

Energy Frontiers Focus Topic Room: Hall 3 - Session EN-TuP

Energy Frontiers Poster Session

EN-TuP1 Effect of Ultra-violet Light on the Degradation in Organic Solar Cells, Kenji Harafuji, Ritsumeikan University, Japan, *H. Sato,* Ritsumeikan University

Organic solar cells (OSCs) offer many desirable properties such as flexibility, low cost, and easy fabrication. The lifetime is, however, still short. The degradation may be driven by light illumination, exposure to external air, and high temperature.

The degradation phenomenon under repetitive light illumination and high-vacuum is experimentally investigated in small molecular OSCs. The OSC has a structure of an indium tin oxide (anode)/copper phthalocyanine (donor, 20 nm)/fullerene (acceptor, 40 nm)/bathocuproine (buffer, 10 nm)/Ag (cathode, 100 nm). Xenon lamp illumination with an intensity of 100 mW/cm² is performed, and an air mass 1.5 global spectrum is obtained using a solar simulator. The repetitive illumination with the period of 30 s is composed of 100 repetitions of 3 s illumination followed by 27 s in the dark. The effect of light wavelength on the degradation is studied with the use of a long-pass filter of cut-wavelength λ_c . The filter allows the transmission of light into the OSC only with its wavelength longer than λ_c . Six kinds of filter with $\lambda_c=0, 320, 370, 400, 550$ and 665 nm are used.

It is found that the OSC degradation is dominated by the UV (ultra-violet) light with wavelength less than 400 nm. The short-circuit current density J_{sc} , open-circuit voltage V_{oc} , and fill factor FF in the case of $\lambda_c=0$ nm (without the filter) are decreased approximately 20%, 40%, and 60% compared with the case of λ_c greater than 400 nm at the 100th illumination, respectively. Resultantly, power conversion efficiency η_p is decreased 80%. The η_p value is decreased 60% with the filter of $\lambda_c=320$ nm, whereas initial η_p is almost kept even at 100th illumination with the filter of $\lambda_c=400$ nm. An S-shaped kink appears near the V_{oc} region in the current-voltage (J - V) characteristics at 100th illumination in the case of λ_c shorter than 400 nm. This shows the increase of series resistance in the OSC. The origin may be due to the disorder of crystal structure at the anode/donor interface. There are no appreciable changes of J - V characteristics between at 1st and 100th illuminations in the case of λ_c longer than 400 nm.

On the other hand, the initial η_p value at the first illumination is much smaller as λ_c is increased in the range of λ_c longer than 400 nm, accompanied by the large decrease of J_{sc} . This is because the total amount of light energy transmitted into active organic layers is decreased as λ_c is longer.

The origin of the degradation by illumination is revealed to be the UV light component with its wavelength shorter than 400 nm. The optimum λ_c value is 400 nm from the compromise between initial efficiency η_p and OSC degradation.

EN-TuP2 Characteristics of DSSC Fabricated at Low Temperature, EunChang Choi, J.U. Wie, B.Y. Hong, Sungkyunkwan University, Republic of Korea

Dye-sensitized solar cells (DSSCs) have been widely investigated as a next-generation solar cell because of their simple structure and low manufacturing cost. To realize a commercially competitive technology of DSSCs, it is imperative to employ a technique to prepare nanocrystalline thin film on flexible organic substrate, aiming at increasing the flexibility and reducing the weight as well as the overall device thickness of DSSCs. The key operation of glass-to-plastic substrates conversion is to prepare mesoporous TiO₂ thin film at low temperature with a high surface area for dye adsorption and a high degree of crystallinity for fast transport of electrons. However, the electron transport in the TiO₂ film synthesized at low temperature is very poor. So, in this study, TiO₂ films synthesized at high temperature were transferred on the selective substrate. We fabricated DSSCs at low temperature using this method. So, we confirmed that the performance of DSSCs using TiO₂ films synthesized at high temperature was improved.

EN-TuP3 Conductivity Enhancement Effect of Sodium Dodecyl Sulfate on PEDOT:PSS for Organic Solar Cell Application, K.-H. Hwang, H.J. Seo, S.-H. Nam, Y.J. Kim, C.Y. Park, Jin-Hyo Boo, Sungkyunkwan University, Republic of Korea

There are many researches on PEDOT:PSS treatment for application to flexible device electrode. Almost PEDOT:PSS treatment is consisted with step adding little bit surfactant to enhancement of adhesion between

PEDOT:PSS and substrate or TCO materials. But basic research about surfactant effect is lacking. We study on the effects of sodium dodecyl sulfate (SDS) with controlling the concentration in aqueous PEDOT:PSS solution, and we confirm the conductivity enhancement of the mixture thin films with surfactant and PEDOT:PSS. Thin films are firstly prepared by spin coating method and then fabricated organic solar cells. To study the structural effects on the resulted electrical properties, thin films are mainly investigated by FE-SEM (Field Emission Scanning Electron Microscopy), AFM (Atomic Force Microscopy), respectively. At the same time, electric properties are also investigated by both 4-point probe and solar simulator.

