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Award Number: DE-EE0003179

Project Title: Purdue Solar Energy Utilization Laboratory

Project Period: 7/01/2010 – 6/30/2011

Recipient Organization: Purdue University
480 Stadium Mall Drive, West Lafayette, IN 47907.

Partners: Purdue University (cost-sharing)

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Project Objective: The objective of this project is to establish and set-up a laboratory that will facilitate research and development of new low-cost and high-efficiency solar energy utilization technologies at Purdue University. The outcome will help spur the creation of solar energy start-up companies and eventually a solar energy industry in Indiana that can help fulfill the growing national demand for solar energy.

Background: Solar energy is well-recognized by the National Academy of Engineering and the Department of Energy as the most promising renewable energy resource. The key problem in utilizing this resource widely is the capital and labor costs of manufacturing. The cost typically scales with the area of the device, and there are two promising approaches being pursued by Purdue faculty to solve this critical problem. One involves developing ultra low-cost conversion devices (photovoltaic and photoelectrochemical) that utilize normal intensity sunlight. The second involves using concentrated sunlight on smaller area ultra high-efficiency conversion devices. In both of these approaches, Purdue team members are pioneering solutions to key problems that differentiate their efforts from the global research community. One such effort is the creation of software (ADEPT) that is currently being used world-wide to simulate the operation of solar cells. The goal of PSEUL is to facilitate the development of these and other innovative solar energy utilization technologies. The grant in this phase is devoted to setting-up a laboratory to characterize, test, and certify the performance of photovoltaic materials and devices. Latter phases of the project will involve expansion of fabrication facilities, funding for applied research projects that have high probability of resulting in commercially viable technology, and seed funding for high-risk high-reward projects.

Progress and Status: There is no new activity to be reported. The installation and implementation of all instruments is complete.

The Purdue Solar Energy Utilization Laboratory (PSEUL) is a versatile user facility providing sophisticated optical and electronic characterization capabilities. Users employ the instruments in PSEUL to characterize various types of samples – nanocrystals and thin films, inorganic and organic materials, completed devices and individual layers – allowing a holistic, bottom-up approach to understanding material and device properties.

Twenty-five graduate students advised by six different professors in four separate departments have been trained as users on instruments in PSEUL:

- Prof. Rakesh Agrawal, Chemical Engineering, 15 students
- Prof. Bryan Boudouris, Chemical Engineering, 4 students
- Prof. Muhammad Alam, Electrical and Computer Engineering, 2 students
- Prof. Mark Lundstrom, Electrical and Computer Engineering, 1 student
- Prof. Joseph Irudayaraj, Agricultural and Biological Engineering, 2 students
- Prof. Lia Stanciu, Materials Science Engineering, 1 student

Several undergraduate students have also been trained as users on equipment in the facility.

Instruments

The project objectives for PSEUL included:

- **Task 1.** Acquisition, Installation, and Testing of a Solar Cell Testing Station
- **Task 2.** Acquisition, Installation, and Testing of an External Quantum Efficiency (EQE) Station
- **Task 3.** Acquisition, Installation, and Testing of a Photoluminescence (PL) System
- **Task 4.** Acquisition, Installation, and Testing of a Deep-Level Transient Spectroscopy (DLTS) System
- **Task 5.** Optimization of Nanocrystal-Ink and Nanowire Solar Cell Performance

During the grant period, it was determined that a time-resolved PL system (in addition to the steady-state system specified in Task 3) would be more beneficial than the EQE station listed in Task 2. Additionally, since DLTS has been reported to be unreliable for thin film samples, Task 4 was amended to the acquisition, installation, and testing of an Impedance Analyzer for capacitance spectroscopies and profiling. The need for a surface profilometer to characterize the thickness and surface roughness of thin films also became apparent. The following list itemizes the instruments purchased under the PSEUL grant and the Task each instrument fulfills:

- Newport Oriel Sol3A Solar Simulator (Task 1)
 - Current-voltage (IV) characteristics
- Horiba/JY FluoroLog-3 Time-Resolved PL (TRPL) Spectrometer (Task 2)
 - Carrier lifetimes
- Horiba/JY LabRAM HR 800 Raman Microscope and PL Spectrometer (Task 3)
 - Raman and steady-state PL emission spectroscopies

- Lake Shore TTPX Cryogenic Probe Station (Task 4)
 - Temperature-dependent device characteristics measurements
- HP/Agilent Impedance Analyzer (Task 4)
 - Capacitance-voltage (CV) and capacitance-frequency (C-f) characteristics
- KLA-Tencor AlphaStep D-100 Surface Profilometer
 - Film thickness, surface roughness

The instruments in PSEUL have provided a plethora of new insight into the fundamental properties that determine solar cell performance. The application of this improved understanding has contributed to new champion efficiencies for inorganic thin film Cu(In,Ga)(S,Se)_2 (CIGSSe) and $\text{Cu}_2\text{ZnSn(S,Se)}_4$ (CZTSSe) solar cells of 14.2% and 9.2%, respectively (Task 5).

