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14. ABSTRACT

The overall goal of the project was to design and demonstrate fiber-based energy harvesting devices that can convert light and heat to electricity, and be integrated into air vehicle structures. Specifically, in Year 1, we set out to design and demonstrate photovoltaic and thermoelectric devices on polymer fibers. In Years 2 and 3, we sought to improve the performance of individual energy converting fibers, as well as to develop models and device architectures that would produce significant gains when many fibers are aggregated. We have successfully demonstrated thermoelectric (TE) and photovoltaic (PV) fibers, achieved substantial improvements in the power conversion efficiency, and developed and validated robust, predictive models for both OPV and TE fibers. Additionally, we developed optics-based approaches to tuning the sensitivity bands of photodetectors, and improving light in-coupling in solar cells and photodetectors. Encouraged by these advances, we have begun the design and construction of a novel apparatus for reel-to-reel coating and encapsulation of active devices on fibers, financed in large part by an AFOSR DURIP grant. We are also actively exploring options for creating a start-up company specializing in multi-functional, energy conversion devices based on the technology developed during this project.

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“Solar and Thermal Energy Harvesting Textile Composites for Aerospace Applications”

Project number FA9550-06-1-0399

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Progress report: 01/01/07 – 09/01/08

Executive Summary:

The overall goal of the project is to design and demonstrate fiber-based energy harvesting devices that can convert light and heat to electricity, and be integrated into air vehicle structures.

Year 1 summary:

Photovoltaic Devices: We developed a computational framework for simulating light in-coupling into fiber-based photovoltaic (PV) cells. Using this framework, we have designed and realized solar cell structures that do not use indium-tin oxide, a brittle and expensive ceramic that is typically used as a transparent electrode in organic solar cells. This achievement is important for integration of PV functionality in woven structures, where significant bending of the fiber occurs. This work has been published in peer-reviewed press (O'Connor et al., *Appl. Phys. Lett.* **89** (2006) p.233502). Additional publications include student posters and presentations at the *Materials Research Society* annual meetings.

Thermoelectric Devices: We developed an analytic framework for predicting the thermal and electrical properties of woven thermoelectric (TE) generators. Using this framework, we designed and demonstrated a generator based on thin-film metallic thermocouple junctions deposited on a fiber. This work has been submitted for publication and was recently published (Yadav et al., *J. Power Sources* **175** (2008) p.909). Additional publications include a student poster at the *Materials Research Society* annual meeting.

Year 2 summary:

Photovoltaic Devices: We demonstrated individual solar cells based on molecular organic compounds deposited onto long fibers. Using archetypal materials (e.g. copper phthalocyanine and C₆₀), these individual PV fibers perform comparably to their planar analogs for normal incidence of light. Our calculations also show that light incident on the cell over a 180 degree range of angles, enhanced light trapping in bundles of PV fibers will enable them to outperform their planar analogs. This is an important result for application in unmanned aerial vehicles (UAVs), in which the angle of incidence of sunlight varies in flight. Furthermore, this result suggests a more general method of enhancing efficiency in low-cost PV systems without solar tracking. This work has been submitted for publication (**update: this work has been published - O'Connor et al., *Appl. Phys. Lett.* **92**, 193306 (2008).**). Additionally, we have explored the fundamental limits of enhancing the efficiency of optical in-coupling in thin-film organic PV cells. The details of the computational framework and design criteria have been accepted for publication (Agrawal et al., *Opt. Express* - accepted).

Thermoelectric Devices: Using the predictions of the analytical model developed in Year 1, we modified the structure of the individual thermoelectric fibers to improve efficiency and ease of fabrication, requiring only one masking step to pattern the junctions. Furthermore, we have demonstrated the use of electroless plating - a highly scalable film deposition method - to form TE junctions on a fiber. Using this approach, we have achieved woven TE generators, in which the TE fiber approaches the design specifications obtained in Year 1 for metallic fibers. A manuscript is being prepared for publication (Yadav et al., manuscript in preparation).

