Tuning the thermoelectric power factor in carbon nanotube films

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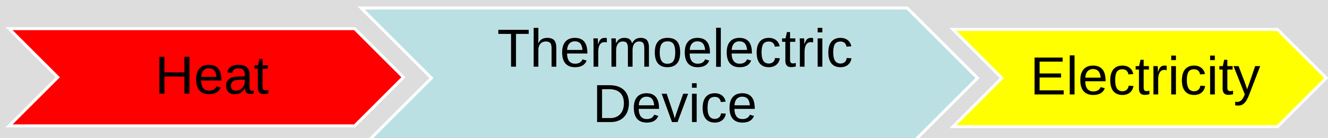
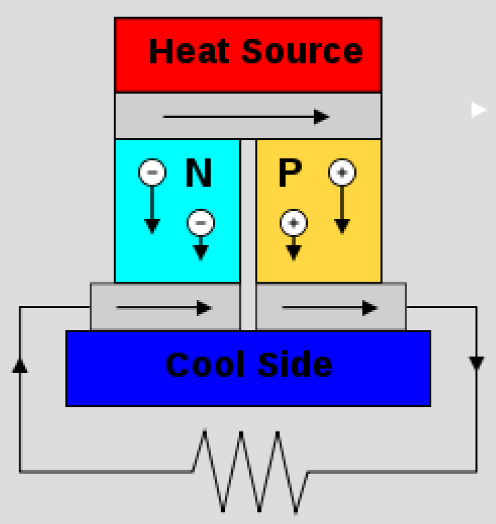
Introduction

Thermoelectrics





Schematic of a thermoelectric device. *(wikipedia)*

$$ZT = \frac{\sigma S^2}{\kappa} T \quad \text{[Eqn. 1]}$$

- High ZT = Good thermoelectric material

  σ - electrical conductivity S - Seebeck coefficient
  κ - thermal conductivity T - temperature
  σS^2 – power factor

- The Mott relation (eqn. 2) shows that to increase the Seebeck coefficient, the energy derivatives at the Fermi level (E_F) of carrier concentration (n) and mobility (μ) should be maximized.

$$S = \frac{\pi^2 k_B^2}{3e} T \left\{ \frac{dn(E)}{ndE} + \frac{d\mu(E)}{\mu dE} \right\}_{E=E_f} \quad \text{[Eqn. 2]}$$

Carbon Nanotubes

- Single walled carbon nanotubes (SWCNTs) are promising thermoelectrics because of their good conductivity and one dimensional density of states.
- E_F can be tuned by doping (black arrows) so that it lies near a Van Hove singularity (blue dashed line), improving the Seebeck coefficient.

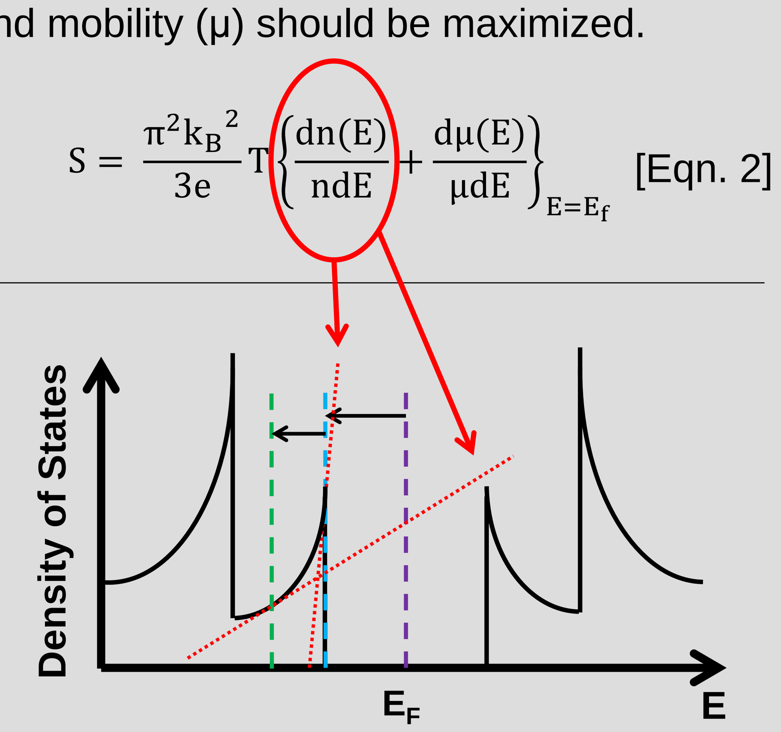
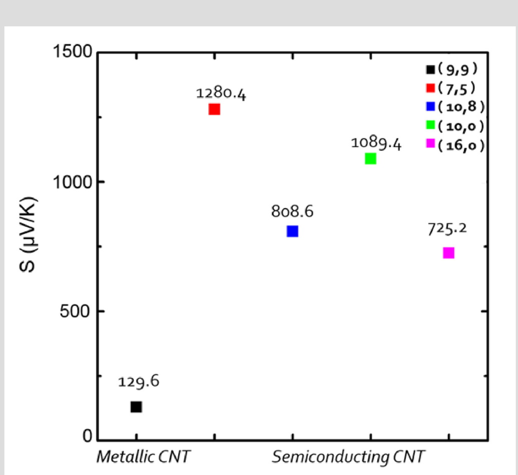