KLA-Tencor AlphaStep D-100 Surface Profilometer

The various layers comprising thin film inorganic and organic solar cells and devices typically do not exceed more than a few microns in thickness. Additionally, the thicknesses of these layers – both individually and relative to one another – and the smoothness of their surfaces can profoundly impact the optical properties of the device. Therefore, the ability to characterize film thickness and surface roughness is paramount for this research. The KLA-Tencor AlphaStep D-100 Surface Profilometer is a relatively economical (e.g. compared to electron microscopy) and very reliable means of measuring film thickness and surface roughness for inorganic and organic films deposited by various methods, including drop-casting, sputtering, spin-coating, and doctor-blading. Figure 1 depicts a scan of a sample consisting of a polymer spin-coated on a glass substrate. The sample has been scratched through the polymer to the glass in order to measure the thickness of the polymer film.

Figure 1. Example profilometer scan for a spin-coated polymer sample.

Newport Oriel Sol3A Solar Simulator

Perhaps the most fundamental (but also the most essential) means of characterizing solar cells is to measure current-voltage (IV) characteristics both in the dark and under solar-simulated illumination. Indeed, this measurement reveals the efficiency and fundamental performance characteristics of the photovoltaic device under test. The Newport Oriel Sol3A Solar Simulator provides illumination that rather precisely mimics the spectral irradiance of the sun with relatively

large-area uniformity (2-in. diameter) for a lab-scale setup. Combined with a thermoelectric, temperature-controlled sample stage, a Si reference solar cell and meter for lamp intensity calibration, and a Keithley 2400-series sourcemeter, the solar simulator provides the capability to determine solar cell efficiency, open-circuit voltage (V_{oc}), short-circuit current (J_{sc}), and fill factor from IV characteristics under illumination. The same measurement with the device in the dark provides a means of calculating the ideality factor and series (R_s) (among other properties) attributed to the material construction of the device. Example dark and illuminated IV and the measured device performance characteristics of an inorganic thin film solar cell with a $Cu_2ZnSn(S,Se)_4$ (CZTSSe) absorber layer are displayed in Figure 2.

Figure 2. IV characteristics for a CZTSSe solar cells with an efficiency of 9.2%.

Similarly, Figure 3 depicts the illuminated IV characteristics for an organic solar cell containing the radical polymer poly(2,2,6,6-tetramethylpiperidinyloxymethacrylate) (PTMA) and achieving an efficiency of 0.33%.

Figure 3. I-V curve under light for a PTMA-containing OPV device with an efficiency of 0.33%.

Lake Shore TTPX Cryogenic Probe Station

The Lake Shore cryogenic probe station offers the capability of measuring device performance characteristics at temperatures as low as 4 K (using liquid He; 77 K using liquid N_2) and as high as 450 K. Since fundamental semiconductor properties are temperature-dependent, these

measurements provide insight into critical parameters influencing device performance. Figure 2 displays IVT measurements for CIGSSe and CZTSSe solar cells between 175 and 350 K.

Figure 4. Current-voltage characteristics of CIGSSe (left) and CZTSSe (right) solar cells at temperatures from 175 to 350 K. The color scheme in the legend of the CIGSSe plot applies for the CZTSSe plot as well.

The Lake Shore probe station is also useful for characterizing radical polymer devices, which degrade in the presence of oxygen and moisture and thus require an inert atmosphere. Figure 5 presents IV data for one such device.

Figure 5. (a) Voltage versus current data demonstrates diode behavior. Inset shows device architecture. (b) Semi-log voltage versus current data demonstrating the preference to transport electrons versus holes.

HP/Agilent Impedance Analyzer

Capacitance spectroscopies and profiling techniques provide valuable information about defect physics that play a role in solar cell performance. These measurements are applicable to both inorganic and organic devices.

CV Measurements in Inorganic Devices

Figure 6 depicts CV data plotted such that the built-in voltage (V_{bi}) and acceptor doping density (N_A) can be inferred. Knowing these values is critical for device modeling and simulation, which accounts for a key component of solar cell research.

Figure 6. CV measurement at room temperature.

CV and C-f measurements in Organic Devices

The accuracy of the measured capacitance data generally is evaluated by monitoring the corresponding dissipation factor. For inorganic semiconductors, the dissipation factor exceeds the tolerance limit of ~ 10 in the forward bias regime, and hence, the forward bias data are generally ignored and not analyzed. In Figure 7, we plot the dissipation factor and the corresponding C-V data for organic devices with different thicknesses (measured by the surface profilometer) and measurement frequencies. The dissipation factor exceeds the tolerance limit of ~ 10 -15 at very high forward bias. However, the capacitance peaks in the forward bias are obtained with $D < 10$ in all cases plotted in Figure 7, indicating an unambiguous signature of deep level traps.