Year 3 summary:

Photovoltaic Devices:

We demonstrated ITO-free, vacuum-deposited, planar, small-molecular organic solar cells with double the power conversion efficiency (~2%) of what our devices achieved previously (~1%). Furthermore, this improved

performance of the ITO-free device is on par with a conventional ITO-based control device. The new device structure consists of a metal-organic-metal multilayer stack, with light coupled in through one of the ultra-thin (non-patterned) metal electrodes; the device exhibits microcavity effects that help maintain a high level of optical field intensity at the electron Donor-Acceptor junction, despite the lower far-field transmittance of the metal electrode. *Our recent findings are significant for several reasons:*

1. The use of non-patterned metal films as transparent electrodes potentially offers a number of advantages, including excellent scalability (via compatibility with low-cost roll-to-roll fabrication, low-temperature processing, the ability to deposit on non-planar substrates)
2. Switching from ITO and similar transparent conducting oxides to the ultra-thin metal electrode increases the power-to-weight ratio of the active structures deposited on any substrate (important for Air Force applications). (Current power densities for the entire PV cell layers - including electrodes and active organic semiconductor - exceed 1 kW/gram at 1 Sun illumination.)
3. Eliminating the brittle layers from the OPV cell structure improved mechanical flexibility and device longevity (also important for Air Force applications)
4. Our detailed analysis of the optical properties of these devices provides general guidelines for the transparent electrode design (based on fundamental, generalized optical and electrical properties of the chosen material set), guiding the search for other candidate electrode materials and pointing the way toward the development of new, exotic metamaterials with optical properties not found in nature.

Additionally, building on the previous years' studies of the fundamental limits of optical in-coupling in organic PV structures, we have developed anti-reflection coatings optimized for broad-band light capture, improving the power conversion efficiency by ~30% over the non-coated fiber. Combining the broad-band optimized coatings with fiber bundle geometries, we predict a 60% improvement over the uncoated single fiber devices.

Thermoelectric Devices:

We have demonstrated woven TE generators, in which several thermoelectric strands ranging from 100 to 500 micrometers in diameter. The woven devices span areas of several square inches, albeit with spaces between the individual junctions on the order of 5 mm. Even at this low weave density, we have achieved power harvesting density exceeding 5 nW/in² for metallic junctions. This design is amenable both to scale up and miniaturization; the fiber spacing can be reduced by a factor of 5 to 10 (with a power density increase by a factor of 25 to 100). Additionally, by employing conventional BiTe alloy films, an additional factor of 10³ gain in power density is projected. A manuscript is being prepared for publication (Yadav et al., manuscript in preparation).

Barrier Coatings:

We also begun developing barrier coating technology for our photovoltaic and thermoelectric fibers. The coatings are currently based on chemical vapor-deposited parylene. To enable rapid deposition onto non-planar fibers, we have developed a novel jet printing approach, where high velocity organic vapor jets are generated by means of a carrier gas and a collimating nozzle aimed at the substrate. Preliminary results suggest the ability to deposit smooth and uniform coatings onto un-cooled substrates.

DURIP:

Based on the encouraging results in Years 1-2, we began the design and construction of a reel-to-reel fiber coating system for photovoltaic and thermoelectric devices.

2. Objectives:

The proposed research focuses on developing novel energy harvesting devices that can be integrated with load-bearing structures in an air vehicle (e.g. a UAV). Several ambient energy sources are available on a UAV: Light, Heat, and Vibration. (**Fig. 1**) The amount of energy available from light and heat exceeds that in vibration, so we focus on these first two modes of harvesting.



Figure 1: Ambient energy available on a UAV, including light, heat, and vibration

Our approach is to create energy harvesting devices in the form of long fibers, that eventually could be woven into lightweight, high-strength multifunctional textiles for seamless integration with aerospace structural composites. (**Fig. 2**) The fiber form factor is a powerful paradigm for these energy conversion devices, since it can lead to improved light trapping in the organic photovoltaic (PV) cells, and allow for a high density of thermocouple junctions, without the use of costly patterning techniques, significantly enhancing the cost-benefit performance.

