Energy Frontiers Focus Topic
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Energy Frontiers Poster Session

EN-TuP2 Mini-band Formation in a Strain-balanced InGaAs/GaAsP MQW Solar Cell Structure Investigated by a Photoreflectance and a Surface Photovoltage Spectroscopy, *Tetsuo Ikari, A. Fukuyama, K. Nishioka, T. Aihara, H. Kuradome,* University of Miyazaki, Japan, *K. Toprasertpong, M. Sugiyama, Y. Nakano*, University of Tokyo, Japan

Embedding of multi quantum well (MQW) structures in an absorption layer of GaAs solar cell is a promising idea for developing higher efficient solar cell devices. Extension of the absorbing region to longer wavelength side enhances the short-circuit current. When the mini-band forms between the QW, further developing of the conversion efficiency would be expected in term of a carrier tunneling without recombination of the photo excited carriers. However, recombination at the QW interface still leads to the degradation of the efficiency. Therefore, we fabricated a strain-balanced InGaAs/GaAsP layer in the intrinsic region of the GaAs *p-i-n* solar cell [1]. The mini-band formation for the samples with different thickness of the barrier region from 5.3 to 1.9 nm was studied by using a photoreflectance (PR) and a surface photovoltage (SPV) spectroscopy at room temperature.

The energies at the Brillion zone edges were detected from the Kramers-Kronig analysis of the PR spectra for estimating the mini-band width as a function of barrier thickness. When the mini-band formed, the ratio of carriers escaped thermally from each QW may change. SPV spectra were, then, measured to know the carrier escaping rate and how this component affects the absorption spectra of the solar cell structures.

The observed PR spectra for the sample with thinnest barrier width of 1.9 nm show two critical energies at 1.274 and 1.312 eV. The energy difference of these critical energies was around 0.038 eV and this energy difference reduces from 0.020 to 0.009 eV for the samples with barrier thickness of 2.7 and 3.6 nm, respectively. Supposing that such energy difference shows the mini-band width, the reduction of the energy with increasing the thickness of the barrier can be understood. The theoretical estimation using a Kronig-Penny model calculation for the width suggests that the mini-band width in the QW is 70 and 0 meV for e1 and topmost hh1 sub-bands. Therefore, the observed mini-band width is smaller than expected. The reason is not clear at present. For the SPV spectra, two broad peaks were observed at 1.29 and 1.32 eV. The energy difference also decreases with increasing the thickness of the barriers. Smaller critical energies for SPV may be explained that these signals detect the maxima energy of the joint-density of states which is larger than the band edge energies. Since the carrier escaping from the QW and radiative and non-radiative recombination rates may be strongly temperature dependent, estimation of the relevant activation energies for carrier escaping from these measurements were useful for further discussion.

[1] M. Sugiyama, *et al.*, J. Cryst. Growth 315 (2011) 1.

EN-TuP5 Cu(In,Ga)Se$_2$ Absorber Layer Deposited by Radiofrequency Magnetron Sputtering, *Romain Meunier, M.-P. Besland, P.Y. Jouan, A. Lafond,* Université de Nantes, France, *P.Y. Thoulon, M. Ricci*, Crosslux Company, France

In the last decades, the deposition of CIGSe thin films by sputtering has seldom been investigated. Besides, the sputtering of a single quaternary CIGSe target would be a real advantage for industrial development. Indeed, sputtering technique exhibits a good compatibility with industrial up-scaling and limits selenium use with respect to toxicity issues. In 1992, Hernandez et al[1] early published on CIGSe layers deposited by sputtering of a single quaternary CIGSe target.

The improvement of plasma discharges at lower working pressures in the last years had allowed news possibilities for CIGS thin films deposited by sputtering. In 2010, Frantz et al[2] succeeded to obtain a CIGSe solar cell with an efficiency of 8.9%.

At IMN laboratory, a dedicated chamber has been home-designed for CIGSe thin films deposition using one step sputtering. CIGSe thin films were deposited on SLG/Mo substrates by radio-frequency magnetron sputtering at ambient temperature. The deposition parameters like pressure or power density have been investigated. Then, CIGS thin films have been annealed at various temperatures in a furnace under Ar flow. The evolution of chemical composition and structural properties of CIGS thin films as-deposited and annealed will be presented.