Figure 7. The capacitance-frequency and capacitance-voltage plots for several organic devices and the corresponding dissipation factors.

Horiba/JY LabRAM HR 800 Raman Microscope and Steady-State Photoluminescence (PL) Spectrometer

The Horiba/JY LabRAM HR 800 is a versatile instrument that offers both the ability to identify distinct chemical compounds in a solid or liquid sample via Raman spectroscopy and a means of measuring the characteristic energy (and energy distribution) of the dominant recombination mechanism in an optically active semiconductor through its PL capability.

Raman Spectroscopy

Raman spectroscopy is a “fingerprinting” technique that identifies compounds by their characteristic bonding structures. Example Raman data for nanocrystal CZTS samples are depicted in Figure 8.

Figure 8. Raman spectra for three samples of CZTS nanoparticles.

Photoluminescence Spectroscopy

The PL data displayed in Figure 9 demonstrates a dominant recombination energy (with a rather broad distribution) roughly 0.1 eV below the estimated band gap for both CZTSSe and CZTGeSse absorber layers.

Figure 9. Example room-temperature PL measurements comparing CZTSSe and CZTGeS_{Se} absorber layers. The vertical, dashed lines denote the estimated band gap for CZTS (1.1 eV) and CZTGeS_{Se} (1.18 eV).

Horiba/JY FluoroLog-3 Time-Resolved Photoluminescence (TRPL) Spectrometer

Since the TRPL intensity measured by the Horiba/JY FluoroLog-3 Spectrometer represents the transient decay of photo-excited carriers in a semiconductor sample, the carrier lifetime can be extracted from TRPL data by applying the appropriate model. The TRPL data in Figure 10 demonstrates a typical decay signal for CZTSSe absorbers, which cannot be fit by a conventional single-exponential model.

Figure 10. TRPL decay for a CZTSSe absorber layer.

Patents: None

Publications / Presentations:

The following publications and presentations include work performed in PSEUL:

“Influence of Ge Doping on Defect Distributions of $\text{Cu}_2\text{Zn}(\text{Sn}_x\text{Ge}_{1-x})(\text{S}_y\text{Se}_{1-y})$ Fabricated by Nanocrystal Ink Deposition with Selenization”

J. Moore, C. J. Hages, M. Lundstrom, R. Agrawal, Proceedings of the 38th IEEE PVSC, Austin, TX, June 2012; awarded Best Student Presentation designation

“Device Limitations and Light-Soaking Effects in CZTSSe and CZTGeS_{Se}”

C. J. Hages, J. Moore, S. Dongaonkar, M. Alam, M. Lundstrom, R. Agrawal, Poster Presentation – 38th Annual IEEE PVSC Meeting, Austin, TX, June 2012; awarded Best Poster designation

“Copper-zinc-tin Chalcogenide Absorbers Derived from Controlled Sulfide Nanocrystals of Wurtzite and Kesterite Structures”

Wei-Chang Yang, Caleb K. Miskin, Charles J. Hages, Peter W. Stephens, Erich A. Stach, and Rakesh Agrawal, 2012 MRS Fall Meeting, Boston, MA, November 2012.

“Improved Performance of Earth-Abundant $\text{Cu}_2\text{ZnSn}(\text{S}_x\text{Se}_{1-x})_4$ Solar Cells through Ge Incorporation”

Charles J. Hages and Rakesh Agrawal, 2012 AIChE Annual Meeting, Pittsburgh, PA, October 2012.

“Characterization of Earth-Abundant $\text{Cu}_2\text{Zn}(\text{Sn}_y\text{Ge}_{1-y})(\text{S}_x\text{Se}_{1-x})_4$ Solar Cells”

Charles J. Hages, Sergej Levchenko, Thomas Unold, and Rakesh Agrawal, accepted for Oral Presentation – 2013 MRS Spring Meeting, San Francisco, CA, April 2013.

“Real-time Investigation of the Sintering Mechanism in Cu-Zn-Sn-S Nanocrystal Films for Photovoltaic Applications”

Nathaniel J. Carter, Roland Mainz, Bryce Walker, Wei-Chang Yang, Alfons Weber, Ole Zander, Sebastian Schmidt, Thomas Unold, and Rakesh Agrawal, accepted for Poster Presentation – 2013 MRS Spring Meeting, San Francisco, CA, April 2013.

“A Synthesis Route to High Efficiency $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ Solar Cells from Nanoparticle Inks”

Caleb Miskin, Wei-Chang Yang, Charles J. Hages, Nathaniel J. Carter, Chinmay Joglekar, Eric A. Stach, and Rakesh Agrawal, submitted for publication, 2013.

“Impedance Spectroscopy for Organic Solar Cells”

Biswajit Ray, Aditya G. Baradwaj, Bryan W. Boudouris, and Muhammad A. Alam, submitted for publication, 2013.