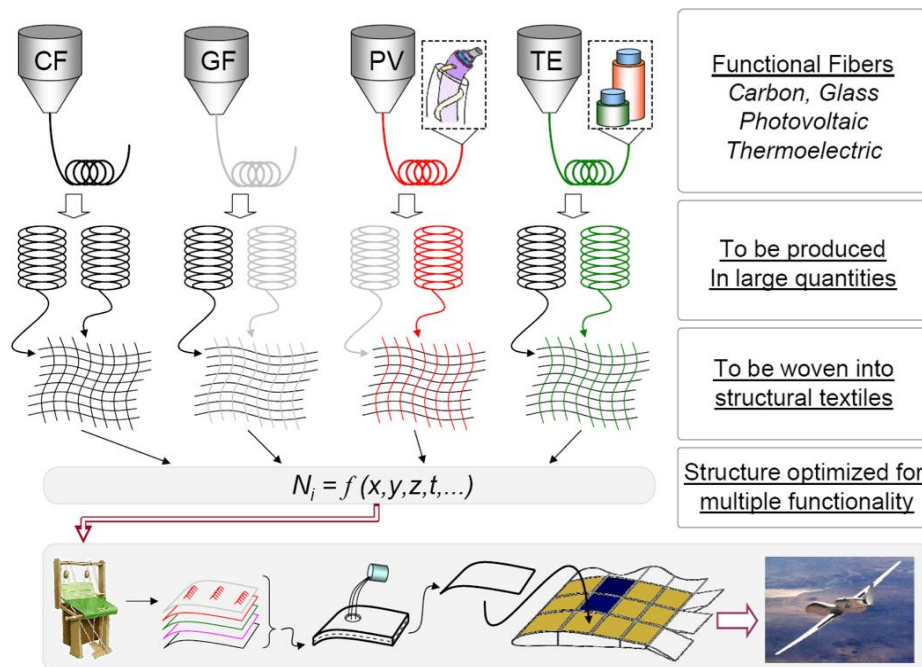


Figure 2: An illustration of the overall approach, wherein energy harvesting is done in specially designed fibers that can be later woven into structural textiles for integration into load-bearing composites.

In the first two years of the project, we focused on modeling and experimentally demonstrating prototype devices, consisting of single fibers capable of the thermoelectric (TE) and PV modes of energy conversion. The results obtained thus far are highly encouraging, and have opened up several exciting new research directions.

3. Status of Effort

This part of the report describes the progress made toward achieving the project goals.

3.1. Organic Photovoltaic fibers:

We are pursuing a solar cell geometry in which the active organic layers and metallic electrodes are formed concentrically around a fiber core, and light is coupled in through the outer electrode. (Fig. 3) This structure is quite different from the conventional planar PV cells, and requires special considerations in its design and for predicting its optoelectronic performance.

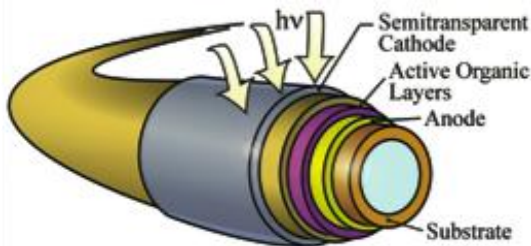


Figure 3: An illustration of the photovoltaic (PV) fiber structure, consisting of very thin active layers deposited concentrically around a fiber core with favorable structural properties.

Modeling of Organic PV Cell Devices

Fresh advances in modeling OPV devices on fibers include the application of multi-layer dielectric coatings to fiber bundles. This architecture (Fig. 4) maximizes light in-coupling in individual fibers and, furthermore, takes advantage of photon recycling in multi-fiber arrays. The modeling combines ray-tracing and transfer-matrix simulations at multiple length scales. Because each component of the model has been independently validated by experiments, we anticipate being able to experimentally realize these gains in the following Years 3-4 of the project.

