UNIVERSITY OF CENTRAL FLORIDA

Research to Improve Photovoltaic (PV) Cell Efficiency by Hybrid Combination of PV and Thermoelectric Cell Elements.

PI: Nicoleta Sorloaica-Hickman**,** Robert Reedy
Students: Kris Davis, Ph.D. CREOL-UCF

Description: Photovoltaic/thermoelectric (PV/TE) cell integration is a promising technology to improved performance and increase the cell life of PV cells. The TE element can be used to cool and heat the PV element, which increases the PV efficiency. Conversely, the TE materials can be optimized to convert heat dissipated by the PV element into useful electric energy, particularly in locations where the PV cell experiences large temperature gradients, i.e. use the thermoelectric module for cooling, heating and energy generation depending on the ambient weather conditions. Thus, the goal of this research effort is to research and develop nanoscale design of efficient thermoelectric materials through a fundamental understanding of the materials properties and to design and build a photovoltaic thermoelectric (PV/TE) hybrid system.
Budget: $161,200
Universities: UCF/FSEC

Progress Summary

Photovoltaic/thermoelectric (PV/TE) cell integration is a promising technology to improved performance and increase the cell life of PV cells. The goal of this research effort is to research and develop nanoscale designs of efficient thermoelectric materials through a fundamental understanding of the materials properties and to design and build a photovoltaic thermoelectric (PV/TE) hybrid system.
There has been one primary approach taken in our laboratory in order to improve the efficiency of the n-type PbTe and Bi_2Te_3 and p-type TAGS and Sb_2Te_3 thermoelectric devices. This is to create controlled shape and size nanostructured materials and to fabricate the TE device using inexpensive, but very accurate techniques. By using n-type and p-type bulk materials in a nanostructured form, it is possible to modify thermoelectric properties in ways that are not possible with bulk materials. The nano form can lead to an improvements in the figure-of-merit, ZT.

Reports of enhanced ZT on thin film structures and nanowires have demonstrated the principle of nanostructuring to improve ZT, although questions remain regarding the accuracy of the ZT reported due to experimental difficulties in measuring the properties accurately. Preliminary theoretical calculation of the phonon and electron transport in PbTe and Bi_2Te_3 doped and TAGS and Sb_2Te_3 superlattices indicated that the primary benefit from nanostructures, a reduced lattice thermal conductivity, require an atomically high density of interfaces and controlled geometry. Because of these requirements, the fabrication process could be laborious and complicated. In order to improve the figure of merit ZT, it is required that the nanostructures have a size smaller than the phonon mean free path but greater than the electron or hole mean free path. Thus, phonons are more strongly scattered by the interfaces than are electrons or holes, resulting in a net increase of the efficiency.

Small size thermoelectric devices based on thick films of n type thermoelectric materials - PbTe and Bi_2Te_3, and p type thermoelectric - TAGS and Sb_2Te_3 are undergoing fabrication and development. There is an increasing need for small thermoelectric devices to provide active spot
cooling and warming for solar cells. The n type thermoelectric materials - PbTe and Bi_2Te_3, and p type thermoelectric - TAGS and Sb_2Te_3 are attractive thermoelectric materials for the operational temperature range (<200 °C, <400 °C) and for their high thermoelectric efficiency . Based on theoretical calculations, the smallness of the thermoelectric legs in these devices (thermoelectric legs have lengths, widths, and thicknesses of the order of microns), the numbers of legs can be of the order of 100 times those of conventional bulk thermoelectric devices.

There has been one primary approach taken in our laboratory in order to improve the efficiency of the n-type PbTe and Bi_2Te_3 and p-type TAGS and Sb_2Te_3 thermoelectric devices. This is to create controlled shape and size nanostructured materials and to fabricate the TE device using inexpensive but very accurate techniques. By using the bulk materials n-type and p-type mentioned above (see Fig 1.) in a nanostructured form, it is possible to modify thermoelectric properties in ways that are not possible with bulk materials. The nano form can lead to an improvement in the figure-of-merit, ZT.

