejnov, D. Susac, J. Stumper*, AFCC, Canada

Low temperature, hydrogen-fueled, proton exchange membrane fuel cell (PEM-FC) based engines are being developed rapidly for near-term implementation in mass production, personal automobiles. Materials and process research aiming to further optimize these systems is focused on understanding and controlling various degradation processes (carbon corrosion, Pt migration, cold start), and reducing cost by reducing or eliminating Pt in the electro-catalyst, especially for the oxygen reduction reaction (ORR). We are using soft X-ray scanning transmission X-ray microscopy (STXM) at the S 2p, C 1s, O 1s and F 1s edges to study a variety of issues related to optimization of PEM-FC materials for automotive applications. STXM provides spectroscopic identification and quantitative mapping of chemical components with 30 nm spatial resolution in both 2D projection and 3D spectro-tomography. Themes of our studies include: mapping ionomer in cathodes of beginning-of-life and end-of-life membrane electrode assemblies [1,2, 3]; investigating Pt-in-membrane [4] and carbon corrosion degradation [3]; studies of alternate electrode technologies (3M nanostructured thin films [5], ink-jet print [6]); and measuring water distributions *in situ* [7]. The O 1s spectra of the 3 phases of water differ from those of membrane electrode assemblies (MEA) constituents allowing direct *in-situ* visualization of water uptake and quantitative mapping of gas and liquid/sorbed water. A newly developed environmental cell for *in situ* studies with controlled humidity and temperature will be described and its current performance will be outlined.

Research funded by AFCC and NSERC. Measurements were made at the Canadian Light Source (supported by NSERC, NRC, CIHR, and the University of Saskatchewan) and at the Advanced Light Source (supported by the Division of Basic Energy Sciences of U.S. DoE).

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- [5] V. Lee, V. Berejnov, M. West, S. Kundu, D. Susac, J. Stumper, R.T. Atanasoski, M. Debe and A.P. Hitchcock, J. Power Sources **263** (2014) 163
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10:20am **EH-WeM8 New Insights into Energy-Related Materials from Advanced Electron Microscopy Methods**, *Gianluigi Botton*, McMaster University, Canada **INVITED**

Electron Microscopy and electron energy loss spectroscopy are invaluable techniques to study the detailed structure and the chemical state of materials at unprecedented spatial resolution. In today's modern electron microscopes, it is possible to tackle problems requiring the highest energy resolution, down to 60meV, and highest spatial resolution, down to the angstrom level, so that atomic resolved spectroscopy with high spectroscopic sensitivity and resolution can be obtained. This leads to the potential of covering excitation phenomena from the mid-infrared, soft-X-rays and even hard-X-ray regime.

In this presentation, various examples of applications of electron microscopy will be given based on a modern electron microscope. After an overview of the imaging conditions used to detect core-shell ordering changes in PtFe, PtRu, PtAu alloy nanoparticles [1,2] graphene and single atoms on doped graphene [3] used for fuel cell catalysts, using a combination of high-angle annular dark-field STEM imaging, EELS elemental mapping and simulations, we will discuss the application of atomic-resolved EELS mapping in to study complex oxide and oxide support materials used to promote strong metal support interaction [4]. Here we demonstrate how electron energy loss spectroscopy can be used to probe the valence change of the oxide following the interaction with the catalyst. This powerful technique can also be used to study of the structure and substitutional effects from single atom dopants in phosphors [5] and metallic alloys.

Additional examples will highlight the application of microscopy technique to the analysis of perovskite structures. These examples demonstrate that compositional and chemical state (valence and coordination) information can be obtained down to the Ångstrom level on surfaces [6].

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11:00am **EH-WeM10 The Use of Massive Ar Clusters for the Sub-Surface Characterization of Organic and Inorganic Materials**, *David Surman*, Kratos Analytical Inc., *J. Counsell, S. Hutton, H. Brannon*, Kratos Analytical Ltd., UK

Over the last several years massive Argon gas cluster ion sources as accessories for sputter depth profiling of organic materials have increased in popularity. These sources utilize Argon cluster ions formed via adiabatic isentropic expansion of Argon gas into a vacuum followed by subsequent electron impact ionization and cluster size selection. In ideal cases the aforementioned massive cluster ions efficiently sputter the surface of organic materials revealing undamaged subsurface structure for analysis. More recently, developments in the technology have expanded the use of these sources to allow for the sputtering of inorganic materials.

Advanced software controlled ion sources and flexible sample handling equipment allow a wide range of experimental conditions to be routinely employed during sputter depth profiling with these massive Argon clusters. In this study we have investigated a variety of parameters such as incident ion energy and cluster size distribution on the effectiveness of the sputtering process and the degree of chemical damage that is induced using X-ray Photoelectron Spectroscopy (XPS) as the monitor. A range of both organic and inorganic materials have been analysed. It has been observed that for most organic materials large cluster sizes with a medium beam energy (typically less than 10keV) are very effective for sputtering with no observable chemical damage. This is in contrast to sputtering of inorganic materials where typically high beam energies (greater than 10keV) and small cluster sizes are required for effective sputtering. The identification of a minimum partition energy for sputtering will be discussed. In addition, it will be demonstrated that, although preferential Oxygen sputtering can be observed on many oxides resulting in the formation of reduced chemical states, this effect is substantially reduced when compared to the use of monoatomic Ar ions.

11:20am **EH-WeM11 Recent Applications and Results in Near Ambient Pressure XPS - In-situ Cell Designs for Liquid Environments**, *Thomas Schulmeyer, A.T. Thissen*, SPECS Surface Nano Analysis, Inc.

Modern devices are often only functional in environments far away from ultrahigh vacuum, which is still considered the standard operating condition for all Surface Science techniques. Due to miniaturization down to the nanoscale, surfaces are increasingly important for device performance. In order to contribute to advanced material analysis in future Photoelectron spectroscopy, Scanning Probe Microscopies and related techniques must be performed in generic or near generic device environments. Such an environment would mean high, elevated or near ambient pressures of defined working gas mixtures, liquid media, potentials or magnetic fields; extremely low or high temperatures might also be necessary. Of course, all standard Surface Science Techniques did not work under these extreme environments previously. This work summarizes and presents existing solutions for present and future development routes to new instruments, and displays how material analysis methods are functional under these working conditions. The opportunities and limitations will be discussed from the perspective of suppliers of scientific instruments. And finally, application examples and results from existing In situ methods will be demonstrated. These methods include: high pressure treatment cells, complete High Pressure or Near Ambient Pressure Photoelectron Spectroscopy or Scanning Probe Microscopy Systems (NAP-PES or NAP-SPM), liquid and electrochemical cells, Liquid sample "manipulators", and concepts and status of equipment working in the highest or lowest temperatures, high magnetic fields and static or dynamic potentials.

