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Project Period: January 13, 2010 to January 12, 2012 with a no-cost extension to June 30, 2012

Date: June 26, 2013

Project Overview

The goals of the research program in the Center for Autonomous Solar power are to conduct research and development in thin film solar cells on flexible substrates for low cost fabrication on roll-to-roll manufacturing. The materials chosen for the cells are earth abundant and non-toxic. The expected outcome is very low cost solar cells that will be competitive in performance and well below current market prices in dollars/watt. Flexible solar cells are useful in building integrated photovoltaic voltaic systems and in military applications in austere environments.

A related research program focuses on ultracapacitors using new materials as well. With sufficiently high energy densities, ultracapacitors can replace batteries for energy storage and offer other advantages in lifetime and in tolerating a wider operating temperature range.

Solar cells consist of three critical layers: a transparent conductor, an n-type layer that is also transparent, and a p-type material that is strongly absorbing. The Center’s research on thin film materials includes replacing the conventional indium tin oxide (ITO) used as a transparent conductor with aluminum doped zinc oxide. Indium is a rare and expensive material, and ITO is brittle, making it less suitable for flexible substrates.

For the n-type material, we have successfully achieved high quality films using zinc sulfide. This layer replaces cadmium sulfide which is much less desirable because of toxicity. The p-type substrates candidates include iron disulfide, zinc phosphide, and copper zinc tin sulfide (CZTS). These materials have near optimum bandgaps, absorb strongly, and have high mobilities (or equivalently, high diffusion constants). We have successfully deposited high quality films of all critical cell layers, including the three candidate p-type layers.

Of the three p-type candidates, CZTS is the most promising. Optimization of the deposition processes has begun. At Binghamton, pulsed laser deposition and chemical vapor deposition have been studied. A subcontract to Clarkson University has begun to deposit this material using a chemical process. These are all alternatives to processes currently used elsewhere (e.g., IBM) that use a highly toxic and unstable gas considered unsafe in academic settings.
Solar cells have been fabricated in the CASP laboratories but have not yet yielded efficiencies that compete with commercial solar cells. Studies are underway to determine the sources of losses and to modify the layers or deposition processes appropriately to successfully transfer the process to a roll-to-roll fabrication line.

On ultracapacitors, research has begun on electrodes and electrolytes to improve energy densities, and significant progress has been made in both electrolytes and electrodes.

In addition to formation of cell layers and complete cells, reliability studies have been conducted on some flexible substrates and layers and summarized below.

Details on processes and progress have been included in quarterly reports. The major technical outcomes are included here.

The Center is a founding member of a consortium of universities and companies in testing solar cells. Funding for this program is provided by the New York State Energy Research and Development Agency (NYSERDA). The Center is also a grantee on a Labor Department education program in solar cells. A small study on a novel technique for non-contact measurements of Hall mobility is also underway and shows very promising results. Funding to support this measurement effort will be sought from another agency.

In sum, the goals of the program have been achieved or exceeded.

**TASK Report**

Major research projects in the center include:

- Transparent conductors for solar cells
- Thin film solar cells using earth abundant materials with three candidate p-type absorbers
- Ultracapacitors for solar energy systems
- Reliability and durability of thin film solar devices
- Thermoelectric solar devices

Considerable progress was made in all of the project areas. The more significant accomplishments include:

1. Successful deposition processes for all cell layers including the CZTS absorber material, two n-type layers, and a transparent coating layer. An antireflection layer process was not developed since it is a non-critical layer. A faculty member affiliated with the center is developing an innovative process for our cells. Early progress indicates that increases of 0.5 to 1% are possible.
2. Successfully development of CZTS solar cells with efficiencies up to 6.5% without the use of selenium and without the use toxic processes or materials.
3. First successful solar cell on Corning’s flexible Willow Glass.
4. Extensive reliability characterizations of transparent conductors on flexible substrates.
5. An innovative thermoelectric material that possesses a high figure of merit ($ZT=2.1$) that compares with the best materials available.
6. New electrode and dielectric materials for ultracapacitors that simplify fabrication and that have high densities measured in farads/gram.

In addition, results in CASP derived from DARPA support have resulted in increased collaboration with industry, in attracting new research funds from NSF, and educated numerous graduate students all of whom are engaged in industrial firms and in other universities in energy related fields.