Reports of enhanced ZT on thin film structures and nanowires have demonstrated the principle of nanostructuring to improve ZT, although questions remain regarding the accuracy of the ZT reported due to experimental difficulties in measuring the properties accurately.[(1)(2)] Preliminary theoretical calculations of the phonon and electron transport in PbTe and Bi_2Te_3 doped and TAGS and Sb_2Te_3 superlattices indicated that the primary benefit from nanostructures, a reduced lattice thermal conductivity, require an atomically high density of interfaces and controlled geometry. Because of these requirements, the fabrication process could be laborious and complicated. In order to improve the figure of merit ZT, it is required that the nanostructures have a size smaller than the phonon mean free path but greater than the electron or hole mean free path. Thus, phonons are more strongly scattered by the interfaces than are electrons or holes, resulting in a net increase of the efficiency. [(2)]

TE Materials Fabrication Techniques

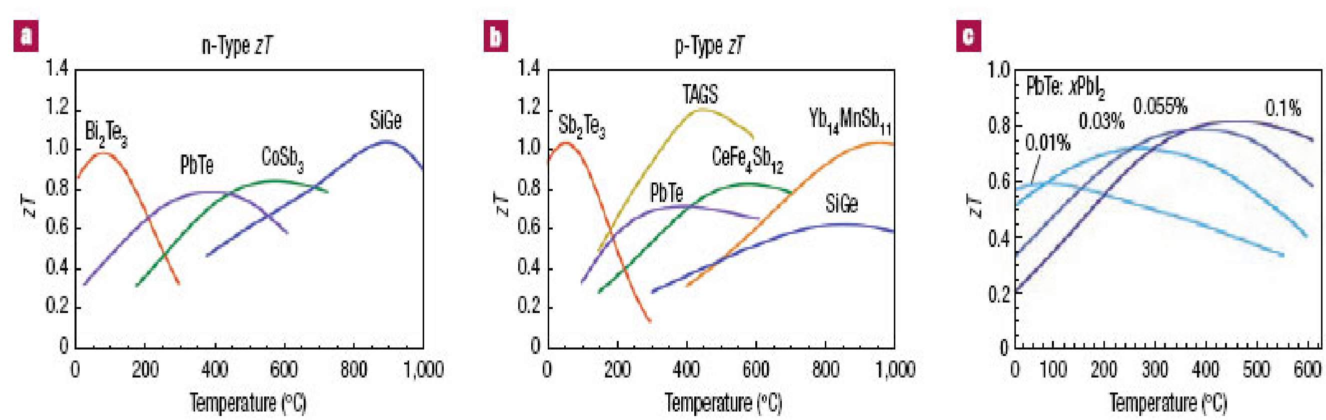


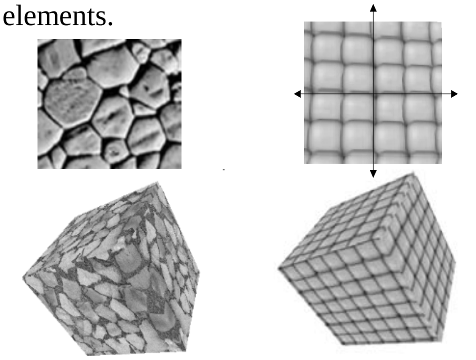
Figure 1. Figure-of-merit*zT* of state-of-the-art commercial materials and those used or being developed by NASA for thermoelectric power generation. **a**. p-type and **b**, n-type **c**. complex alloys with dopants (G. Jeffrey Snyder & Eric S. Toberer Nature Materials **7**, 105-114 (2008)

One major challenge is to create a material with nanoscale structures throughout using inexpensive and fast bulk procedures. Once the bulk material has been fabricated, the next challenge is to optimize the fabrication conditions so that the efficiency is improved. In our case, the optimization is difficult because the effects of the fabrication conditions on the nanostructures formed is not known and the material's thermoelectric properties are not always clear. Finally, we have to fabricate a thermodynamically stable material which can retain its nanoscale structures while being used in a practical device. If the nanostructures dissolve during the course of operation, the thermoelectric properties will return to those of the bulk material, removing any increase in efficiency that the nanostructured material was supposed to give.

For this work CDV and inkjet printing techniques were used to fabricate the bulk materials of nanostructure. These methods are simple in theory, but are rather involved in practice.

First, we use a CVD technique (Figure 2), formerly developed by a research team from Clemson [(3)]. This technique is particularly effective in synthesizing doped PbTe and Bi_2Te_3 particles with typical sizes from 0.1 to 10 □m. We are still in the process of optimizing this method with the main goal to use it for fabrication of large quantities of a specific size and shape (Figure 2 (b) and (c)) that possesses a rather narrow size distribution. The regular shape of the starting particles, coupled with the rather simple crystal structure and multiple constituents of the matrix material, enables us to control any change in the surface morphology and structure, as well as the migration of the elements.

