Thermoelectric Transport in Novel Quantum Confined and Organic-Inorganic (Hybrid) Nanostructured Materials

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Quantum Confined Core-Shell Nanowires

***Abstract*: The thermal conductivities of crystalline nanowires have reached values comparable to their amorphous counterparts. However, the enhancement of the thermoelectric efficiency due to phonon-boundary scattering still fails to achieve large *ZT*. A greater improvement in *ZT* could be achieved if increases are made to the Seebeck coefficient (*ZT* is proportional to S^2). we are working with band structure engineering by creating core-shell nanowires as means to increase *S* because one or two dimensional hole/electron gases in undoped band engineered nanowires exhibit large mobilities. The lack of impurity scattering in the conduction channel would result in an increase of both *S* and *σ*.**

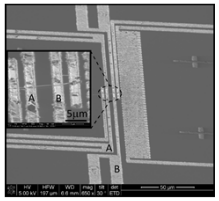
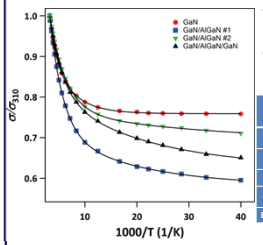


Figure 1. SEM images of the core-shell GaN/AlGaN nanowire placed on the characterization platform. Electrical and thermal contacts were realized by placing a top metal layer by SEM-lithography. After thermal annealing, ohmic contacts are observed. Larger bumps on the metal leads are the result of the gold-aluminum intermixing. ***k*** was obtained with the self-heating method. The Seebeck coefficient was acquired by measuring the thermal voltage and temperature diff. between leads A and B.



GaN Nanowire

- $\sigma(T) = \sigma_0 + \sigma_1 \exp(-E_a/k_B T)$

For Core-Shell

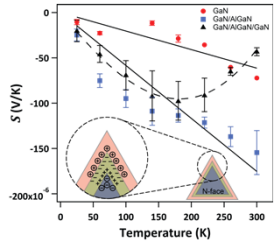
- $\sigma(T) = \sigma_0 + \sigma_1 \exp\left(-\frac{E_1}{k_B T}\right) + \sigma_2 \exp\left(-\frac{E_2}{k_B T}\right)$

	σ_0 (S/cm)	σ_1 (S/cm)	E_{a1} (meV)	σ_2 (S/cm)	E_{a2} (meV)
GaN	90.1	90.7	63.8	-	-
AlGaN/GaN(1)	43.4	77.0	69.0	12.4	5.4
AlGaN/GaN(2)	33.8	36.3	54.4	7.3	1.0
GaN/AlGaN/GaN	31.2	35.3	69.9	10.9	4.8

Error represent 95% confidence interval of the regression

Figure 2. Left: Electrical conductivity as function of temperature for GaN (control) and 2 types of core-shell nanowires. Electrical conductivities as function of *T* does not follow the phonon-carrier scattering expected mechanism for 2-DEG in core/shell nanowire. Right: Carrier thermal activation equations employed to model our samples. E_{a1} energy level is similar to the reported for **Oxygen doped GaN and this energy level is also observed in core/shell nanowires.** E_{a2} shows a **very shallow channel that is comparable to the activation energy of electron gas.** The double channel model yields meaningless E_{a1} and E_{a2} for GaN nanowires. The heavily doped core dominates the electrical conductivity. The large residual conductivity (σ_0) of the core is also contributing to temperature behavior of the data.

Quantum Confined Core-Shell Nanowires



Core-shell Contribution Model

$$S = \frac{S_{EG}\,\sigma_{EG} + S_{GaN}\,\sigma_{GaN}}{\sigma_{EG} + \sigma_{GaN}}$$

$$S = S_{EG}\frac{\sigma_{EG}}{\sigma_{GaN}} + S_{GaN} \quad for\ \sigma_{EG} << \sigma_{GaN}$$

Figure 3. Observed Seebeck coefficient versus *T* for our nanowires. Solid lines represent the fitting of experimental data with *A T*. Dashed line is the fitting with $A'T+B'T^{\alpha}$. Adding a AlGaN shell resulted in **doubling the Seebeck** coefficient and the core-shell model (right) indicates the strong enhancement of the 2-DEG electrons. A quantum confined electron gas layer is thought to be reached by the electrostatic repulsion by the doped GaN core and the N-face forcing the *EG* to be confined on the corner. An additional GaN shell actually decreases the Seebeck coefficient. The presence of 2-DEG electrons influences the outer AlGaN-GaN shell-shell by producing holes. Inset: hypothetical charge distribution of GaN/AlGaN/GaN core/shell/outer-shell nanowire. Charges in circles represent either 2-DEG or 2-DHG while the others are polarization charges.