References

1. Hernández Rojas, J. L. et al.. Appl. Phys. Lett. 60, 1875–1877 (1992)

2. Frantz, J. A. et al. Thin Solid Films 519, 7763–7765 (2010).

EN-TuP6 Developments in Power Efficient Dissociation of CO$_2$ using Non-Equilibrium Plasma Activation, *Waldo Bongers, A.P.H. Goede, M.F. Graswinckel, S. Welzel,* Dutch Institute for Fundamental Energy Research, The Netherlands, *M. Leins, J. Kopecki, A. Schulz, M. Walker,* Universität Stuttgart, Germany, *M.C.M. van de Sanden*, Dutch Institute for Fundamental Energy Research, The Netherlands

In the framework of an emerging Solar Fuel program the first and essential CO$_2$ dissociation step of CO$_2$ into CO and O$_2$ has been studied. The focus was thereby on high energy efficiency of the process using non-thermal (non-equilibrium) microwave plasmas without the use of rare materials. The plasma was generated by tangentially injecting CO$_2$ gas in a quartz tube placed inside a low loss 915 MHz TM$_{010}$ circular waveguide mode cavity. Powers were used up to 10 kW. The feed gas expanded supersonically after the cavity to quench the plasma and prevent vibrational-translational relaxation losses. These experiments resulted in power efficient conversion (more then 50%) of large CO$_2$ flows (up to 75 standard liter per minute) with 11% conversion yield. The product formation was measured downstream the plasma at the expansion in a calibrated mass spectrometer.

The research at the plasma Solar Fuels facilities of DIFFER concentrates on optimization of power efficient selective vibrational CO dissociation. This can be achieved by means of several novel methods: like tuning the optimal kinetic energy range of the electrons by controlling the reduced electric field in the microwave cavity or make use of the relaxation time difference of translational and vibrational modes of CO controlled by modulating the microwave field. First results were obtained with a 2.45 GHz 1kW microwave plasma source. The source consists of a quartz tube with a tangential gas injection system placed inside a circular TEM mode coaxial cavity coupled to a TE$_{10}$ rectangular waveguide mode cavity. The configuration of the coaxial cavity allows control of the electric field. With an input of 7 standard liter per minute of CO$_2$ energy efficiencies 15% to 36% were obtained (based on CO$_2$ depletion) in the pressure range from 1Bar (atmospheric) till 0.2 Bar. An update on these new research developments will be shown.

EN-TuP8 GLAD & SAD-GLAD Nanorod Array Catalyst Electrodes for Polymer Electrolyte Membrane Fuel Cells, *Fatma Yurtsever, M. Begum, M. Yurukcu, M.F. Cansizoglu, A.U. Shaikh,* University of Arkansas at Little Rock, *W.J. Khudhayer,* University of Babylon, Iraq, *N. Kariuki, D.J. Myers,* Argonne National Laboratory, *T. Karabacak*, University of Arkansas at Little Rock

Polymer electrolyte membrane (PEM) fuel cell technology is one of the promising alternative

energy systems for an environmentally friendly, sustainable energy economy. However, PEM

fuel cells require an expensive platinum catalyst which raises the cost of the fuel cell. In this

study we investigated the electrocatalytic oxygen reductive reaction (ORR) activities of Pt and

Pt-Ni alloy catalyst thin film coated on Cr and Ni base nanorod arrays, respectively, and also

ORR of Pt-Ni alloy nanorods. Cr and Ni nanorods were used as low cost, high surface area

metallic supports for the conformal Pt and Pt-Ni allow thin film, respectively. Nanorods were

grown on glassy carbon electrodes using a magnetron sputtering glancing angle deposition

(GLAD) technique and conformal coating of catalyst thin film on the base nanorods were

achieved using a small angle deposition (SAD) technique. Pt-Ni alloy nanorods were also grown

using GLAD. The electrocatalytic ORR activity of the nanostructured electrodes were

investigated using cyclic voltammetry (CV) and rotating disk electrodes (RDE) in a 0.1M

aqueous perchloric (HClO$_4$) acid solution. The electrochemical active surface area (ECSA),

surface area specific activity (SA), and mass activity (MA) values were determined and

compared to the Pt and Pt-Ni alloy catalyst results in the literature. The results from GLAD Pt-Ni

alloy nanorods exhibit higher values of ECSA compared to geometric area of the nanorods. The