Details of the progress made in the task areas follow.

Successful deposition of transparent conductors using an Atomic Layer Deposition (ALD) instrument acquired with DARPA funding was made. Most of the research emphasis was placed on aluminum doped zinc oxide (AZO) that has a high transparency and higher durability than the industry standard of indium tin oxide (ITO). Extensive studies comparing ITO and AZO have been conducted on glass and plastic substrates.

Likewise thin film solar cells were successfully fabricated with efficiencies of up to 6.5% from Copper Zinc Tin Sulfide (CZTS) cells with no antireflection coating. With an antireflection coating, these cells compare with the best cells fabricated anywhere. The first CZTS solar cell fabricated on Corning’s Willow Glass exhibited good efficiency.

New dielectric and electrode materials were developed for ultracapacitors including a solid gel electrolyte that simplifies the manufacturing of ultracapacitors because it eliminates a separator layer, reducing the layers from 5 to 3. The performances of devices developed measured in Farads/gram (a measure of energy density and size) exceed those currently manufactured.

Reliability studies of thin film coatings and devices have been conducted to investigate the lifetimes of devices under severe environmental conditions. These include aluminum doped zinc oxide and indium tin oxide on flexible substrates.

An innovative thermoelectric material using nanostructures has been developed that has a high thermoelectric figure of merit and consists of silicon and tin.

DARPA support has made possible the development of a high quality research laboratory staffed by talented graduate students. As a result of the successful research activities, additional external support to sustain the research has been acquired, regional industries have benefited, and graduating students have gained employment at the MS, doctoral, and postdoctoral levels in
industries and academia in areas related to their research in CASP. Employers include Brookhaven National Laboratories, the Global Foundries, BAE, CISCO, and the University of Kansas. All of the positions are in energy and power related fields.

Each task area will be described with a summary of the results.

1. **Transparent conductors for solar cells**

   Aluminum doped zinc oxide (AZO) films were deposited using an atomic layer deposition (ALD) instrument that produced very high quality films. The ALD produces conformal layers that help minimize pinholes or other defects that can promote leakage. We have also been successful in producing good quality films with sputtering. The roll-to-roll line at Binghamton University is ready to test deposition of AZO on a variety of flexible substrates. One of the more promising substrates is a 75 micron thick flexible glass (Willow Glass) manufactured by Corning. Corning has recently produced rolls of the glass and tested it on the Binghamton roll-to-roll line. Glass offers several advantages to solar cells including the ability to tolerate higher temperatures and serve as more effective barrier to moisture that can damage any solar cell material. We have prepared samples of AZO on flexible substrates and tested their reliability. In addition to flexible glass, we have also tested transparent coatings on PEDOT, a flexible plastic and tested them in environmental chambers. The durability of the glass, which is subject to cracks, is, of course, and important issue and will continue to be a topic for investigation.

   A 1000 hour test on a variety of AZO coated substrates was recently concluded. The test cycled temperatures and humidity hourly between low temperatures and low humidity to higher levels: 80° C and 80% humidity. The samples included films deposited by a commercial firm and sputtered films deposited by CASP. This thinnest samples (less than 200 nm) exhibited apparent damage. The thicker films did not exhibit obvious damage; however additional characterization of the films will be studied in the future.

   ![An example of the Willow Glass product from Corning](image)
In addition to Willow Glass, indium tin oxide and PEDOT have been studied on PET, a popular plastic film. Indium Tin Oxide (ITO) is the most widely used TCO for displays and solar cells. It has good optical and electronic properties but is brittle when subject to flexing and bending. Of interest is the durability of the TCO's in damp heat. Samples of Poly (3, 4-ethylenedioxythiophene) (PEDOT) with two different resistances (150Ω and 225Ω) coated on polyethylene-terephthalate (PET) and indium tin oxide (ITO) coated on PET were used in experiments. PEDOT showed good mechanical properties with a small resistance change and no clear cracks or deformation that formed on the surface under cyclic bending. However, the resistance of ITO significantly increased with the cyclic bending due to clear cracking that initiated in the center of sample and propagated toward the edges. The design of experiment (DOE) approach was used to study the effect of different parameters. Additionally, a damp heat experiment on similar samples was conducted by applying 85°C temperatures and 85% relative humidity on them for 1000 hours. The electrical resistance dramatically increased for both materials. Scanning electronic microscopy (SEM), Energy Dispersive Spectrometry and transmission tests were conducted to further understanding of the damp heat effect on the film composition and transparency.
2. Thin Film Solar Cells