Photo-Thermoelectric Solar Power Cell

***Abstract*: Combining photovoltaic (PV) and thermoelectric (TE) components allow a larger portion of the solar spectrum to be absorbed and converted into electricity. Porphyrin films are excited by wavelengths in the UV-vis regions. TE materials, like Bi_2Te_3 nanowires will capture the thermal energy (IR) Utilization of the IR region leads to electricity generation from the solar cell in the dark and also can improve the overall efficiency of the device.**

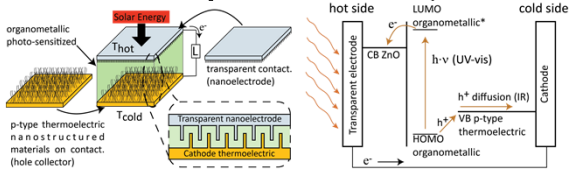


Figure 1. Left: Conceptual representation of proposed PV-TE solar power generation cell. Right: band structure indicating porphyrin photo-excitation. Electrons and holes flow to anode and cathode respectively are also included.

Porphyrin on ZnO and Bi_2Te_3 NWs

Photoconductivity of Sn/Zn nanosheets on ZnO nanowire

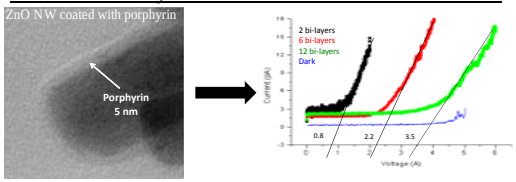


Figure 2. Observed photoconductivity (white light) for porphyrin bilayer (ZnTTPS⁻ and SnTNEtOHPyP⁴⁺) deposited onto ZnO nanowires. A characteristics diode behavior is observed for our sample. Dark case resulted in negligible conduction due t the lack of photo-activated carriers. The threshold voltage scales with the thickness of the bilayer.

Photoconductivity of Sn/Zn nanosheets on p-type Bi2Te3 nanowire

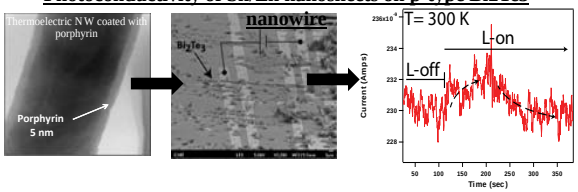


Figure 3. photoconductivity studies (white light) for porphyrin bilayer (ZnTTPS⁻ and SnTNEtOHPyP⁴⁺) deposited onto p-type Bi_2Te_3 nanowires. During the photo-excitation, the current increases followed by a decrease due to either light thermal heating of the sample or carrier recombination within the porphyrin.

Photoconductivity of SnTNEtOHPyP⁴⁺ on n-type Bi2Te3 nanowire

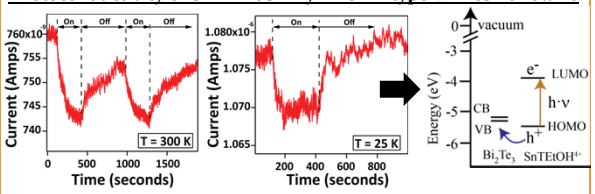


Figure 4. Left 2 figures: photoconductivity studies (blue light) for SnTNEtOHPyP⁴⁺ deposited onto n-type Bi_2Te_3 nanowires. After initial charging, a clear temperature dependence is observed during photoactivation and carrier dark recombination. Mobility of carriers within the porphyrin film is responsible this observation. Right: band diagram indicating that the **hole injection into n-type Bi2Te3** is energetically favorable.

Current Work: PV-TE Components Integration

The present phase of this project will seek to incorporate a photoconductive porphyrin film/n-ZnO nanowire photovoltaic complex with the thermoelectric Bi_2Te_3 p-nanowire component of the hybrid solar cell. The porphyrin should adsorb as smooth as possible to the Bi_2Te_3 to maximize the interface between the ZnO electrode and the TE cathode to optimize charge transfer and improve cell efficiency. The following milestones are necessary for the integration process:

- **p-type Bi_2Te_3 nanowires are being synthesized by a solution method in our lab group at New Mexico State University.**
- **A single nanowire PV-TE solar cell measurement are expected to be carried out with a within few months.**

Conclusions

- **Nanostructured materials with high mobility of 1;2-DEG carriers are a novel approach to increase *ZT*. This work presents evidence of room temperature quantum confinement due to electrostatic repulsion of the electron gas. Spontaneous hole-gas formation is also reported.**
- **Hybrid solar cells could increased efficiency, lower cost of production, and simplify scale-up factors. The NWs effectively coated with porphyrins show exceptional potential for creating the hybrid device. Photo-activation of thermoelectric hybrid was observed and the transfer of carrier across the organic-inorganic boundary is possible for our materials**

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