11:40am **EH-WeM12 Dynamic H₂O/GaP (111) Interfacial Chemistry Monitored by Near-Ambient Pressure XPS in Real Time**, *Xueqiang Zhang, S. Ptasinska*, University of Notre Dame

A photoelectrochemical (PEC) solar cell for water splitting can convert solar energy into chemical energy and store it in the form of hydrogen, a molecule regarded as a promising candidate for sustainable and clean fuels [1]. PEC solar cells using phosphide-based III-V semiconductors are known to have higher efficiency than other materials. They are, however, usually limited by issues such as photocorrosion or decreased electron extraction efficiency due to formation of interfacial oxide species, which becomes

especially critical when operating electrodes (typically, semiconductors) are exposed to aqueous electrolytes [2]. Therefore, It is desirable to understand the process of water interactions with semiconductors and possible oxidation and reduction mechanisms at the H₂O/semiconductor interface, especially under near realistic conditions.

In the present study, water dissociative adsorption on a GaP (111) surface was investigated using near ambient pressure X-ray photoelectron spectroscopy (NAP XPS) at various pressures and temperatures. The interfacial chemistry was tracked by recording high resolution photoemission spectra of Ga 2p_{3/2}, O 1s and P 2p. In the pressure-dependent study (room temperature, ~300 K), enhanced surface Ga hydroxylation and oxidation were observed with an increase of water vapor pressure, which was also mirrored by the photoemission spectra of O 1s. In the temperature-dependent study, surface Ga hydroxylation and oxidation were further enhanced at temperatures below 673 K. While a large-scale conversion of surface O-Ga-OH species into Ga hydroxide, along with surface P oxidation, was observed at a temperature of 773 K. The formation of Ga and P oxide/hydroxide networks with a schematic formula of Ga_aP_bO_c(OH)_d (a, b, c and d represent a ratio of different elements and groups) is suggested. Our results can be compared with recent theoretical findings [3, 4] and lead to a better understanding of water splitting mechanisms and photo-corrosion on semiconductor surfaces.

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Energy Harvesting & Storage

Room: Mauka - Session EH-WeP

Energy Harvesting & Storage Poster Session

EH-WeP1 Lifetime Prediction of Encapsulated Organic Photovoltaic Modules in Accelerated Conditions, SungHyun Kim, N. Kim, Korea Electronics Technology Institute (KETI), Republic of Korea

Organic photovoltaic (OPV) modules consisting of ITO/ZnO/photoactive layer/PEDOT:PSS/Ag inverted structure were fabricated using slot-die coating method and encapsulated by a barrier film deposited on polyethylene terephthalate (PET). Effective water vapor transmission rate was measured in both the transient and steady-state regimes of PET with a barrier layer. Acceleration tests were conducted under 65°C and 85% relative humidity to investigate the degradation of OPV modules. Total amount of water vapor into OPV module was calculated and correlated with the degradation rate of it. The lifetime of encapsulated OPV module under ambient condition is calculated and will be presented in the conference.

EH-WeP2 Effect of Surface Roughness on the Contact Resistance between the Gas Diffusion Layer and Bipolar Plate in a Polymer Electrolyte Membrane Fuel Cell, Changhee Choe, J.J. Lee, Seoul National University, Korea, Republic of Korea

In a polymer electrolyte membrane fuel cell (PEMFC), one of the most important factors affecting the performance is ohmic loss arising from the contact resistance at the interface of the gas diffusion layer (GDL) and bipolar plate (BP). As a method to reduce the contact resistance between the bipolar plates and gas diffusion layer, the contact area of the bipolar plates were increased by inducing roughness on the surface. The environment of the highly porous GDL being pressed by an external compaction pressure was simulated, and the contact area between the GDL and bipolar plates was calculated. The calculated contact resistance using the contact area was compared with the experimental contact resistance results of the bipolar plates polished with various grades of abrasive paper. As the average surface roughness increased, the contact resistance values decreased, which is in good agreement with the results of this study. In a single cell test, the efficiency of the cell increases when the rough bipolar plate is used.

EH-WeP3 Fully flexible and Transparent Piezoelectric Touch Sensor is based on ZnO nanowires with BaTiO₃, MoolKyul Kang, J.H. Park, K.I. Lee, Korea Electronics Technology Institute (KETI), Republic of Korea, *B.K. Ju,* Korea University, Republic of Korea, *C.S. Lee,* Korea Electronics Technology Institute (KETI), Republic of Korea

ZnO nanowires (NWs) can be grown by chemical approach at low temperature (<100 °C) on any substrate and any shape substrate. A relatively small force is required to induce the mechanical agitation, so that it can be fabricated sensitive devices.[1] But piezoelectric device based on ZnO NWs, which can not improve the piezoelectric properties of a single material due to a low piezoelectric d constant of ZnO NWs ($d \approx 12\text{pC/N}$).

In this paper, we demonstrated fully flexible and transparent piezoelectric touch sensor based on ZnO NWs, and composed that touch sensor with BaTiO₃ of Perovskite structure for improving piezoelectric properties. In order to maintain the flexibility of sensing spot, the BaTiO₃ (10 wt%) are dispersed in flexibility-improved SiO₂ capping solution and coated on ZnO NWs surface as a capping layer by spray coating method. Also, By replacing Indium tin oxide (ITO) electrodes with transparent flexible CNT-Ag nanowires electrode, the flexibility of the entire structure was enhanced. ITO is commonly used as transparent electrodes. However due to its high cost and limited supply of indium, the fragility and lack of flexibility of ITO layer, its alternative are being sought. It is expected that conductive films using carbon nanotubes and Ag NWs could be a prospective replacement of ITOs.