MA of the Pt-Ni nanorods was found to be a factor of 2.3 to 3.5 higher than that of pure Pt

nanorods of the same dimensions and increasing with increasing Ni contents. However, the SA

enhancement was only observed for the nanorods with the highest Pt contents. In addition, both

the SAD-Pt/GLAD-Cr and GLAD-Pt-Ni alloy nanorods were found to have higher stability

against loss of ECA during potential cycling in the acidic electrolyte. Our preliminary results on

the SAD-Pt-Ni/GLAD-Ni nanorod arrays will also presented

EN-TuP9 XPS Study of Ternary Chalcogenide Semiconductors Deposited by a Solution-based Method for Solar Cells Applications, *Francisco Aguirre-Tostado, R. Garza-Hernandez,* CIMAV-Monterrey, Mexico, *R. Mayen-Mondragon,* UNAM-Punta, Mexico, *E. Martinez-Guerra*, CIMAV-Monterrey, Mexico

The use of solution-based methods for semiconducting thin film deposition is of great importance for large area photovoltaics applications, enabling as well the deposition on flexible substrates. Chalcogenide semiconductor materials present p- and n-type characteristics that are attractive for photovoltaics applications. The optimization of device structure for a solar cell requires an atomistic understanding of the structure and chemical reactions taking place during deposition and post-deposition processes. In this regard, X-ray photoelectron spectroscopy (XPS) is uniquely suited for tracking chemical reactions occurring at the surface and interface of sub-nanometric layers. The chemical analysis and thermal stability for surface and interface reactions of binary and ternary chalcogenide semiconductors is presented. CuS, ZnS, SnS$_2$, CdS thin films and some of its combinations were deposited by the successive ionic layer absorption and reaction method (SILAR) under controlled environment next to the XPS analysis load-lock chamber. Step by step XPS analysis of the SILAR process reveals an incubation period that depends on temperature and ion concentrations. The stability of the heterostructures is discussed in terms of chemical reactivity and inter-diffusion.

EN-TuP10 Enhanced Photovoltaic Response of Pb$_{0.95}$La$_{0.05}$Zr$_{0.54}$Ti$_{0.46}$O$_3$ Thin Film Based Solar Cells, *Vaishali Batra, G. Cabot, S. Kotru*, University of Alabama

Ferroelectrics materials have generated considerable interest in the field of ferroelectric photovoltaic (FE-PV) in recent years and are still being researched as potential alternative material for future photovoltaic applications. However, the PV response from these FE-PV devices is still very low. In this work, various approaches are adopted to improve the PV response from the FE-PV devices. The ferroelectric material used for fabricating the capacitor type solar cells was Pb$_{0.95}$ La$_{0.05}$Zr$_{0.54}$Ti$_{0.46}$ O$_3$ PLZT) in thin film form, prepared using chemical solution deposition method. In one approach, a thin layer of lead titanate (PTO) was introduced as a seed layer to control the (001)/ (100) orientation and to suppress the (110) orientation of the PLZT films. Presence of seed layer was seen to show a remarkable effect on the ferroelectric and the photovoltaic properties of the devices. Another approach used was the incorporation of silver nanoparticles (SNPs) in PLZT matrix. The narrow band gap nanoparticles (NP) embedded in PLZT films enhances the optical absorption in Pt/PLZT/Pt by extending the absorption spectra from ultraviolet to a fraction of the visible light spectrum. Results showing the effect of seed layer and incorporation of NP on PLZT devices will be presented.

EN-TuP11 Influence of Orientation and Size in Crystallite on Various Properties in Al-doped ZnO Films for Solar Cell Transparent Electrode Applications, *T. Minami, Toshihiro Miyata, T. Yamanaka*, Kanazawa Institute of Technology, Japan

We have recently reported that impurity-doped ZnO thin films appropriate for transparent electrode applications in thin-film solar cells were related more to the content rather than the kind of impurity doped into the films as well as to the deposition method used [1]. This paper describes the influence of the orientation and size in crystallite on the resulting optical absorption and the obtainable surface texture structure and carrier mobility in Al-doped ZnO (AZO) thin films prepared with different types of magnetron sputtering deposition (MSD) methods. The AZO thin films were prepared with a thickness of 500-3500 nm on OA-10 glass substrates at a sputter Ar gas pressure of 0.2-12 Pa and a temperature of room temperature (RT)-350ºC by d.c. MSD or r.f. power superimposed d.c. MSD. The surface texture formation was carried out as a result of MSD under the appropriate deposition condition or by wet-chemical etching (in a 0.1% HCl solution at 25ºC). For example, when the AZO films were prepared with increasing a