Diagram of the 1-D density of states in s-SWCNTs. m-SWCNTs have a small, non-zero DOS in between the first two Van Hove singularities



- Recent studies have shown that SWCNT films enriched in semiconducting SWCNTs (s-SWCNTs) have higher Seebeck coefficients than in films enriched in metallic SWCNTs (m-SWCNTs).

Density functional calculations of the Seebeck coefficient of m- and s-SWCNTs, demonstrating the large Seebeck coefficients possible with s-SWCNTs.

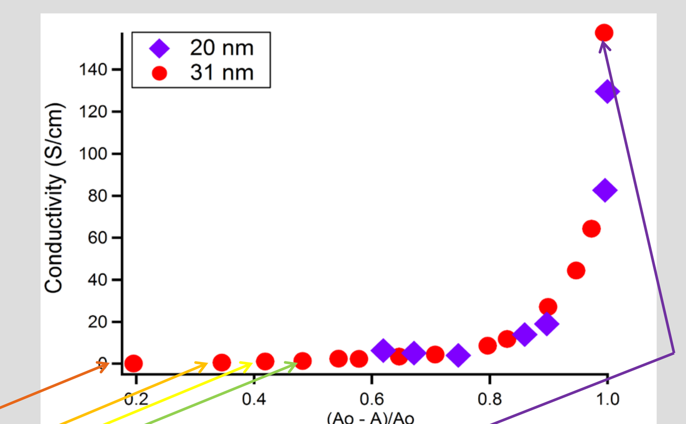
Objective

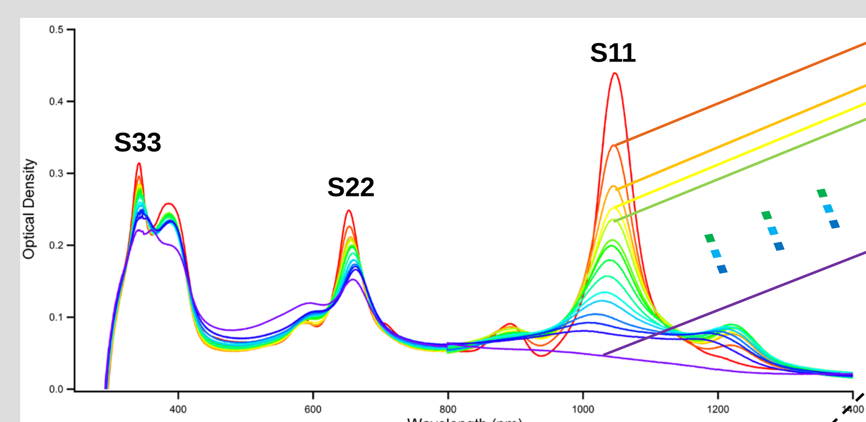
- To demonstrate that the Fermi level and carrier concentration of s-SWCNT films can be tuned to optimize their thermoelectric power factor.
- To engineer multi-chiral SWCNT films which have high Seebeck coefficient at high carrier concentrations..

Results and Discussion

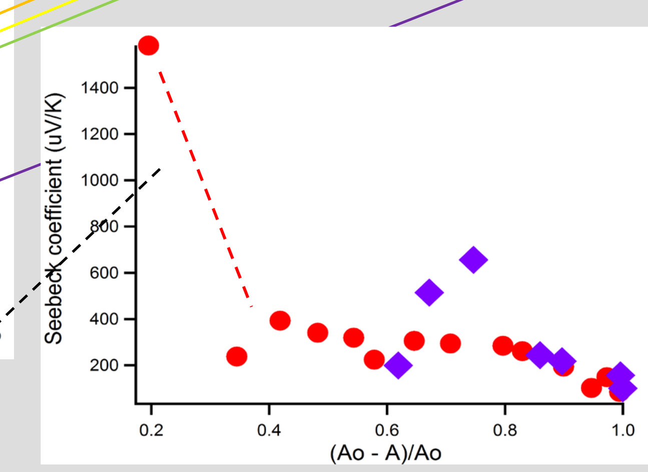
Single-chiral (7,5) SWCNT films

- A 20 nm (7,5) film and a 31 nm (7,5) film were doped incrementally. The conductivity and Seebeck coefficient were measured at each doping step.
- The shift in Fermi level and degree of doping is judged by the bleaching of the S11 peak.