The ZnO NWs based sensor generated the output voltage of ~ 50 mV. The sensor with BaTiO₃ generates a higher output voltage (~1.2 V) than a ZnO NWs based sensor. We confirmed that the output voltage of sensor with ZnO NWs and BaTiO₃ was dramatically increased. We measured the resistance of capping layer and CNT-Ag NWs electrode during the periodic bending. When bent and flexed over 1,000 cycles, the films did not show significant degradation in sheet resistance compared to Ag thin film and ITO film on the same PET substrate. The bending test results conducted to confirm the mechanical stability of capping layer and CNT-Ag NWs as a electrode. The measurement results suggest that the our Piezoelectric touch sensors are suitable for flexible device such as flexible touch sensor, wearable and rollable touch panel.

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EH-WeP4 Analysis of Steam Reforming Reaction by Vibrationally-Excited Methane Based on First-Principle Molecular Dynamics Simulation, Naoki Yokoyama, Y. Higuchi, N. Ozawa, H. Yugami, M. Kubo, Tohoku University, Japan

For an environmentally-friendly energy system, hydrogen is expected as a resource to replace fossil fuels. Recently, steam methane reforming (SMR) is mainly used for hydrogen production. However, the promotion and the cost reduction of hydrogen production in SMR is strongly desired for stable supply of hydrogen because SMR requires a large amount of heat. To increase hydrogen production, Maegami et al. proposed the vibrationally-excited method, in which infrared light vibrationally excites a C-H bond of a CH₄ molecule [1]. While hydrogen production is promoted by the vibrational excitation of a CH₄ molecule, the detailed analysis at atomic scale is necessary for higher efficient hydrogen production. Thus, by using the first-principles molecular dynamics (FPMD) simulation method, we examined the effect of vibrational excitation of the C-H bond on chemical reaction dynamics for hydrogen generation from CH₄ and H₂O.

To reveal the chemical reaction dynamics, we simulated collision process of a H₂O molecule with a CH₄ molecule in the vibrationally-excited state by using our development FPMD code "Violet" [2]. The vibrationally-excited state was reproduced by extending a C-H bond. After the collision, a dissociation of C-H bond was observed. Moreover, the H atom of the dissociated C-H bond reacted with a H atom of the H₂O molecule, and H₂ and CH₃OH were generated. Next, to examine the effect of vibrational excitation, we simulated collision processes with the collision angle from -60° to 60° and collision energy from 9 eV to 20 eV in the ground state and the vibrationally-excited state. In the ground state, hydrogen molecules were generated in the range of collision angle from -50° to -10° and collision energy from 17 eV to 20 eV. On the other hand, in the vibrationally-excited state, hydrogen molecules were generated in the range of collision angle from -60° to 0° and collision energy from 14 eV to 20 eV. Therefore, in the vibrationally-excited state, H₂ molecules were generated in a wider range of collision angle and lower collision energy than those in the ground state. This simulation result suggests that the H₂ generation was promoted by vibrational excitation, which is consistent with the experiment [1]. We also examined the later process after the H₂ and CH₃OH were generated. Accordingly, CH₂(OH)₂, HCHO, HCOOH, and CO were observed as intermediate products. Consequently, we indicated the chemical reaction dynamics of H₂ generation from H₂O and vibrationally-excited CH₄ in gas phase.

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EH-WeP7 The Integration of XPS and Ar-Gas Cluster Ion Sputtering to Study the Corrosion of Stainless Steel Surfaces, D. Surman, Kratos Analytical Inc., *Helen Brannon, J. Counsell, S. Hutton,* Kratos Analytical Ltd., UK, *J. Morrison,* University of Birmingham, UK, *C. Blomfield,* Kratos Analytical Ltd., *A. Roberts,* Kratos Analytical Ltd., UK

Stainless steels are vital construction materials in all areas of industry, combining excellent corrosion resistance with good mechanical properties. For these reasons, stainless steels are used extensively in power stations of all varieties – of particular interest is the use of stainless steel in Pressurised Water Reactor (PWR) type nuclear power plants, such as the Sizewell B power station, Suffolk, UK.

The corrosion of steel in contact with hot, pressurised water in a PWR is a common problem. This side reaction is undesirable due to the reduced heat transfer efficiency caused by the deposited oxide layers.

Stainless steel's corrosion resistance is derived from the formation of a passivation layer at the surface of the material. Under atmospheric conditions this is thought to be a vanishingly thin layer of Chromia (Cr₂O₃), however, under conditions found in the coolant cycles of a PWR, it is thought that the passivation layer grown forms a double layer – the inner layer consisting of corrosion resistant, non-stoichiometric Chromite (FeCr₂O₄), while the outer layer consists of non-stoichiometric Nickel Ferrite (NiFe₂O₄). The thickness of this film is believed to vary with the steel surface finish, and the Environment Degradation Group at the University of Birmingham has recently begun a programme to study the dependence of corrosion rate and passivation layer thickness on surface finish, system chemistry and temperature.

The samples were ground to a 120 and 1200 grit finish using silicon carbide paper to produce samples with significantly difference roughness levels

(approximate R_a values of 1050 and 110 nm, respectively), before being inserted into a flowing rig, where they were exposed to deoxygenated water at pH 10 and 300°C at a pressure of 10 MPa. Sets of samples were removed from the rig every 250 hours, up to 1000 hours total exposure time.

X-ray photoelectron spectroscopy (XPS) was used to determine the type of corrosion chemistry that occurs. It was combined with a high energy, medium sized argon gas cluster source, which is shown to be advantageous compared to a conventional monatomic argon when depth profiling such layered structures, causing reduced structural and chemical damage from the ion beam sputtering process. Data acquisition at small analysis areas gives well resolved spectra, revealing the multi-layered oxide structures produced from the corrosion process. [1] Depth profiling of the Passive Layer on Stainless Steel using Photoelectron Spectroscopy, Wendy Fredriksson, Uppsala University [2] Applied Surface Science, 257, (2011), 2717–2730 [3] The Radiochemistry of Nuclear Power Plants with Light Water Reactors, By Kark-Heinz Neeb

EH-WeP9 Current Enhancement in Hybrid Solar cells prepared with Quantum Dots and PFN, D. Esparza, J. Oliva UC, T. Lopez, I. Zarazua, Elder De la Rosa, Centro de Investigaciones en Optica A.C., Mexico

This work presents a hybrid solar cell made with quantum dots and poly [(9,9-bis(3'-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN), which is commonly used as electron transport layer in organic solar cells. Those cells were fabricated by Successive Ionic Layer Adsorption and Reaction (SILAR) method and spin coating. The configuration used in this work was: TiO₂/PbS/PFN/CdS/ZnS. The presence of PFN produced an increase of 33% in the short circuit current (J_{sc}) respect to the sample of reference: TiO₂/PbS/CdS/ZnS. Such increase in current caused an increment of the cell efficiency from 2.6% to 3.6%. PTB7 was also used as donor in our hybrid solar cells instead of quantum dots, when the PFN is added in this system, the current increased 60% respect to the cell of reference and the efficiency increased from 1.1% to 3.0%.