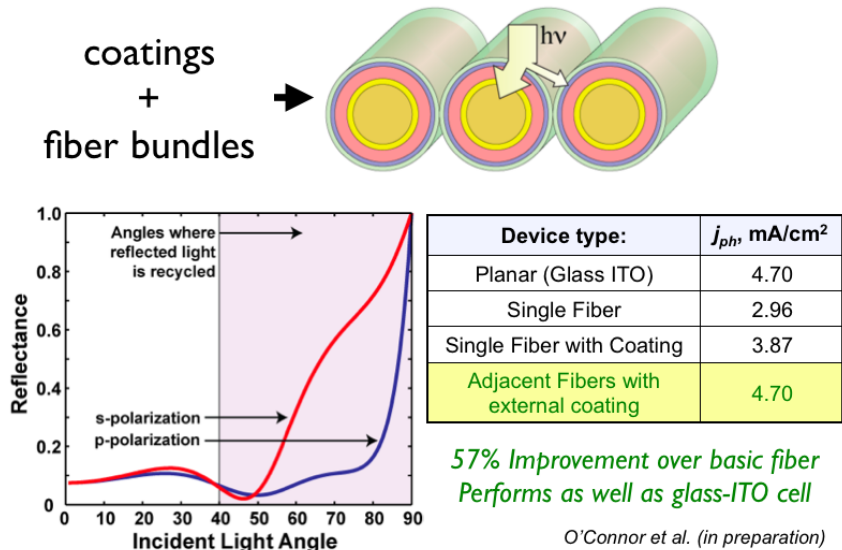


Figure 4: Combining the beneficial effects of multi-layer anti-reflection coatings and photon recycling in bundles, light trapping efficiency is increased, leading to a nearly 60% improvement of efficiency in fiber-based OPV cells, compared to single, uncoated fibers. The fact that the novel device architecture does not use ITO, yet achieves parity with conventional, ITO-based cells is an important advance.

Improved efficiency of ITO-free (metal-organic-metal) cells

We have demonstrated improved power conversion efficiency of planar OPV cells using a metal-organic-metal layer structure. Importantly, these devices now match the efficiency of conventional ITO-based cells, which we have also improved this year. As Fig. 5a shows, the ITO-free device exhibits a slightly lower short circuit current density (J_{SC}), but compensates with a higher open circuit voltage (V_{OC}). Further analysis of how J_{SC} varies with anode thickness reveals that the device performs unexpectedly better (red line in Fig. 5b) than the far-field transmittance of the anode would suggest (grey lines in Fig. 5b). The enhanced performance is due to the mi-

cavity effects dominating the thin-film OPV cell, in which the far-field optical transmission of the electrode is less important than its ability to place the antinode of the optical field close to the donor-acceptor junction in the organic layers. Detailed optical modeling allows us to map out the performance of a wide range of electrode materials (**Fig. 5c**), and predicts that silver is not far from the conventionally employed ITO with respect to the J_{SC} values it can allow.

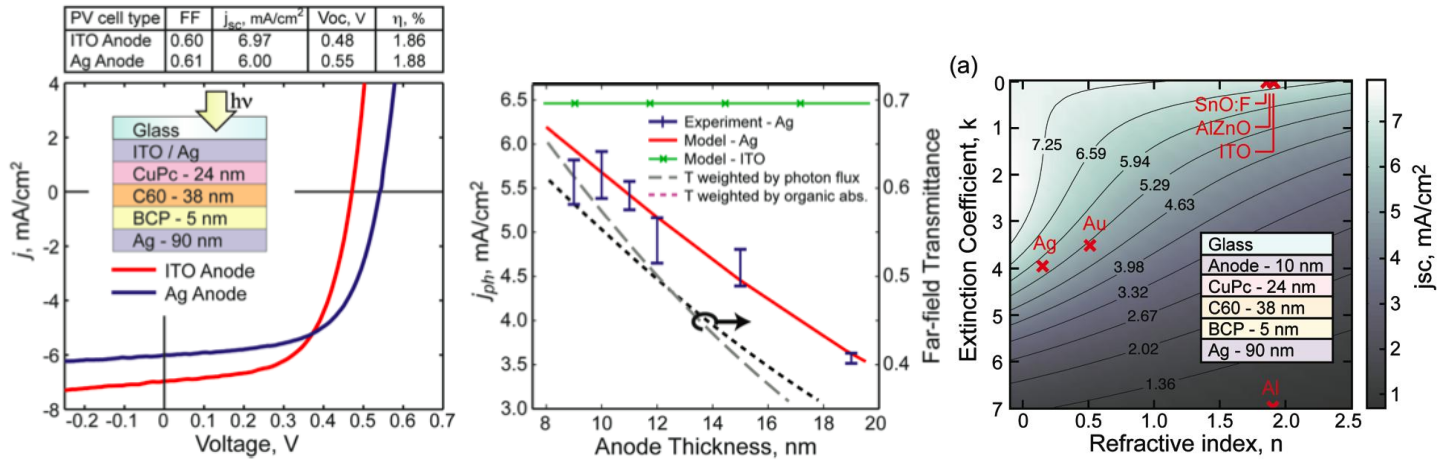


Figure 5: (a) A plot of the short circuit current density (J_{SC}) versus circuit voltage (V_{OC}) for a conventional OPV cell deposited on ITO and a metal-organic-metal cell deposited on glass. Their efficiencies are comparable. (b) A comparison of how J_{SC} and far-field transmittance vary with the silver anode thickness. Devices perform significantly better than what would be expected from simple transmittance measurements on the anode. (c) A contour plot of the predicted J_{SC} for any combination of extinction coefficient and refractive index of the anode material (averaged over the absorption spectrum of the active organic layers). These full optical models shed light on the physics underpinning the observed behavior, providing clear guidance for material design.