Figure2.



a. CVD system customized in our laboratory for thermoelectric materials, **b** and **c** shape and sizes controlled nanostructure

We are also using this fabrication technique to deposit extremely smooth films that can be layered with different materials within the confines of arrays of micro/nanoscale capillaries in PV cells.

The second fabrication technique that was tried and optimized is the inkjet materials technique (Figure 3, **a** and **b**). The general approach is to dissolve the row materials used for the TE in different solvents, and then put the resulting solution in the printer's cartridge. Process parameters that must be optimized include the pH of the solution; the concentrations of materials in the solution; the temperature of the solution; homogeneity of the solution; the deposition voltage and current density; the surface finish of the cathode and post-deposition annealing.

The main factors that need to be controlled during the printing process are drop volume, drop shape and formation, printing distance and its impact on print quality, evaporation kinetics of the droplet, surface energy of the substrate and surface tension of the droplet, penetration or spreading parameters and film thickness. Furthermore, ink rheology varies and one must be able to print liquids ranging from low to relatively high viscosity, hot melts, phase-changing inks, etc. However, viscosity range is rather limited. The phase separation kinetics can be controlled by the drop size and substrate temperature which affects the annealing time. Upper limit for viscosity is dictated by the printer. In this research, the printer has an upper limit for viscosity of 15 cP and the surface tension 30 ~ 32 dynes/cm. Despite these difficulties, several inks processes have been developed which are expected to show the creation of stable nanocomposites and microcomposites with improved properties over those of their bulk counterparts.

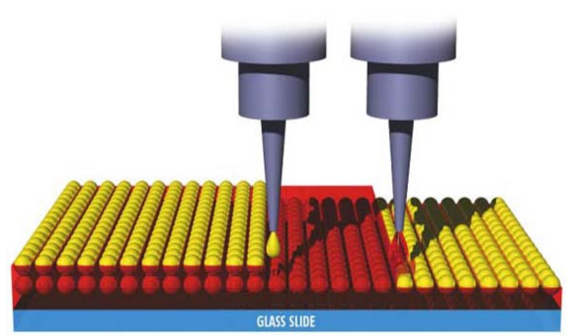


Figure 3. Materials printing system (Dimatrix) and deposition sketch

In comparison with other conventional semiconductor-fabrication techniques, the printing technique offers several advantages for fabrication of the thermoelectric materials and legs. Fabrication rates achievable by printing are in the range of microns per minute, fast enough for mass production of devices in the desired size range. Whereas, lower growth rates by the conventional techniques are better suited to fabrication of submicron-sized devices. The compositions of films grown by printing can be controlled via the concentrations of the constituents of the aqueous deposition solutions. The thermoelectric materials can be deposited onto the contact pads through the holes in the masks. Thus, conventional integrated-circuit-fabrication techniques can readily be combined with printing deposition for mass production of submillimeter thermoelectric devices.

Thermoelectric Microdevice

A thermoelectric module would contain thermoelectric legs made from thick films of n- and p-type semiconductors, plus multiple metal layers and outer layers made from high-thermal-conductivity materials. The thermoelectric legs would be connected electrically in series and thermally in parallel (Figure 4).

Small size thermoelectric devices based on thick films of n type thermoelectric materials - PbTe and Bi_2Te_3, and p type thermoelectric - TAGS and Sb_2Te_3 are undergoing fabrication and development. There is an increasing need for small thermoelectric devices to provide active spot cooling and warming for solar cells. The n type thermoelectric materials - PbTe and Bi_2Te_3, and p type thermoelectric - TAGS and Sb_2Te_3 are attractive thermoelectric materials for the operational temperature range (<200 °C, <400 °C) and for their high thermoelectric efficiency . Based on theoretical