EH-WeP11 On the Role of Plasma System for CO₂ Dissociation, H.Y. Chang, Korea Advanced Institute of Science and Technology (KAIST), South Korea

The CO₂ capture and storage technology (CCS technology) needs immediate action, but does not have complete solutions yet due to the efficient and economical CO₂ conversion problems. In this presentation, the governing fundamental quantities will be identified to obtain the maximum energy efficiency and capacity for CO₂ dissociation. Several CO₂ conversion ideas will be introduced, describing the advantages and disadvantages of each conversion techniques. The plasma reactor has been known as one of the most promising candidate for CO₂ dissociation. However, the problems on how to achieve high efficiency, stable discharge at atmospheric pressure, and reliability at high power density should be solved. The ICP(Inductively coupled plasma) source will be introduced along with other sources such as microwave, DBD(Dielectric barrier discharge), and DC for the efficient CO₂ dissociation. In this presentation, the technical issues for the mass production of CO₂ conversion will also be discussed.

EH-WeP15 Positive Temperature Coefficient of CdS/Cu(In,Ga)(S,Se)₂ Solar Cell, Sangmok Kim, C.-W. Jeon, Yeungnam University, Republic of Korea

In the recent years, Cu(In, Ga)Se₂ (CIGS)-based thin-film solar cells with efficiency of readily over 20% have been reported by several groups, therefore, it is strongly expected to replace the crystalline silicon solar cell rapidly. Unlike crystalline silicon cell of a homo-junction, CIGS thin-film solar cell consists of hetero-junction between absorbing layer and CdS buffer layer. In CBD (Chemical Bath Deposition)-CdS, which is commonly used for a high efficiency CIGS solar cell, the kind and concentration of source materials and bath temperature is known to affect the characteristics of the CIGS/solar cell as well as CdS film properties. In general, the efficiency of solar cell decreases with increasing ambient temperature due to the reduction of band gap energy of absorber layer and higher reverse saturation current at an elevated temperature. In other words, temperature coefficient (TC) of a solar cell is normally negative. [1] While this tendency is observed in the CIGS/CdS solar cells, according to this study, it was confirmed that the behavior of TC depends on the synthesis conditions of the CdS. In this study, we prepared several solar cells of ZnO/CdS/CIGS/Mo/glass with different CdS deposition conditions by changing [Cd] and [S] in the solution over the range of [Cd]=15~135mM, [S]=12.5~50mM. And the variation of TC's were monitored by measuring IVT (Current-Voltage-Temperature) in the temperature range of 10~50°C. Some of solar cells with high [Cd] of low [S] were found to have positive TC's. In these devices, while Voc decreased as expected with increasing temperature, fill factor increased on the contrary. The enhancement of fill factor stemmed from the lower series resistance at higher operating

temperature. The thermal characteristics of the solar cells depending on the [S]/[Cd] composition ratio in the solution will be discussed with the results of IV, CV, QE measurements. Acknowledgement This research was financially supported by the Ministry of Knowledge Economy(MKE), Korea Institute for Advancement of Technology(KIAT) and Dae-Gyeong Leading Industry Office through the Leading Industry Development for Economic Region. References [1] A.Virtuani, D. Pavanello, and G. Friesen, 25th European Photovoltaic Solar Energy Conference and Exhibition/5th World Conference on Photovoltaic Energy Conversion. 2010, p6-10

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. Beliatis, 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).

Thursday Morning, December 11, 2014

Energy Harvesting & Storage

Room: Lehua - Session EH-ThM

Nanotechnology & Energy

Moderator: Jin-Hyo Boo, Sungkyunkwan University, Korea

8:00am **EH-ThM1 Improving the Photoconversion Efficiency of Quantum Dots Sensitized TiO₂ Solar Cells Prepared by SILAR and Electrophoresis Method**, *I. Zarazua*, Centro de Investigaciones en Optica, Mexico, *D. Esparaza, A. Sanchez, A. Cerda, T. Lopez-Luke, Elder De la Rosa*, Centro de Investigaciones en Optica A.C., Mexico **INVITED** One of the most studied hybrid-type nanostructured solar cells is the Gratzel or dye sensitized solar cell (DSSC). DSSCs typically consist of TiO₂ NCs acting as a highly porous, wide bandgap semiconductor for electron collection, and dye molecules adsorbed onto the TiO₂ NCs surface acting as sensitizers to harvest solar light. An alternative to DSSC is the utilization of quantum dots (QDs), e.g., CdSe, CdTe, CdS, PbS, PbSe, Bi₂S₃, and InP, as sensitizers to replace the expensive ruthenium dyes. QDs have large extinction coefficients in the visible region and, after bandgap excitation, undergo charge separation, injecting electrons to the conduction band of the metal oxide

The quantum dots (QD) has been recently drawing great attention as a material for solar energy conversion. The quantum dots sensitized titanium dioxide (TiO₂) was synthesized by different chemical methods such as successive ionic layer adsorption and reaction (SILAR), and electrophoresis (EP). Titanium dioxide (TiO₂) films consisting of a 150 nm compact layer, a 6 μm layer made of 40 nm TiO₂ nanoparticles (NPs) and a 7 μm scattering layer made of 400 nm TiO₂ NPs, were composited with several QDs such as CdS, PbS, ZnS, and Bi₂S₃ by SILAR and EP. Multisensitized configurations as PbS/CdS/ZnS and CdS/Bi₂S₃/ZnS were analyzed obtaining a photoconversion efficiencies of 3.75% and 2.52% respectively. These efficiencies are due to high photocurrents (14.3 and 10.2 Ma/cm², respectively) obtained by the correct combination of near infrared and visible light photoabsorption. Photoconversion efficiency was increased to 5% by combining both sensitizers method in the appropriate way. It also was studied the effect of depositing Gold Nanoparticles (Au NPs) by electrophoresis in CdS SILAR sensitized solar cells, results show that Au NPs slightly reduces the photocurrent (from 8.7 to 7.4 Ma) by reducing the photoabsorption of the CdS QDs, but at the same time strongly increases the FF (from 51 to 58%) and Voc (from 510 to 560 Mv). Electrochemical measurements suggest that Au NPs help to prevent recombination processes in the solar cell. In this paper, a detailed analysis of charge transport on both configurations is presented; taking advantage of impedance spectroscopy (IES) a detailed analysis of each interface is also presented.