sputter gas pressure from 0.4 to 12 Pa at a deposition temperature of 350ºC, the films exhibited the red shift with tailing in both the absorption edge and plasma edge as the sputter pressure was increased. With increasing the sputter gas pressure, the deposited films exhibited the increase of etching rate and the decrease of etch pit size obtained from the etching, whereas the pyramid type textured surface was formed at a pressure above approximately 6 Pa. It was also found that both in the c-axis orientation and the crystallite size as well as the carrier mobility in the deposited films were decreased by increasing the sputter gas pressure. It should be noted that the sputter gas pressure dependence described above was strongly dependent on the thickness of deposited films and MSD method used. In addition, the result described above was considerably affected by after heat-treatment with rapid thermal annealing (RTA) in air. Consequently, observed sputter gas pressure dependences such as the expanded tailing of absorption coefficient, etching characteristics and decrease of mobility were mainly correlated to the degradation of crystallinity as evidenced by the c-axis orientation and the crystallite size.

[1] T. Minami, T. Miyata, and J. Nomoto, Materials Science and Engineering, **34**, 012001 (2012).

EN-TuP13 Surface Analytical Investigation on Organometal Triiodide Perovskite, *Yongli Gao, C.G. Wang, C.C. Wang,* University of Rochester, *X.L. Liu,* Central South University, Changsha, China, *J.S. Huang,* University of Nebraska Lincoln

In a little over a year, there has been an unexpected breakthrough and rapid evolution of highly efficient solid-state hybrid solar cells based on organometal trihalide perovskite materials. This technology has the potential to produce solar cells with the very highest efficiencies while retaining the very lowest cost. We have measured the electronic density of states of CH$_3$NH$_3$PbI$_3$ using ultraviolet photoelectron spectroscopy (UPS), inverse photoemission spectroscopy (IPES), and x-ray photoelectron spectroscopy (XPS). The valence band maximum (VBM) and conduction band minimum (CBM) positions are obtained from the UPS and IPES spectra, respectively, by liner extrapolation of the leading edges. With the Fermi level close to the VBM, the sample is slightly p-type, with the E$_{VBM}$=0.76 eV, E$_{CBM}$=-0.9 eV, and transport energy gap 1.7 eV. The ionization potential (IP) of 6.16 eV can be obtained from the sum of the UPS measured E$_{VBM}$ and the work function of 5.40 eV. The XPS spectra reveal an obvious deficiency of N is, whereas the concentrations of I and Pb are close to the expected values. The existence of O and excessive C indicate that the surface is contaminated, and the contamination is reduced by 12-20% by thermal annealing in vacuum. The interface between CH$_3$NH$_3$PbI$_3$ and TiO$_2$ is also investigated. As CH$_3$NH$_3$PbI$_3$ layer thickness increases, one sees a gradual shift of the vacuum level cut-off. At the CH$_3$NH$_3$PbI$_3$ thickness of 8.2 nm, the shift saturates, signaling the end of the interface dipole formation. The evolution of the VB is even more gradual, and it appears to mature only at the thickest layer. Given the UPS probing depth of ~1.5 nm and the typical interface formation in other systems, the saturation of the vacuum level cut-off at 8.2 nm in CH$_3$NH$_3$PbI$_3$/TiO$_2$ is surprisingly large. It points at the possibility that the films are not truly uniform. On the other hand, the interface dipole of 0.7 eV CH$_3$NH$_3$PbI$_3$ and TiO$_2$ is important for further understanding of the energy level alignment and charge transfer across the interface.

EN-TuP14   Synthesis, Characterization and Hydrogen-Storage Performance of Nanoporous Graphene-based Adsorbents, *Claus Rebholz, N. Kostoglou,* University of Cyprus, *V. Tzitzios, C. Tampaxis, G. Charalambopoulou, T. Steriotis, K. Giannakopoulos,* National Center for Scientific Research Demokritos, *Y. Li, K. Liao, K. Polychronopoulou,* Khalifa University of Science, Technology & Research

In the present work, we synthesized and systematically characterized two novel graphene-based nanomaterials, a reduced graphene oxide sponge and a microwave-exfoliated graphene oxide. Their textural properties were determined by N$_2$ adsorption/desorption at 77 K, while additional characterization techniques were employed in order to elucidate further their structure, surface chemistry and morphology such as X-Ray Diffraction (XRD), Fourier-Transform Infrared Spectroscopy (FT-IR), Field-Emission Scanning Electron Microscopy (FE-SEM) and High-Resolution Transmission Electron Microscopy (HR-TEM). Both nanomaterials were additionally evaluated for their H$_2$ storage performance and were critically compared to commercially available carbons (e.g. graphene nanoplatelets, carbon nanotubes) based on systematic H$_2$ adsorption/desorption measurements at 77K between 0-1 bar. Maximum H$_2$ gravimetric capacities ~0.5 wt% and ~0.7 wt% were recorded at 77 K and 1 bar for the reduced GO sponge and the microwave-exfoliated GO, respectively. A linear relationship was found between the H$_2$ uptake values and the BET specific surface area of the materials included in this study.