Several deposition techniques have been developed for Copper Zinc Tin Sulphide (CZTS). These include sputtering of individual layers of copper, zinc, and tin followed by sulfurization; co-sputtering of Co-sputtering using Cu (DC Power) and SnS (RF power) and ZnS (RF Power) followed by sulfurization; and Pulsed Laser Deposition (PLD) followed by sulfurization. A third process involving evaporation of Cu, Zn, and Sn followed by sulfurization has also been successfully developed. All of the fabrication processes led to similar efficiencies varying from 5 – 7% even without an antireflection coating. An example follows in the figures below. For the sputtered cells, consistently high efficiencies were achieved. Higher efficiencies can be achieved if selenium is added; however, selenium involves toxic processes, contrary to our central goals of our research program.

To achieve higher efficiencies, processes must be done in a closed system, a facility we lack. A closed system means that the entire deposition process for all layers can be done without breaking vacuum. We believe that fundamental improvements in the CZTS are needed, and that will remain a focus of our research. We have not used an antireflection film because that would divert our research focus. Another faculty member not supported by DARPA is developing a process and has already demonstrated some initial success. At a later time, we will incorporate his process.
I-V curve of a CZTS cell showing 6.5% efficiency. No antireflection coating.

Cross section of a standard cell and the fabricated cell. Again, there is no antireflection coating.

After deposition of the CZTS films and sulfurization, an etching of the surface is performed before deposition of the subsequent layers. The n-p contact is the most critical, and the etch process was refined for maximum efficiencies.

To better understand the CZTS layer, quantum efficiency together with cell modeling has been conducted on this p-type absorber. The results are shown in the following figures.

Quantum efficiency measurements for etched (red) and unetched CZTS surface.
It is apparent that the quantum efficiency (number of electrons produced per photon) improves with etching of the deposited and annealed CZTS layer. The etch removes surface imperfections arising from the annealing processes.

Extensive modeling of the CZTS cell and comparisons with quantum efficiency reveal that photogeneration of carriers contributes to the solar cell current only for a region close to the interface. The remaining electron carriers are lost to recombination in the bulk of the CZTS. Additional studies are needed to determine the reasons for the recombination due to defects. We are investigating Rutherford Back Scattering measurements to characterize defects in the film.

In sum, CZTS thin film solar cells have been fabricated that exhibit good efficiencies that are comparable with the highest efficiencies observed in the world. Nevertheless, a better understanding of the losses in the film and measures that can be taken to reduce recombination are needed for commercial cells.

3. Progress in Ultracapacitors

Good progress has been made in ultracapacitors. The high capacitance of ultracapacitors arises from high surface area electrodes and an effective electrolyte. Most commercial devices use liquid electrolytes that are infused between the electrodes. Further, a separator layer is required in commercial cells to prevent charge flow between electrodes. Hence, commercial devices consist of 5 layers: electrode, electrolyte, separator, electrolyte, and electrode.

We have successfully developed a gel electrolyte with commercial quality performance that does not require a separator, simplifying manufacturing and lower costs. A patent disclosure has been filed for this material. In addition, research has been conducted on improved electrode materials. A detailed description follows.

All-solid-state thin ultracapacitors have been fabricated using current pulse polymerized poly (3, 4-ethyleneoxythiophene) (PEDOT) over carbon fiber paper and ionic liquid based gel polymer electrolyte. The PEDOT-coated carbon paper electrodes were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) which confirm the porous morphology of PEDOT at the Nano scale and a high degree of ClO₄⁺ dopant ion conjugation. The performance characteristics of the ultracapacitor cells have been evaluated by ac impedance spectroscopy, cyclic voltammetry and galvanostatic charge-discharge techniques. The PEDOT electrode shows specific capacitance of ~ 154.5 F g⁻¹, which correspond to the cell area-normalized capacitance of 85 mF cm⁻². The maximum specific energy and specific power of the solid-state ultracapacitor cell, calculated from charge-discharge characteristics, are 6.5 Wh kg⁻¹ and 11.3 kW kg⁻¹, respectively. The solid-state ultracapacitor shows good cycle durability and time stability. The thin, lightweight, gel electrolyte based ultracapacitor shows considerable potential for low-cost, high-performance energy storage applications.
The capacitor shows excellent stability as shown below. The cell characteristics did not change significantly over a 3-month period.