We acknowledge financial support from CONACYT through grant 134111, UC-MEXUS program, CEMIE-Sol (P28), and European Community Seven Framework Programme (FP7-NMP-2010-EU-MEXICO) and CONACYT under grant agreements 263878 and 125141, respectively. D. Esparza, Andrea Sánchez and Andrea Cerda acknowledge scholarship from CONACYT.

8:40am **EH-ThM3 Applications of pure ZnO and the Mn-doped ZnO on Dye Sensitized Solar Cells**, *P.X. Feng, Xiaoyan Peng, Y.M. Li*, UPR, Puerto Rico

Mn-doped ZnO nanopowders have been prepared by the sol-gel technique using zinc and manganese (II) acetates as precursors. The crystalline structural investigations reveal that as prepared nanostructures with low Mn doping concentration have single hexagonal phase and are grown along the preferred c-axis. The chemical bonding structure in Mn-doped ZnO nanopowders was examined using X-ray photoelectron spectroscopy techniques, which indicate substitution of Mn²⁺ ions into Zn²⁺ sites in ZnO lattice. Temperature-dependent Raman spectra of the nanocrystals displayed suppression of luminescence and enhancement in full width at half maximum in pure ZnO nanocrystals with increase in temperature, which suggests an enhancement in particle size at elevated temperature. Furthermore, the magnetic measurement of Mn-doped ZnO nanostructures exhibits the ferromagnetism at room temperature.

The characteristics of dye-sensitized solar cells (DSSCs) with pure ZnO and Mn-doped ZnO nanopowders have also been investigated. The enhancement of the performance of DSSCs achieved using Mn-doped ZnO nanopowders is attributable to the introduction of the spontaneous polarization direction of ferroelectric materials with the electric field which

will efficiently block the back transfer of electron from fluorine doped tin oxide to the I⁻/I₃⁻ redox couple.

9:00am **EH-ThM4 Infrared Spectroscopic Study of Adsorption of Carbon Monoxide and Other Surface Reactions at the Ruthenium Dioxide Particle Film Aqueous Solution Interface**, *Jim McQuillan, S. Aloi*, University of Otago, New Zealand

Ruthenium dioxide is renowned as a highly active oxidation catalyst as well as a material with supercapacitor properties. Its heterogeneous catalyst behaviour has been extensively studied in surface science using well-defined crystal faces under high vacuum conditions. These studies have led to a good understanding of its active sites and the roles they play in solid/gas interface reactions such as the oxidation of adsorbed carbon monoxide. At the same time, the importance of ruthenium dioxide as an electrocatalyst has led to many electrochemical studies of RuO₂ electrodes immersed in aqueous solutions. These studies, somewhat contrasting with those in surface science, have sought to elucidate the basis of the 'pseudocapacitor' behaviour of hydrous RuO₂ which must involve both faradaic and non-faradaic processes. In spite of extensive efforts the details of the electron and proton transfer processes at RuO₂ electrodes remain obscure and there have been few spectroscopic studies addressing questions about the molecular nature of processes at the hydrous RuO₂ interface.

We have used *in situ* attenuated total reflection infrared (ATR-IR) spectroscopy to examine hydrous RuO₂ particle films deposited on diamond and ZnSe prisms immersed in flowing aqueous solutions. The adsorption behaviour of oxalate has been shown to be very similar to that of oxalate adsorbing on TiO₂ involving bidentate chelation. Adsorbed carbon monoxide exhibits several peaks indicating a diversity of sites as previously observed in its adsorption to RuO₂ (110) under high vacuum. Adsorbed carbon dioxide/carbonate is formed from the oxidation of adsorbed CO. Both the adsorbed CO and adsorbed carbonate spectra are sensitive to the presence of CO and O₂ as redox agents in solution which suggests that surface ruthenium ions may undergo changes in oxidation state via redox species in solution. These novel *in situ* spectroscopic results are the first from the RuO₂ aqueous solution interface and will be discussed in comparison with those from surface science and electrochemistry.

9:20am **EH-ThM5 Effect of Different Synthesis Routes of NaTaO₃ and the Presence of Metal-Based Nanoparticles as Co-Catalyst on the Hydrogen Production**, *Leticia M. Torres-Guerra, I. Juarez-Ramirez, C. Gomez-Solis, D. Sanchez-Martinez, J.C. Ballesteros-Pacheco*, Universidad Autonoma de Nuevo Leon, Mexico **INVITED**

Significant attention has been paid on the investigations of new photocatalysts metal-oxides because of their ability to harness the sun energy to drive fuel-producing reactions, such as water splitting. The compound NaTaO₃ has been studied in the last 10 years as photocatalyst in this reaction. According to the results obtained by several authors, high activity on this reaction was found by using NaTaO₃ material prepared by solid state route. This result is associated with the high crystallinity of the powder. However, there are other factors that also influence the physicochemical properties of semiconductor material such as specific surface area, microstructure, optoelectronic properties among others. Therefore the synthesis of metal-oxides can be carry out by soft chemical methods in order to modify and control the morphology, which allows to increase sites for hydrogen evolution. In our research group we have explored the performance of sodium tantalate, NaTaO₃ and RuO₂/La:NaTaO₃ prepared by several synthesis methods such as solid state reaction, sol-gel, hydrothermal, ultrasonic, solvo-combustion on photoinduced reactions. The sodium tantalate phase with perovskite structure has been synthesized by solvo-combustion path at low temperature (180°C) and using nanoparticles of RuO₂ as co-catalyst. This material showed considerably high photocatalytic activity for hydrogen production around 9,800 μmol.h⁻¹.g⁻¹, twice greater than those results obtained when the material was prepared by solid state method. The activity is associated with the material high crystallinity and the presence of the second phase, Na₂Ta₄O₁₁ in small concentration after annealed at 600°C. The formation of nanosteps between NaTaO₃ nanoparticles also contributed to the reaction efficiency. In addition, it was found that the crystalline structure formed by chains enhances mobility among linked octahedra and separation of hole-electron pairs, which increases the photoactivity of the material in these processes. From photoelectrochemical study was proposed the reaction mechanism that occurs during the water splitting on NaTaO₃ single and doped phase. Additionally, experiments of the electrochemical impedance spectroscopy were realized in order to obtain Mott-Schottky plots to determine the flat band potential of NaTaO₃, RuO₂/La:NaTaO₃.