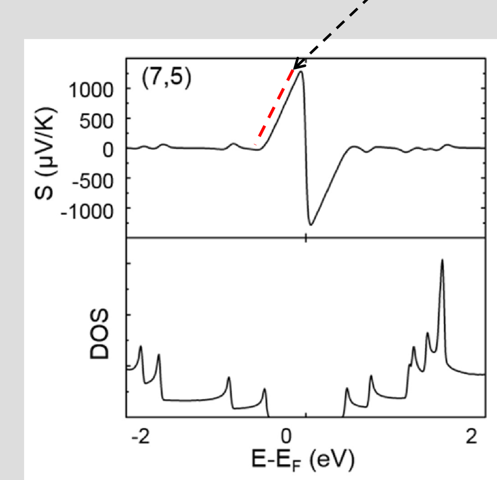


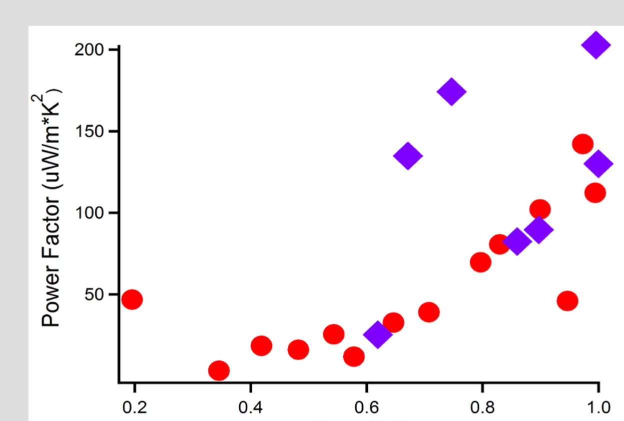


Absorbance spectra of the 31 nm (7,5) film as it is incrementally doped.



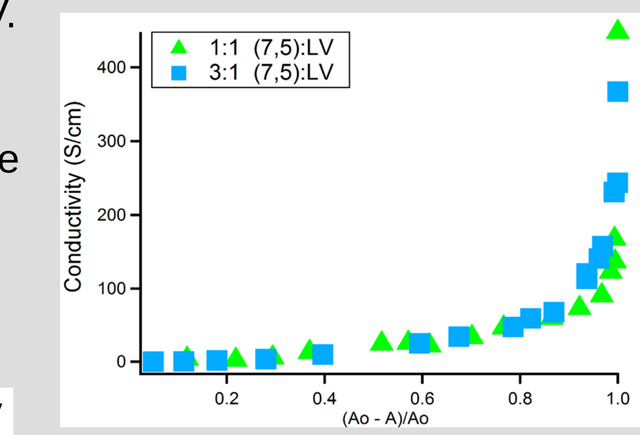
Density functional calculated Seebeck coefficient as a function of the position of the Fermi level