![Graph showing capacitor characteristics over time](image)

The plots show the charge/discharge behavior immediately after fabrication, after one month, and after three months. Note that the difference in one month to three months is nearly negligible.

4. Thermoelectric Devices – High figure of merit (ZT)

In this program, the development of sustainable, silicon based thermoelectric materials with large figure of merit (>3) is underway. Previously, it has been shown through molecular dynamics simulations that the thermal conductivity of Si containing random monolayers of Sn can be reduced by factors up to 3000 (i.e. to values of approximately 0.050 W/m-K) when 20% of the Si [100] planes are randomly selected and replaced with Sn. The random, mass altered atomic planes produce Anderson localization of the lattice vibrations, which results in a dramatically reduced lattice thermal conductivity. Under conditions in which the mass-altered planes are the predominant source of charge carrier scattering, the expected ZT of such a solid for heat/transport in the cross-plane direction is expected to be greater than 8.

We have focused on examining the electrical properties of the random multilayer thin films formed from Si and Sn. As described previously, the process of record for these nanostructured materials is to utilize room temperature sputtering of the thin films, to prevent Sn agglomeration, followed by a rapid thermal annealing process at 400 °C for 10 sec to improve the crystallinity of the thin film. A new mask set for improved hall mobility characterization has been designed and the results for
the Si:Sn random multilayer thin films are shown in the figure. The data indicate that the as-
deposited films have an in-plane mobility of approximately 0.2 cm$^2$/V-sec at a carrier
concentration of $10^{17}$/cm$^3$. While the mobility in this case is low, the fact that the addition of
-20% Sn in the form of randomly located atomic planes did not produce significant increases in
the carrier concentration is promising given that, generally, carrier concentrations below
approximately $10^{19}$/cm$^3$ are required for large Seebeck coefficients. Following the RTA process,
the mobility is observed to increase by approximately one order of magnitude, to a value of 2.4
cm$^2$/V-sec, while the carrier concentration is reduced to approximately $5 \times 10^{16}$/cm$^3$.

While the in-plane mobility extracted from the Hall measurements is promising, these
nanostructured materials are designed to minimize the cross-plane lattice thermal conductivity.
Thus, the cross-plane charge carrier mobility is critical in determining the efficiency of the
material. To estimate the cross-plane charge carrier mobility, a series of metal-semiconductor-
metal structures, with different cross-sectional areas was created (see inset of figure 2), the
resistance of each structure was then determined from current-voltage curves generated between
-4V and 4V. We note that the I-V curves were linear indicating ohmic contact between the
metals (Cr in this case) and the random multilayer structure. The extracted resistance as a
function of $1/r^2$ is shown in figure 2. A plot of resistance versus $1/r^2$ should produce a line whose
slope is determined by the thickness of the random multilayer thin film as well as its resistivity.
From this slope, and the carrier concentrations
determined from the in-plane measurements, the
cross-plane mobility can be extracted. In doing so,
the values are found to be consistent with those
produced from in-plane measurements.

An initial estimate of the room temperature
Seebeck coefficient has been generated using the
metal-semiconductor-metals structures. The
temperature dependence of the resistivity of the
electrodes from these structures was utilized to
measure the temperature difference across the
random-multilayer thin film when the sample was
subjected to a heat pulse. The voltage response of
the structure indicates that the Seebeck coefficient
is approximately 1.1 mV/K, a value similar to that
of silicon.

Based on the extracted charge carrier mobility and initial Seebeck coefficient estimate, it is
expected that the Si:Sn random multilayer will have a room temperature value of ZT of 2.1 when
the carrier concentration in the silicon is increased to $10^{19}$ carriers/cm$^3$. 