10:20am **EH-ThM8 Tailored Nanomaterials for Electrochemical Applications**, *Vojislav Stamenkovic*, Argonne National Laboratory

Research that is aimed to fundamental understanding of processes for electrochemical energy conversion and storage will be presented. Atomic scale insight at the topmost surface layer is essential in order to understand and control properties of catalytically active materials. Therefore, well-defined surfaces have been in focus of our research that is executed in ultra-high vacuum (UHV) systems merged with electrochemical cells. Properties such as surface structure, surface and bulk compositions, electronic properties and surface defects are established by UHV surface specific tools. Well-characterized surfaces are then transferred to the ambient pressure electrochemical cell under strictly controlled conditions, and formed electrified solid-liquid interface is being characterized in order to obtain direct correlation between fundamental properties of materials and electrochemical behavior.

Our recent work, has been demonstrated that fine tuning of surface properties can lead towards unprecedented improvements in their functional behavior [1]. This presentation will address unique approach that is capable of utilizing structure-function relationships in the design of multimetallic materials for electrochemical systems. The following topics will be discussed: 1) well-defined materials obtained by varying their surface structure, composition profile and electronic properties in UHV; 2) atomic/molecular insight into formation of the electrified solid-liquid interfaces; 3) identification of the active and the most vulnerable surface sites under reaction conditions; 4) insight into chemical nature between the surface atoms, reactants, and molecular species in the electrolyte; 5) design and synthesis of tailored nanomaterials with desired size, shape and composition profile [2,3]; 6) ex-situ and in-situ characterization of tailored electrochemical interfaces.

This synergistic approach encompasses highly diverse experimental methods that span from UHV to rational synthesis of nanomaterials, has been proven to serve as a foundation in the development of practical materials for electrochemical applications such as batteries, fuel cells and electrolyzers. Reaction rates and durability of tailored nanomaterials for the electrochemical oxygen reduction, hydrogen evolution and hydrogen oxidation are improved over 30-fold compared to state of the art catalysts.

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10:40am **EH-ThM9 Photo-Electrochemical Energy Conversion and Storage**, *A. Hankin, Geoff Kelsall*, Imperial College London, UK

Global (mean) power demands of ca. 1.5×10^{13} W, projected to double by 2050, could be provided from the earth's ultimate power source, ca. 1.2×10^{17} W of incident solar radiation, if adequately efficient, robust and economic transducers are developed. However, the diurnal nature of solar power requires that such transducers are coupled to energy storage, preferably in chemical bonds for high specific energy / energy density, and to fuel cells for subsequent conversion to electrical energy. Such systems could decarbonise power sources, manage intermittency of renewable power sources and smooth the dynamics of electrical power demands. This can be achieved if electrons from photovoltaic panels are used, for instance, to electrolyse water to form (oxygen and) hydrogen, which can be oxidised subsequently in fuel cells. Alternatively, solar energy can be used directly, and potentially more cheaply, for photo-electrochemical reduction (and oxidation) of water in an environmentally benign route to hydrogen (and oxygen).

As in photovoltaic cells, a semiconducting material may be used to absorb solar photons with energies ($h\nu$) greater than the semiconductor's band gap, generating electrons in its conduction band (e_{CB}) and highly oxidising electron 'holes' in its valence band (h_{VB}). The semiconductor needs to be chosen judiciously, so that: (a) electrons at its conduction band edge have sufficient energy to reduce water to hydrogen, and (b) holes at its valence band edge are sufficiently energetic to oxidise water to oxygen. Though the feasibility of such processes is well established, practical reactor systems have yet to be deployed, because the semiconductors also need to be stable, well-matched to the solar spectrum and achieve acceptable photon-to-hydrogen energy conversion efficiencies. Unfortunately, no single material yet meets all these criteria, to enable such artificial photosynthetic reactors to be: efficient, robust and cheap, of which only any two properties are achievable at present.

200 nm thin films of n-type α -Fe₂O₃ photo-anodes were produced by automated spray pyrolysis of iron(III) salts dissolved in ethanol onto F-doped SnO₂ coated glass or perforated titanium substrates heated to 450 °C and with an open area of ca. 17 %. These photo-anodes were deployed in laboratory-scale photo-electrochemical reactors, designed initially for photo-assisted electrolysis only, rather than spontaneous photo-electrolysis;

a metal cathode supported hydrogen evolution with an electrical energy input.

Results will be reported for the thermodynamic and kinetic constraints on such processes, together with the effects of experimental variables on H₂ production rates.

11:00am **EH-ThM10 Gate-Modulated Thermoelectric Characteristics of Silicon Nanowires on Plastic Substrates**, *Youngin Jeon*, Korea University, Republic of Korea, *J. Choi, K. Cho*, Korea University, *S. Kim*, Korea University, Republic of Korea

Recently, several novel concepts of thermoelectric technologies have been reported as a promising source of next-generation regeneratable energy. Moreover, silicon nanowire (Si NW) based thermoelectric devices are an attractive research area due to their advantages such as non-toxicity, abundance, and low-cost manufacturing, which can lead to new opportunities in broad areas of commercial electronics. The efficiency of energy conversion has been intensively studied by modulating the dimensionless thermoelectric figure of merit, $ZT = \sigma S^2 T / \kappa$, where σ is the electrical conductivity, S is the thermoelectric power (Seebeck coefficient), κ is the thermal conductivity, and T is the absolute temperature. Numerous studies indicate that the use of Si NW enables the improvement of ZT due to their low-dimensional properties. Nevertheless, it is still difficult to achieve high ZT value because σ , S and κ are interdependent. Therefore, the modification of these parameters in Si NW can enhance the thermoelectric properties. Among various methods, the field-effect modulation, applying electric fields on thermoelectric materials, may be one of the prominent ways to modulate the thermoelectric parameters. In this study, we fabricate a gated Si NW thermoelectric device constructed on a thermal-insulating plastic substrate, and examine the field-effect modulation of thermoelectric characteristics.