Keywords: PEDOT, SDS, Surfactant, Organic solar cell, Electrical conductivity

EN-TuP4 Study of the Synthesis of Cu₂ZnSnS₄ Thin Films by Reactive Magnetron Co-Sputtering, P.-A. Cormier, Rony Snyders, University of Mons, Belgium

Cu₂ZnSnS₄(CZTS) has attracted significant attention for thin film solar cells because it is composed on earth abundant and non-toxic elements and, has an optimal band gap of 1.5 eV. The control of the film stoichiometry is critical during the growth of CZTS thin films. We previously demonstrated the possibility to grow close to stoichiometric and phase pure crystallized CZTS thin films by reactive magnetron co-sputtering [1]. The films were close to stoichiometric (Zn/Sn=1.1-1.4, Cu/[Zn+Sn]=0.9-1.1). Nevertheless, it has been suggested that Cu-poor Zn-rich CZTS have would present the best solar cell performances [2].

Therefore, in the present work, aiming to better control the film stoichiometry and to deeper understand the relationship between the chemical composition of the deposited film and its phase constitution and ultimately to reach the best performances of the cell, two Cu poor CuSn targets presenting Cu/Sn ratio of 1.5 (CuSn1.5) and 1 (CuSn1) have been utilized. In both case, the effect of the sputtering power (P_{CuSn}) on the material properties has been studied. The films were characterized by multiwavelength Raman spectroscopy (785 and 325 nm), by X-Ray Diffraction (XRD), and by Energy-dispersive X-ray spectroscopy (EDX).

As expected, the phase constitution is affected by increasing P_{CuSn} . Using the CuSn1.5 target, its evolution is similar than the one observed using the CuSn2 target [1]: at low P_{CuSn} , the films mainly contain CZTS, with a low content of ZnS. Increasing the power, CZTS disappears to the profit of SnS, Cu₄Zn clusters, S₆ and ZnS. On the contrary, using the CuSn1 target does not allow the formation of CZTS dominated films. Indeed, even for the low P_{CuSn} conditions, ZnS dominates the Raman spectra. For medium power ($P_{CuSn}=45$ W), the film is composed by SnS, S₆, ZnS and CZTS while for higher powers, the films are similar than the one obtained with the CuSn1.5 and CuSn2 targets and the CZTS is replaced by Cu₄Zn clusters. For all sets of data, the concentration in Zn is stable. Therefore, the decomposition of the CZTS material seems to be related to the increase of the Cu and Sn concentrations and to the decrease of the S one, which deviates from the theoretical values in CZTS. Based on these data, a phase diagram can be built.

Finally, one film of each region was synthesized and used in solar cell devices in order to investigate the influence of the phase constitution on the cell performance with efficiency up to 1.8%.

[1] Cormier et al., Acta Materialia, accepted for publication subjected to minor revisions (2015)

[2] Mitzi et al., Solar Energy Materials & Solar Cells 95 (2011)

EN-TuP5 Development of Low Cost, Solution Deposition Method for High Efficiency Cu₂ZnSn S_xSe_{4-x}(CZTSSe) Thin Film Solar Cells, Cheik Sana, S. Shahriar, J. Galindo, D. Kava, D.R. Hodges, University of Texas at El Paso

Non-vacuum, solution based processing of earth abundant Cu₂ZnSnS_xSe_{4-x}(CZTSSe) has attracted considerable interest as a material capable of driving economical and terawatt capacity photovoltaic module production. It has already shown promising results with solar cells efficiency up to 12.6%. The interest to CZTSSe as an absorber layer for thin film solar cells is due to its large absorption coefficient of over 10⁴ cm⁻¹ in the visible range, its tunable optical band on-vacuum solution based method to deposit Cu₂ZnSnS_xSe_{4-x}(CZTSSe) was investigated. In this approach, a precursor solution of CZTSSe is formed by reacting metal sources copper (II) acetate monohydrate, zinc (II) acetate dehydrate, tin (II) chloride dehydrate and elemental powders of sulfur and selenium powders in a solution of 2-methoxyethanol. The slurry was then spincoated followed by annealing at different temperatures. Optical, structural and electronic characterization of thin films were performed using scanning electron microscope (SEM), X-ray diffractometer (XRD), raman spectrometer, UV-Vis spectrophotometer,

4 point probe and Hall Effect Measurement System. Film thickness was measured using Dektak 150 surface profilometer. X-Ray diffractograms show different shifts of the kesterite/stannite (112) peak, which indicates the presence of CZTSSe. The three major peaks of the (1112), (220), and (312) planes had respective 2θ in the vicinity of 28° , 47.5° and 56° . The shift of the peaks depends on the ratios of S/Se in the synthesized material. The lattice constants decrease linearly with increasing contents of S in the precursor solution. Raman spectroscopy showed traces of both quaternary CZTS and CZTSe.