The resistance of a Si:Sn random multilayer thin film as a function of the inverse square of the radius of a metal-semiconductor-metal
This figure of merit translates into 15% to 20% efficiency, depending on the temperature difference obtained in the system, and compares well with any other practical thermoelectric material now available.
CASP Publications

Conference Papers/Presentations:


Ink-Based FeS2 Thin-Film Absorber Formed by Annealing, Tara P. Dhakal, Lakshmi K. Ganta, Charles R. Westgate, 38th IEEE PVSC 2011 conference proceedings, submitted on June 2, 2012 and accepted on June 14, 2012


Parag Vasekar, Siva Pramod Adusumilli, Daniel Vanhart and Tara Dhakal, “Development of zinc phosphide as an absorber using chemical reflux technique”, accepted for publication in MRS conference proceedings, Boston, November 2011. (accepted in June 2012)

Parag Vasekar, Siva P Adusumilli, Daniel Vanhart, Tara Dhakal and Seshu Desu, "Development of zinc phosphide as a p-type absorber", submitted to 38th photovoltaic specialists' conference proceedings, Austin, June 2012. (submitted in May 2012)


Hamasha, M. M., Alzoubi, K., Dhakal, T., Qasaimeh, A., Lu, S., Westgate, C. R., “Stability of Aluminum Thin Films on Flexible Substrate under Thermal and Isothermal Conditions”, ISMTA Conference and Exhibition, October, 16-20, 2011; Fort Worth, TX, USA.

Alzoubi, K., Choi, G., Hamasha, M. M., Alkhazali, A. S., DeFranco, J., Lu, S., Sammakia, B. and Westgate. C. R., “Comparisons of the mechanical behaviors of poly (3, 4-
ethylenedioxythiophene) (PEDOT) and ITO on flexible substrates”, (Material Science Society Fall Meeting & Exhibit, November 25-30, Boston, Massachusetts, USA)

Alzoubi, K., Alkhazali, A. S., Choi, G., Hamasha, M. M., Albahri, S., DeFranco, J., Lu, S. and Westgate, C. R., “Comparisons of the thermal stability of poly (3, 4-ethylenedioxythiophene) (PEDOT) and ITO on flexible substrates”, (Material Science Society Fall Meeting & Exhibit, November 25-30, Boston, Massachusetts, USA)

Hamasha, M. M., Dhakal, T., Ganta, L. K., Westgate, C. R., “Effect of pre-annealing temperature on the quality of Cu2ZnSnS4 thin film deposited by sol-gel method” (Material Science Society Fall Meeting & Exhibit, November 25-30, Boston, Massachusetts, USA)

Graphene-Based All-Solid-State Supercapacitor with Ionic Liquid Gel Polymer Electrolyte.
(Submitted on 28 March 2012, Accepted on 19 June 2012)

Pulse Polymerized Poly(3,4-ethylenedioxythiophene) Electrodes For Solid-State Supercapacitors with Ionic Liquid Gel Polymer Electrolyte.
(Submitted on 28 March 2012, Revised on 5 August 2012)

Poly(3,4-ethylenedioxythiophene)-Graphene Composite Electrodes For Solid-State Supercapacitors with Ionic Liquid Gel Polymer Electrolyte.
G. P. Pandey, A. C. Rastogi, ECS transactions, 221st ECS Meeting Proc. 2012 (Under Review)
(Submitted on June 6, 2012) G. P. Pandey

Graphene-Based All-Solid-State Supercapacitor with Ionic Liquid Gel Polymer Electrolyte.


Polyacrylonitrile and 1-Ethyl-3-Methylimidazolium Thiocyanate Based Gel Polymer Electrolyte for Solid-State Supercapacitors with Graphene Electrodes. October 7-12, 2012, 222nd ECS Meeting (PRiME 2012), Honolulu, Hawaii. (Accepted for Poster Presentation) G. P. Pandey


Book Chapters


Journal Publications


Solid-State Supercapacitors based on Pulse Polymerized Poly(3,4-ethylenedioxythiophene) electrodes and Ionic Liquid Gel Polymer Electrolyte.

Synthesis and Characterization of Pulsed Polymerized Poly(3,4-ethylenedioxythiophene) Electrodes for High-Performance Electrochemical Capacitors.