Figure 1 shows the optical image of our gated thermoelectric device on a plastic substrate. The structure of the device with a NW channel length of 50 μm is similar to a NW field-effect transistor. N-type Si NWs with a doped concentration of 10^{17} cm^{-3} are present between the electrodes and a gate electrode is located at the middle of the Si NWs. And a heater electrode is used as a heating source. We investigate the seebeck voltage variation of the gated thermoelectric device with the gate bias is applied. Figure 2(a) exhibits the seebeck voltage versus temperature variation characteristics of the device with V_{GS} from 0 to 5 V. Our device shows the good gate controllability of the channel potential, which implies the capability of the electrical conductivity modulation for the Si NWs. Thus, as V_{GS} decreases, the conductivity of the Si NWs also decreases accordingly, leading to the increase of the seebeck voltage with the same temperature variation. Therefore, as shown in Figure 2(b), the seebeck coefficient, defined as $- \Delta V / \Delta T$, is able to modulate with the gate voltage variation. Our study suggests that the gated thermoelectric device with n-type Si NWs on a plastic substrate reveals its potential use as a next-generation energy harvesting device.

11:20am **EH-ThM11 Transition Metals Ion Implantation into AlInN/GaN Thin Films**, *Abdul Majid*, University of Gujrat, Pakistan, *Zhu*, Chinese Academy of Sciences, Beijing

A lot of work has been done on Mn doping in III-V [1] but work on Mn and other TM ions doping in AlInN is still lacking. Out of III-Nitrides, AlInN is the only ternary alloy which is capable of lattice matching with GaN and is potential candidate for use as distributed Bragg reflectors, cladding layers and several other electronic /optoelectronic devices[2]. Like several other materials, the doping of AlInN with TM elements is expected to produce diluted magnetic semiconductors (DMS) based on it. Realization of AlInN based DMS will be exciting due to wide direct band gap and lattice matching capability at 17% indium content with GaN. This work is one of initial detailed reports on TM doping into AlInN. Transition metals ions of Cr, Mn, Co and V were implanted MOCVD grown wurtzite AlInN/GaN thin films at doses 5×10^{14} to 5×10^{16} ions/cm². The structural properties of the materials were studied by X-ray diffraction and Rutherford backscattering spectroscopy (RBS) techniques. XRD analysis revealed that GaN related peak for all samples remains at its usual Bragg position of $2\theta=34.56^\circ$ whereas a shift in AlInN peak taken place from its position of $2\theta=35.51^\circ$ for as-grown sample. RBS analysis provided interesting results with clear shift in position of indium related peak pointing to migration of indium atoms towards interface of heterostructures. Moreover this peak has observed to be splitted into two peaks which is indication of depth wise redistribution of indium atoms within the material. The measurements of magnetization versus temperature as well as applied magnetic field measured using SQUID magnetometer indicated room temperature ferromagnetism in the films. The density Functional Theory based calculations of Transition metals doped AlInN predicted that TM ions will preferably substitute In sites in the alloy. In order to model the experimental results and explore the mechanism of ferromagnetic exchange interactions in the materials, detailed density functional theory (DFT) based calculations

were performed. The electronic and structural properties of pure and TM doped AlInN were computationally investigated using ADF-BAND program which performs calculations using Kohn-Sham under Local Density Approximation. We modeled 64 atoms supercell with 3x3x3 mesh in the form Al₂₇In₅N₃₂ for pure AlInN and Al₂₇In₃Mn₂N₃₂ (2 Mn atoms substitutes 2 In atoms), Al₂₆In₅Mn₁N₃₂ (Mn substitutes Al) and Al₂₆In₅Mn₁N₃₂ (Mn substitutes Al) supercells for Mn doped AlInN. The literature suggests that Fermi level should lie within spin up Mn band predicting Mn:AlInN to be in half metallic state like other Mn doped III-Nitrides [3]. The calculated results indicate that Mn d band is partially filled for Al₂₇In₄Mn₁N₃₂ and Al₂₇In₃Mn₂N₃₂ whereas completely empty for Al₂₆In₅Mn₁N₃₂. It can be said that, either one or two Mn atoms substituting In sites produces expected half metallic AlInN whereas Mn substituting Al sites turns out to be unacceptable option. It is therefore concluded that Mn will preferably substitute indium in AlInN.

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De la Rosa, E.: EH-ThM1, **17**; EH-WeP9, **14**
Dunin-Borkowski, R.E.: EH-WeM3, **10**
Dutta, M.: EH-TuP10, **5**

— E —

Ebert, P.: EH-WeM3, **10**
Eisele, H.: EH-WeM2, **10**
Esparaza, D.: EH-ThM1, **17**
Esparza, D.: EH-WeP9, **14**

— F —

Feng, P.X.: EH-ThM3, **17**
Fu, W.: EH-TuM8, **3**
Fujita, T.: EH-WeM4, **10**
Fukata, N.: EH-TuP10, **5**

— G —

Galazka, Z.: EH-WeM2, **10**
Garay Dixon, A.: EH-TuP11, **6**
García-Fernández, T.G.F.: EH-WeE4, **15**
García-Segundo, C.G.S.: EH-WeE4, **15**
Garza-Hernández, R.: EH-MoM3, **1**
Gomez-Solis, C.: EH-ThM5, **17**
Guglietta, G.W.: EH-TuM5, **3**

— H —

Han, J.: EH-TuP13, **6**
Hankin, A.: EH-ThM9, **18**
Hernández-Rodríguez, N.: EH-TuM6, **3**
Higuchi, Y.: EH-WeP4, **13**
Hilfiker, M.: EH-TuM11, **4**
Hitchcock, A.P.: EH-WeM6, **11**

Hoffman, P.: EH-WeE8, **15**
Hutton, S.: EH-WeM10, **11**; EH-WeP7, **13**
Hwang, S.M.: EH-TuP11, **6**

— I —

Ianno, N.J.: EH-TuM10, **4**; EH-TuM11, **4**
Intonti, F.: EH-WeE7, **15**
Iwakiri, H.: EH-TuP4, **5**