3.2. Thermoelectric Fibers:

Conversion of heat to electricity - thermoelectric generation - can be accomplished by connecting two dissimilar materials (metals or semiconductors) in a series of junctions, and sandwiching the junctions between a hot source and a cold sink, as shown in the slide. The voltage produced by the junction is proportional to the temperature gradient between the hot and cold sides. (**Fig. 6a**) We can reproduce the conventional series-connected junction geometry in the form of thin-film segments deposited along fibers. Weaving these fibers can position the junctions as required for power generation. (**Fig. 6b**) The TE generator is optimized by maximizing the temperature gradient, minimizing the thermal conductivity, and maximizing the Seebeck coefficient and electrical conductivity. We can predict the power density for a weave consisting of junctions of different types of materials - in **Fig. 6c**, metallic junctions are modeled.

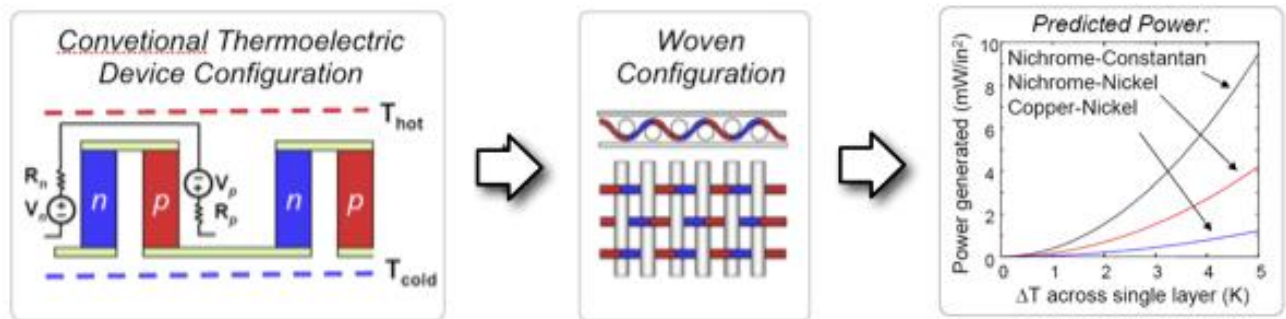


Figure 6: An illustration of how the conventional thermoelectric device geometry can be adapted to fiber substrates, along with predictions for power generated by metal-based TE fibers.

Experimental Demonstration of a Woven Fiber-Based Thermoelectric Generator

We have also demonstrated woven thermoelectric generators utilizing several TE fibers at once. Several fiber diameters have been explored, varying also the TE segment length and weave density, and spanning square inches. An example of a woven mat is shown in **Fig. 7a**, along with a diagram of the test set-up and a plot of the

measured power. We note that for smaller fibers, increased weave density, and greater temperature gradients, the power density increases dramatically. The thinness and flexibility of these mats suggests that multi-layer TE fabrics can be used to efficiently span temperature gradients using individual layers tuned to work at their maximum ZT point. We plan on further increasing the power density of TE weaves, and to incorporate semiconducting films for projected thousand-fold improvement of efficiency.