EN-TuP7 Synthesis and Characterization of Electron Beam Deposited $\text{Cu}_2\text{ZnSn}_{1-x}\text{Si}_x\text{S}_4$ Thin Films, Alejandro Alvarez Barragan, S. Exarhos, J. Hernandez, L. Mangolini, University of California - Riverside

Nowadays, $\text{Cu}_2\text{In}_x\text{Ga}_{1-x}\text{Se}_4$ (CIGS) and CdTe are the leading commercially available compounds in thin film photovoltaics technology. Nevertheless, the scarcity of In and Te, and the toxicity of Cd, are considerable threats that may hinder the production and increase the cost of these materials in the near future. Replacement of In, Ga, and Se in CIGS with Zn, Sn, and S yields the promising quaternary compound $\text{Cu}_2\text{ZnSnS}_4$ (CZTS). This material has a favorable direct band gap of 1.5 eV. Further, each of its constituent elements is earth abundant and non-toxic. These two attractive characteristics make it plausible to launch CZTS as the wave of the future in thin film PV. We now present the synthesis process of CZTS by electron beam evaporation and a subsequent sulfurization step¹. A thin film of Zn, Cu, and Sn stacked layers was obtained upon localized heating of their respective metallic sources. The as-deposited layers were subsequently sulfurized under a vacuum inside a sealed quartz tube at temperatures ranging from 500°C to 600°C . One of the main difficulties that has been reported for CZTS synthesis is the stoichiometric control of the material. Secondary, unwanted phases such as CuS, SnS_2 , ZnS, and Cu_2SnS_3 may nucleate if the initial atomic percentage of the layers or the sulfurization parameters are off a small window in which CZTS can be produced^{2,3}. Extreme care was taken to prevent this issue. Characterization techniques such as Energy Dispersive Spectroscopy (EDS), X-ray Diffraction (XRD), and Raman Spectroscopy were heavily employed to confirm the presence of CZTS crystals. We are also presenting preliminary results regarding the synthesis of a $\text{Cu}_2\text{ZnSn}_{1-x}\text{Si}_x\text{S}_4$ structure. To the best of our knowledge, synthesis of this compound by the E-beam evaporation and sulfurization process is yet to be reported. Previous theoretical and experimental data regarding its wide band gap add up to the interest of engineering this material for optoelectronic applications⁴.

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EN-TuP8 Optical and Photocatalytic Properties of Nanostructured Ce-TiO₂ Mixed Oxides, R. Ramirez-Lopez, Escuela Superior de Ingenieria Quimica e Industrias Extractivas-IPN, Mexico, Isaias Hernandez-Perez, Universidad Autonoma Metropolitana- Azcapotzalco, CBI, Mexico, R. Suarez-Parra, Instituto de Energias Renovables, UNAM, Mexico, RT. Hernandez-Lopez, Universidad Autonoma Metropolitana- Azcapotzalco, CBI, Mexico, A. Garcia-Sotelo, E. Campos, M. Melendez-Lira, Cinvestav-IPN, Mexico

The use of nano-crystalline TiO_2 is a promising strategy for photocatalytic remediation of wastewater due to its broad ability to remove various pollutants in aqueous media. In order to use a major part of the spectral solar distribution it would be necessary to reduce the bandgap of TiO_2 based materials. In this study, a series of nanocrystalline CeO_2 - TiO_2 powders were successfully synthesized by sol-gel at room temperature, employing titanium isopropoxide and cerium nitrate as precursors, with nominal 2, 5, 10, 20 and 50 % of CeO_2 : TiO_2 molar ratio. The crystalline structure, surface morphology and optical properties of synthesized samples were characterized using powder XRD, TEM, SEM, XPS. The optical band gap was determined by DR-UV-Vis spectroscopy and the emission spectrum by photoluminescence spectroscopy. Photocatalytic activity was evaluated by the photodegradation of Orange II azo dye, employing two different sources of irradiation 365 and 425 nm. Structural characterization showed that the Ce- TiO_2 particles crystallized into the anatase phase. TEM micrographies shown clearly the formation of nanocrystals. The optical bandgap energy shows a red shift for all synthesized samples compared with pure TiO_2 . The

results shown that the incorporation of 5 % CeO_2 effectively improves the photocatalytic activity compared with pure TiO_2 at UV; while Ce incorporation activates it for 425 nm excitation still the nominal 5% shows the best performance. The results are discussed in terms of the electronic structure modification by Ce incorporation in the TiO_2 matrix.