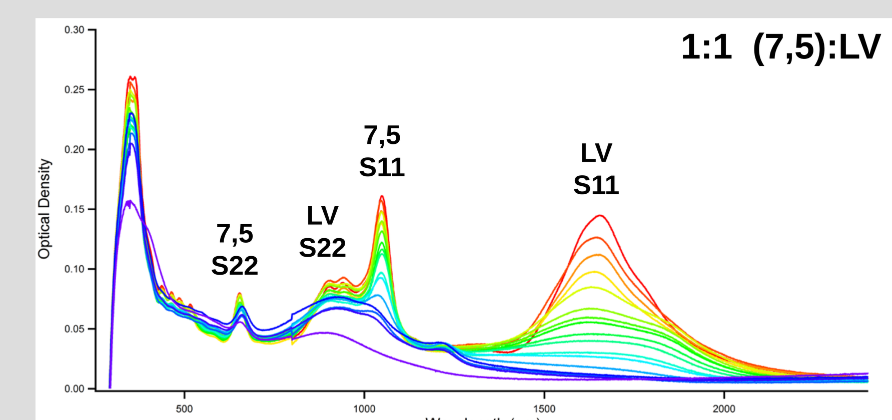


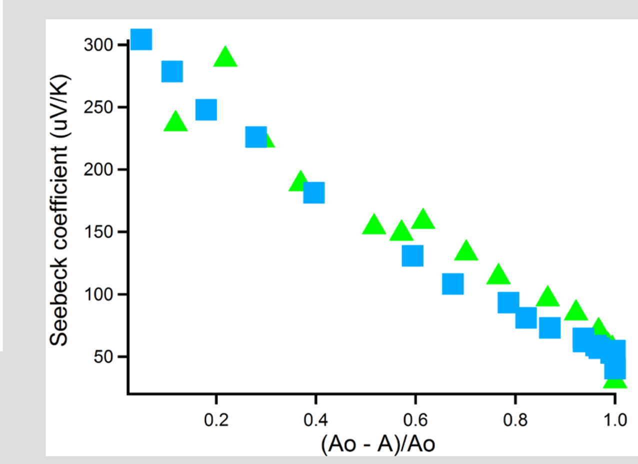


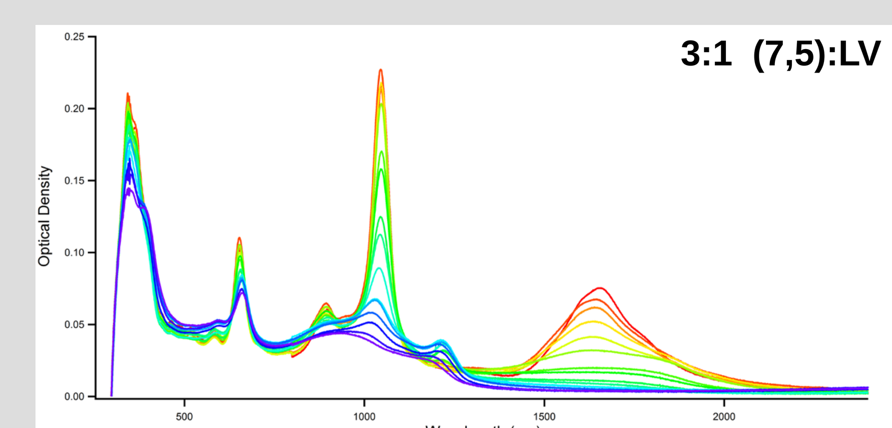
Multi-chiral (7,5)/LV SWCNT films

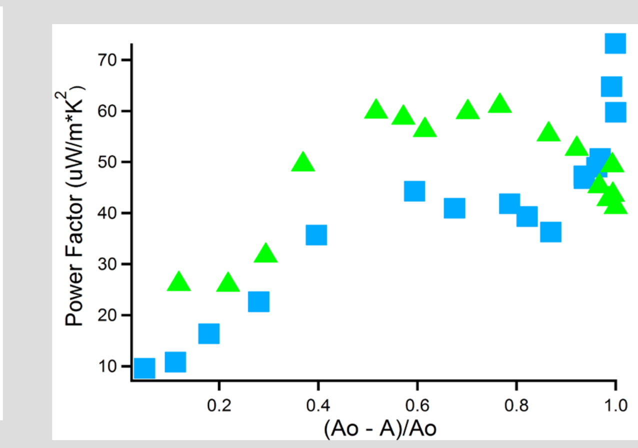
- (7,5) SWCNTs were mixed with LV SWCNTs in mass ratios of 1:1 (7,5):LV and 3:1 (7,5):LV.
- By having SWCNTs with different band gaps, it was hoped that a high conductivity would be achieved in the LV SWCNTs and a high Seebeck coefficient in the (7,5) SWCNTs.











Materials and Methods

- **Ink Preparation:** (7,5) nanotubes were dispersed by poly[9,9-dioctylfluorenyl-2,7-diyl] (PFO) in toluene, and laser vaporization (LV) nanotubes were dispersed by PFO-*alt-co*-(6,6'-{2,2'-bypyridine})] (PFO-BPy). The mixtures were homogenized by tip sonication. Impurities and excess polymer were removed from the solutions by ultracentrifugation.
- **Film Preparation:** Films were fabricated by ultrasonic spraying.
- **Doping:** Films were doped in solutions of triethyloxonium hexachloroantimonate in dichloroethane.
- **Measurements:** Electrical conductivity was measured by 4-point probe method, while Seebeck coefficient was measured on a home-built system.

Conclusions and Future Work

- The carrier concentration and Fermi level of (7,5) SWCNT films were sensitively tuned to optimize the films' power factor.
- The power factors of 100-200 $\mu W m^{-1} K^{-2}$ for the optimized (7,5) films are the highest reported for SWCNT thin films.
- The Seebeck coefficients are the highest reported for SWCNTs, remaining above 200 μV/K even at high conductivities, when the highest previously reported Seebeck coefficient for SWCNTs was ~160 uV/K.
- Distinct effects from the (7,5) and LV SWCNTs in the multi-chiral films were not observed. Further investigation is required.
- X-ray photoelectron spectroscopy can quantify the Fermi level shift induced by doping, and will allow the measured results to be compared to the DFT calculations

Acknowledgements

- This work was supported in part by the U.S. Department of Energy, Office of Science, Office of Workforce Development for Teachers and Scientists (WDTS) under the Science Undergraduate Laboratory Internship (SULI) program.
- I would like to thank Azure Avery, Jeff Blackburn, and Andrew Ferguson for guiding me through this project and always being available for advice. I would also like to thank Linda Lung, Marcus Giron, and Madison Martinez of the Education Staff for their support throughout the internship.