EN-TuP15 Vacuum Deposition Of Photosystem 1 Films In P-Doped Silicon Surface To Improve The Efficiency Of Bio-Photovoltaic Cells, *CarlosFelipeRezende Facchini, L.T. Manera, P. Mazzafera, R.V. Ribeiro, E. Kiyota*, University of Campinas, Brazil

The high efficiency which some organisms perform photosynthesis and its abundance around the globe, coupled with high world energy demand in the coming years and the low competitiveness of current photovoltaic devices in comparison with other forms of energy, inspired us to build a Bio-photovoltaic device composed of a heavily p-doped silicon substrates and a tandem of protein complex called Photosystem 1 (PS1) found in the thylakoid of leaves.

The process extraction of PS1 complexes from spinach essentially consists of two general steps: the extraction of thylakoid membranes from the spinach leaves and the isolation and purification of PS1 complexes from the thylakoids.

For the deposition of PS1 films onto silicon substrates we use a simple and straightforward method. The procedure entails depositing a volume (100μL) of an aqueous PS1 suspension on to a silicon surface modified with 3-aminopropyl-triethoxysilane (APTS) and applying a negative pressure (~70 mTorr) to remove the solvent from the PSI solution via vacuum deposition process. The thermodynamic driving force for the formation of these films arises from hydrophobic interactions between neighboring protein complexes in the film and by tuning the silicon Fermi energy by doping. This promotes the alignment of silicon bands with redox active sites of PS1, which leads to the formation of dense and resilient films.

Iterative depositions were similarly performed and for two deposition steps, a thickness of ~600nm was achieved, thereby increasing the efficiency of the bio-hybrid cell.

These results represent significant progress toward affordable, biologically-inspired renewable energy conversion platforms.

EN-TuP16 Cross Sectional Mapping of CdTe PV Devices with Scanning Capacitance Microscopy, *Gilad Zorn, B.A. Korevaar, J.R. Cournoyer, K. Dovidenko*, GE Global Research Center

Scanning capacitance microscopy (SCM) is a powerful method for mapping dopant variation in semi-conductor and PV devices. In SCM a conducting AFM tip is used to scan the surface in contact mode. The tip and sample surface form a metal–insulator–semiconductor structure. Simultaneous with the topography data collection, an AC bias is applied to the sample while the tip is grounded. The resulting oscillation of carriers near the tip, leads to a modulated capacitance (dC/dV), which is measured by a capacitance-sensing circuit. The capacitance measured by the SCM sensor varies as the carriers move towards (accumulation) and away from (depletion) the probe. When the sample is fully depleted the measured capacitance is that of the oxide plus the depletion layer. When carriers are accumulated at the surface, the measured capacitance is that of the oxide layer. The magnitude of the change in capacitance (dC) for a given change in voltage (dV)depends on the carrier concentration. For heavily doped materials the carriers do not move far. Hence, the measured capacitance variation between accumulation and depletion is small. The opposite is true for lightly doped semiconductors which yield a large capacitance change. The sign of the measured dC/dV signal changes between n-type and p-type. In p-type semiconductors, as the sample voltage becomes more negative relative to the tip, the width of the surface depletion layer will increase. Hence, the total capacitance will decrease. If the sample voltage is positive, accumulation will occur, and the capacitance measured will be that of the oxide layer only. For n-type samples the effects are opposite.

This work describes SCM cross-sectional mapping of CdTe devices, focusing on the role of the various processing steps during the device fabrication. These steps include CdTe deposition, $CdCl_2$-treatment, and a copper-step. Generally it is accepted within the CdTe community that as deposited CdTe is lightly doped and could be both n-type or p-type depending on the deposition temperature and process. The effect of the $CdCl_2$ treatment is typically presented as a way to create so-called A-centers, which dope the CdTe p-type. The final copper-step then fills the A-centers and creates Cu on Cd-sites, which further dopes the CdTe p-type to levels in the range of $5x10^{13}$ to $5x10^{14}$ cm^{-3}. Here SCM is used to demonstrate the role of the various processing steps with regards to carrier density. SCM dopant map could clearly distinguish n and p-type CdTe as well as the p-n transition across the interface. It was found that the doping distribution across the CdTe layer depends on the type of the copper treatment.

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