EN-TuP9 Hybrid Photoelectrode Based on Two-Dimensional Materials Decorated BiFeO₃ Thin Films for Efficient Solar Water Splitting, C.M. Yoon, H. Lee, J. Lee, H. Lee, Taekjib Choi, Sejong University, Republic of Korea

Semiconducting metal oxides have been attracted much interest as photoelectrodes for solar water splitting because of their stable photochemical activity in aqueous solutions. However, photoelectrochemical performance is usually limited by poor charge carrier separation. Thus, hybrid photoelectrodes combined with semiconducting ferroelectric materials offer promising potential for achieving efficient solar water splitting by promoting photogenerated-charge carrier separation due to spontaneous electric polarization leading to an increase in the electric field. In this study, we have fabricated two-dimensional materials decorated BiFeO_3 thin films as hybrid electrodes. The structural and optical properties of single and hybrid electrodes were comparatively characterized. The hybrid electrodes exhibited a stronger absorption of visible light and produced a higher photocurrent than that of single electrode. For hybrid electrodes, photoelectrochemical characterization demonstrated a large enhancement of the interfacial charge transfer kinetics as well as an efficient charge carrier separation, which greatly contributed to the improved photoelectrochemical performances. In addition, we will discuss the effect of electric polarization on interface reduction/oxidation (REDOX) through electrolyte ions. Therefore, our results provide useful information for developing highly efficient hybrid photoelectrodes for solar water splitting.

EN-TuP11 Improvement in Photovoltaic Response of PLZT Thin Film Capacitors with ITO Electrodes, Sushma Kotru, V.N. Harshan, V. Batra, The University of Alabama

Ferroelectric thin films of perovskite-type structure are of practical interest because of their excellent ferroelectric, dielectric and optical properties. Recently these materials have generated lot of research interest for photovoltaic applications (PV). Photovoltaic properties of $\text{Pb}_{0.95}\text{La}_{0.05}\text{Zr}_{0.54}\text{Ti}_{0.46}\text{O}_3$ (PLZT) thin film capacitors prepared using solution based method with various top electrodes having different work functions are investigated. The results demonstrate that ITO (Sn doped In_2O_3), a transparent conducting oxide, as top electrode, enhances the magnitude of photo voltage and photo current as compared to metal electrodes. The photovoltaic efficiency is enhanced by orders of magnitude with ITO as top electrode when compared to metal electrode devices. Thus the choice of transparent conducting oxide as an electrode holds potential for improving the photovoltaic response of ferroelectric thin film capacitors.

EN-TuP14 Rational Design of Battery Architecture at Nanoscale: Self-Aligned Batteries Inside Nanopores via Atomic Layer Deposition, C. Liu, E. Gillette, Xinyi Chen, A.J. Pearce, A.C. Kozen, M. Schroeder, K. Gregorczyk, S.B. Lee, G.W. Rubloff, University of Maryland, College Park

A self-aligned nanostructured battery entirely confined within a single nanopore offers a powerful platform to investigate the rate performance and cyclability limits of nanostructured storage devices. Atomic layer deposition (ALD) has enabled such a structure that embeds coaxial nanotubular electrodes and electrolyte confined inside a single anodic aluminum oxide (AAO) nanopore, realizing an ultrasmall full cell battery with $\sim 1\mu\text{m}^3$ volume ($\sim 1\text{fL}$). These nanopore batteries display exceptional power-energy performance and cyclability when tested as massively parallel devices ($\sim 2\text{billion}/\text{cm}^2$). The extraordinary thickness and conformality control of ALD and the highly self-aligned nanoporous structure of AAO are crucial to fabrication of precise, self-aligned, regular nanopore batteries. Using controlled-conformality ALD processes, we optimized metal nanotube current collector (Ru or Pt) length at two ends of AAO nanopores to provide fast electron transport to overlying anode and cathode materials, while keeping them spatially and electrically isolated. Crystalline V_2O_5 was deposited as lithium ion storage material inside the metal nanotubes using O_3 as the oxidant. Subsequently, the V_2O_5 was electrochemically prelithiated at one end to serve as anode while pristine V_2O_5 without Li at the other end served as cathode, enabling the battery to be cycled between 0.2V and 1.8V. Capacity retention of this full cell is 95% at 5C rate and 46% at 150C, with more than 1000 charge/discharge cycles. Further increase of full cell output potential is also demonstrated for SnO_2 and TiO_2 anodes in asymmetric full cells with V_2O_5 cathodes. These results reveal the potential of ultrasmall, self-aligned/regular, densely packed nanobattery structures as a building block for high performance energy storage systems and as a test bed to study ionics and electrochemics at nanoscale with a variety of geometrical modifications.

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