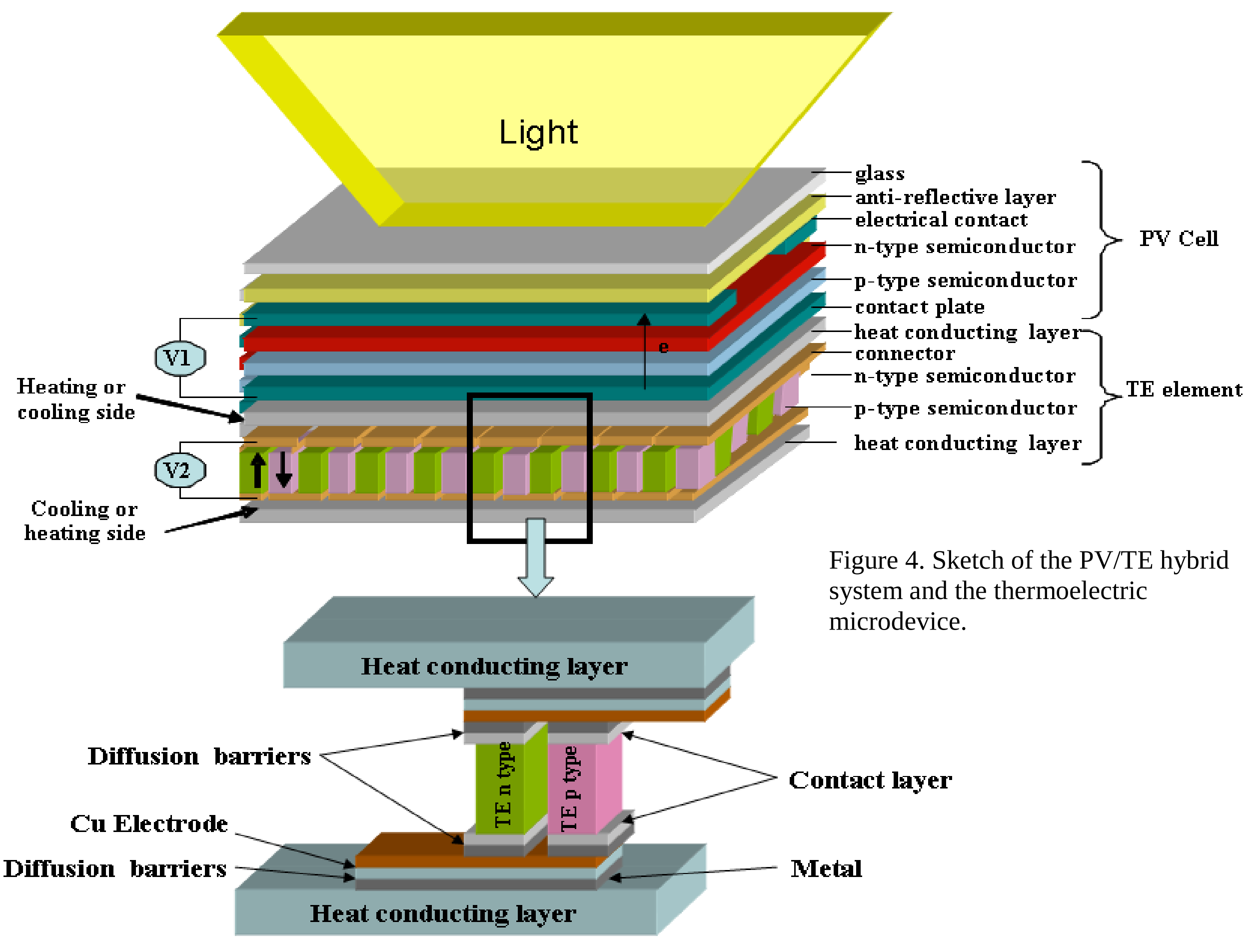


Figure 4. Sketch of the PV/TE hybrid system and the thermoelectric microdevice.

calculations, the smallness of the thermoelectric legs in these devices (thermoelectric legs have lengths, widths, and thicknesses of the order of microns), the numbers of legs can be of the order of 100 times those of conventional bulk thermoelectric devices.

The thermoelectric legs (shown in figure 4) are integrated with contact, diffusion-barrier, and electrode layers, all sandwiched between two thermally conductive, electrically insulating outer layers that are placed in contact with the solar cell.

As we mentioned before the n and p legs are made by CDV deposition and printing using an aqueous solution. The other parts of the device are fabricated by various conventional integrated-circuit-fabrication techniques, including photolithography and vacuum deposition.

References

1. R. Venkatasubramanian, E. Siivola, T. Colpitts and B. O'Quinn, *Nature*, 2001, **413**, 597
2. G. Jeffrey Snyder & Eric S. Toberer *Nature Materials* **7**, 105 - 114 (2008)
3. B. Zhang, J. He, X. Ji, and Terry M. Tritt, Amar Kumbhar, APPLIED PHYSICS LETTERS **89**, 163114 _2006_