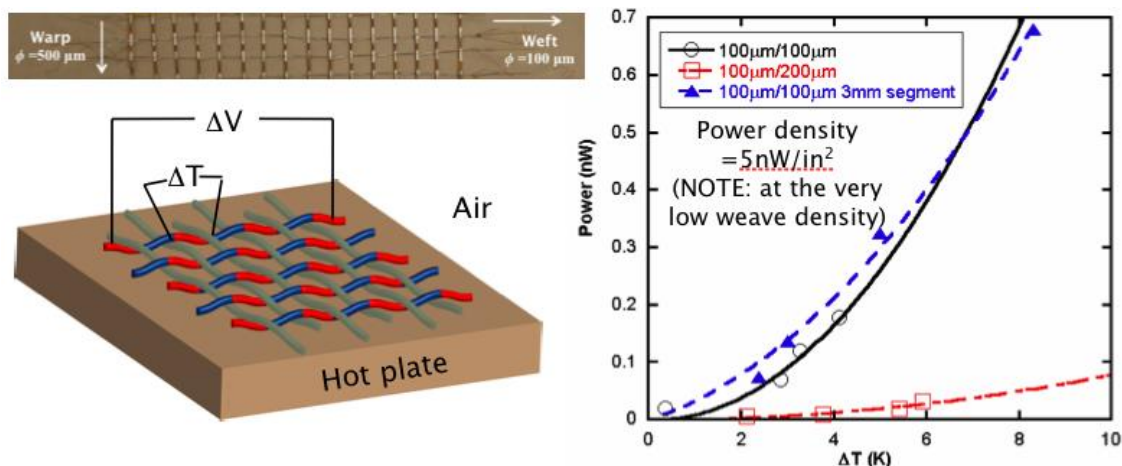


Figure 7: (a) Photograph of a woven TE generator spanning several inches. (b) A diagram of the test set-up for measuring the power generation. (c) A plot of the power generated by the mat for a given (mild) temperature gradient.

3.3. Encapsulation and reel-to-reel coating:

We are also actively developing jet deposition approaches for depositing encapsulating films onto active devices on fibers. One possibility includes the chemical vapor deposition of parylene, adaptable for reel-to-reel processing. This approach builds on the PIs previous invention of organic vapor jet printing for planar optoelectronic devices, and is illustrated in **Fig. 8**.

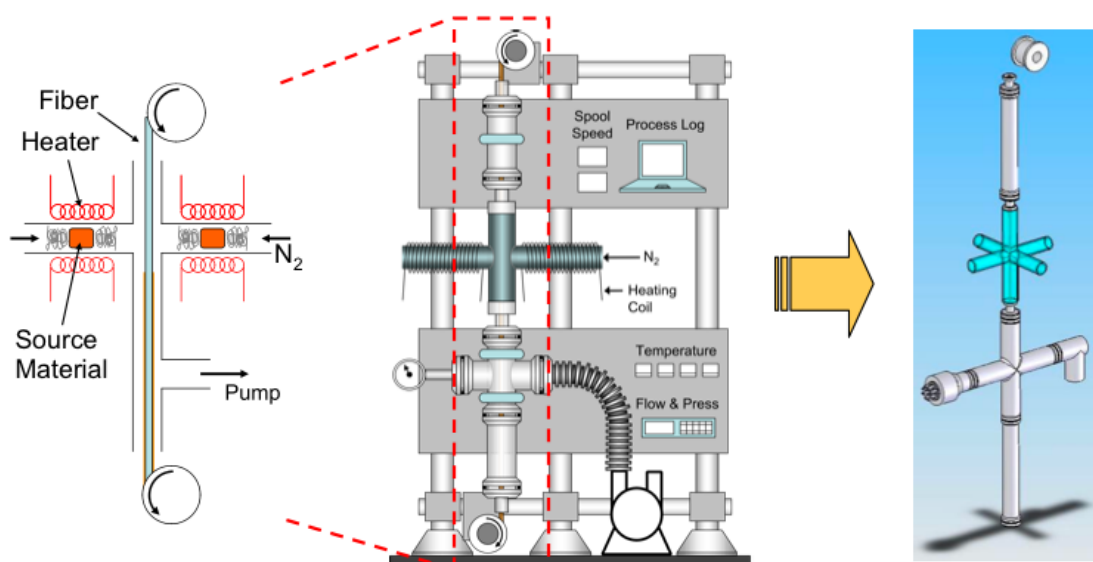


Figure 8: A conceptual illustration of a reel-to-reel coating apparatus, where the layers (e.g. parylene-based barrier films) are deposited onto a fiber that is translated at high velocity through the deposition chamber.

4. Accomplishments/New Findings:

In this section we briefly summarize the major accomplishments described in more detailed in Section 3.