— J —

Jeon, C.-W.: EH-TuP16, **7**; EH-WeP15, **14**
Jeon, Y.: EH-ThM10, **18**
Jeong, D.-S.: EH-TuP12, **6**
Ju, B.K.: EH-WeP3, **13**
Juarez-Ramirez, I.: EH-ThM5, **17**
Jun, Y.: EH-TuP14, **6**
Jung, J.P.: EH-TuP17, **7**

— K —

Kang, M.K.: EH-WeP3, **13**
Kelsall, G.: EH-ThM9, **18**
Kenis, P.J.A.: EH-TuE9, **8**
Kim, D.J.: EH-TuP17, **7**
Kim, G.: EH-TuP9, **5**
Kim, H.-G.: EH-TuP16, **7**
Kim, H.S.: EH-MoM10, **1**
Kim, J.: EH-TuP14, **6**
Kim, J.H.: EH-TuP15, **6**; EH-TuP17, **7**
Kim, J.-H.: EH-TuP4, **5**
Kim, N.: EH-WeP1, **13**
Kim, S.: EH-ThM10, **18**; EH-WeE10, **16**; EH-WeP15, **14**
Kim, S.H.: EH-MoM10, **1**; EH-WeP1, **13**
Kim, S.-H.: EH-TuP16, **7**
Kim, W.K.: EH-TuP13, **6**; EH-TuP14, **6**
Kubo, M.: EH-WeP4, **13**
Kwon, M.-S.: EH-TuP16, **7**

— L —

Leblebici, S.Y.: EH-WeE7, **15**; EH-WeE9, **16**
Leblebici, Y.: EH-WeE8, **15**
Lee, C.S.: EH-WeP3, **13**
Lee, H.: EH-TuP12, **6**
Lee, J.: EH-WeE7, **15**
Lee, J.J.: EH-WeP2, **13**
Lee, J.S.: EH-TuP8, **5**
Lee, K.I.: EH-WeP3, **13**
Lee, V.: EH-WeM6, **11**
Lenz, A.: EH-WeM2, **10**
Li, Y.: EH-WeE9, **16**
Li, Y.M.: EH-ThM3, **17**
Lim, J.Y.: EH-TuP15, **6**
Lim, S.B.: EH-TuP6, **5**
Liu, X.: EH-TuE1, **8**
Lopez, T.: EH-WeP9, **14**
lopez-Luke, T.: EH-ThM1, **17**
Lyubinetzky, I.: EH-WeM1, **10**

— M —

Majid, A.: EH-ThM11, **18**
Markovic, M.: EH-TuE7, **8**
Martínez-De León, J.M.DL.: EH-WeE4, **15**
Mathies, A.: EH-WeE8, **15**
McQuillan, A.J.: EH-ThM4, **17**
Melli, M.: EH-WeE7, **15**; EH-WeE9, **16**
Miyazawa, T.: EH-TuM8, **3**
Moon, K.: EH-TuP14, **6**
Morrison, J.: EH-WeP7, **13**
Munehika, K.: EH-WeE7, **15**

— N —

Nakamichi, M.: EH-TuP4, **5**

— O —

Ogletree, D.F.: EH-WeE7, **15**
Oliva UC, J.: EH-WeP9, **14**

Oshima, M.: EH-TuE3, **8**
Ozawa, N.: EH-WeP4, **13**

— P —

Park, C.: EH-TuP12, **6**
Park, C.H.: EH-TuP15, **6**
Park, D.: EH-TuP9, **5**
Park, H.: EH-TuP13, **6**; EH-WeE10, **16**
Park, J.H.: EH-MoM10, **1**; EH-WeP3, **13**
Park, Y.J.: EH-TuP5, **5**; EH-TuP6, **5**
Peña, L.: EH-TuM6, **3**
Peng, X.Y.: EH-ThM3, **17**
Portz, V.: EH-WeM3, **10**
Ptasinska, S.: EH-WeM12, **11**

— R —

Rejón, V.: EH-TuM6, **3**
Riech, M.: EH-TuM6, **3**
Roberts, A.: EH-WeP7, **13**
Roy Choudhury, K.: EH-TuM5, **3**
Ryu, H.-S.: EH-TuP14, **6**
Ryu, I.: EH-TuP9, **5**

— S —

Sakurai, T.: EH-TuM8, **3**
Salmeron, M.B.: EH-MoM8, **1**
Sanchez, A.: EH-ThM1, **17**
Sánchez-Aké, C.S.A.: EH-WeE4, **15**
Sanchez-Martínez, D.: EH-ThM5, **17**
Sarkar, A.: EH-TuM10, **4**; EH-TuM11, **4**
Sato, K.: EH-TuP10, **5**
Schnedler, M.: EH-WeM3, **10**
Schulmeyer, T.S.: EH-WeM11, **11**
Schwartzberg, M.: EH-WeE8, **15**
Sharp, I.D.: EH-WeE9, **16**
Shlesinger, I.: EH-WeE9, **16**
Song, J.D.: EH-MoM10, **1**
Soukup, R.J.: EH-TuM10, **4**; EH-TuM11, **4**
Stamenkovic, V.S.: EH-ThM8, **18**
Stumper, J.: EH-WeM6, **11**
Surman, D.: EH-WeM10, **11**; EH-WeP7, **13**
Susac, D.: EH-WeM6, **11**

— T —

Tamura, M.: EH-WeE3, **15**
Tenopala, F.T.: EH-WeE4, **15**
Thissen, A.T.: EH-WeM11, **11**
Toma, F.M.: EH-WeE9, **16**
Torres-Guerra, L.M.: EH-ThM5, **17**
Trejo, N.: EH-MoM1, **1**

— U —

Urias-Cordero, F.: EH-TuM11, **4**

— V —

Valverde-Alva, M.A.V.A.: EH-WeE4, **15**
Villagrán-Muniz, MVM.: EH-WeE4, **15**

— W —

Wang, S.: EH-TuM8, **3**
Weber-Bargioni, A.: EH-WeE7, **15**; EH-WeE9, **16**

— X —

Xia, H.: EH-TuM8, **3**

— Y —

Yim, S.: EH-TuP9, **5**
Yokoyama, N.: EH-WeP4, **13**
Yoon, D.H.: EH-TuP5, **5**
Yugami, H.: EH-WeP4, **13**

— Z —

Zarazua, I.: EH-ThM1, **17**; EH-WeP9, **14**
Zhang, XQ.: EH-WeM12, **11**
Zhu: EH-ThM11, **18**
Zielinski, R.: EH-WeM2, **10**