4.1 Fiber PV:

i. Doubled the performance of planar OPV cells

The power conversion efficiency of single-junction, small molecular organic PV cells made in our laboratory now approaches 2%. This is near the limit for the given material system in a single-junction, planar configuration. Polymer-based OPV cells fabricated on planar substrate now exceed 2.75%.

ii. Eliminated ITO while maintaining the high power conversion efficiency

Our new cell design eliminates brittle transparent conducting oxides in favor of malleable thin metal films, without the loss of power conversion efficiency.

iii. Developed comprehensive optical models of OPV cells

We now have predictive optical models for OPV cells, where any combination of substrate, active layers, electrodes, external coatings, incident spectrum and light direction can be simulated, predicting the photocurrent of a device with high accuracy.

vii. Combination of anti-reflection coatings and photon recycling in fiber bundles

We used our models to develop a combination of fiber bundles, wherein each fiber contains a 6-layer anti-reflection coating. The power conversion efficiency for the entire bundle beats that of ITO-based devices, with significant further gains possible in view of our recently developed, efficient metal-organic-metal OPV heterostructure.

4.2. Fiber TE

i. Woven TE generators with improved power density

We have applied two methods developed in Year 2 of the project to realizing larger TE meshes, achieving power density of 5 nW/in², and pointing to concrete ways of improving the efficiency.

4.3 Encapsulation and reel-to-reel deposition methods

i. Begun construction of a novel parylene deposition apparatus suited for coating fibers.

ii. Begun construction of a novel reel-to-reel fiber coating apparatus that will incorporate the apparatus from 4.3-i.

5. Personnel Supported:

Faculty:

University of Michigan – Max Shtein (PI), Kevin Pipe (co-PI)

Stanford University – Peter Peumans (sub-contractor)

Graduate Students:

University of Michigan – Brendan O'Connor,* Abhishek Yadav,* Shaurjo Biswas, Steven Morris

Stanford University – Mukul Agrawal

* O'Connor and Yadav have recently defended their Ph.D. theses. O'Connor is currently a post-doctoral fellow at NIST (on a congressional fellowship) and will be joining NC State University as an assistant professor in 2010/2011. Yadav is currently a post-doctoral researcher at the University of Michigan, actively seeking a faculty position.

6. Publications in peer-reviewed literature:

1. B. O'Connor, K-H An, Y. Zhao, K. Pipe, M. Shtein, "Enhanced electric field distribution in organic photovoltaics using external coatings." *Applied Physics Letters* 89, 233502 (2006)
2. B. O'Connor, K-H An, Y. Zhao, K. Pipe, M. Shtein, "Fiber shaped organic light emitting device" *Advanced Materials* 19, 3897 (2007)
3. B. O'Connor, K. Pipe, M. Shtein, "Fiber based organic photovoltaic devices" *Appl. Phys. Lett.* 92, 193306 (2008)
4. A. Yadav, K. Pipe, M. Shtein, "Fiber-based thermoelectric generator" *Journal of Power Sources* 175, 909 (2008)
5. B. O'Connor, C. Haughn, K. H. An, K. P. Pipe, M. Shtein, "Transparent and conductive electrodes based on unpatterned, thin metal films." *Applied Physics Letters* 93, (2008) 223304.
6. Mukul Agrawal and Peter Peumans, "*Broadband optical absorption enhancement through coherent light trapping in thin-film photovoltaic cells,*" *Optics Express* **8**, (2008) 5385
7. M. Agrawal, P. Peumans., "Broadband optical absorption enhancement through coherent light trapping in thin-film photovoltaic cells." *Optics Express*, 16, 5385 (2008)
8. K. H. An, B. O'Connor, K. P. Pipe, M. Shtein, "Organic photodetector with spectral response tunable across the visible spectrum by means of internal optical microcavity." *Organic Electronics* 10, (2009) 1152.
9. K.H. An, M. Shtein, K.P. Pipe, "Surface plasmon mediated energy transfer of electrically-pumped excitons." *Optics Express* 18, 4048 (2010)

7. Interactions/Transitions:

a. Participation/presentations at meetings, conferences, seminars, etc.

Students and advisors have been giving presentations at the meetings of Materials Research Society, Electronic Materials Society, and SPIE Photonics West, SAMPE, CLEO/QELS. Shtein has given several invited lectures at leading universities and conferences in the last year.

b. Consultative and advisory functions to other laboratories and agencies, especially Air Force and other DoD laboratories.

N/A

c. Technology Assists, Transitions, and Transfers.

We are currently exploring the options for starting a company that will specialize in multi-functional energy conversion devices based on the technology developed in this project.

8. New discoveries, inventions, or patent disclosures.

Several patent disclosures have been filed, based on this research.

9. Honors/Awards:

Brendan O'Connor – a student working on the photovoltaic fibers – received an honorary fellowship from the Michigan Memorial Phoenix Energy Institute.