The Study of ZnSnN₂ for possible Thermoelectric and Photovoltaic Applications

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Abstract

In order to replace semiconductors that rely on rare Earth and costly elements, the search for analogous semiconductors formed by plentiful elements began. A recently developed material, ZnSnN₂, is the analog to In₁−ₓNₓ. In this project, the Seebeck and Hall effects are measured along with the electrical conductivity. The carrier concentration can then be determined from the Hall coefficient. Using the method of four coefficients and a general theory of these properties, the bounds on effective mass are determined corresponding to the different possible scattering parameters. The results show that samples with carrier concentrations around 6×10²¹ cm⁻³ exhibit properties consistent with the model, but not samples with a higher concentration of 1.02×10²² cm⁻³.

Background

Semiconductors are important in many electrical applications including almost all modern computers. A desired semiconductor is In₁−ₓNₓ due to its band gap energies. The increase in demand of indium has led to volatility in its price. Many semiconductors do not have the facilities in place to recycle the costly and rare elements. ZnSnN₂ is the direct analog to In₁−ₓNₓ. This can be easily seen by the position of the elements on the periodic table. Indium is sandwiched by zinc and tin. In essence, the group III element is replaced by II-V ones. ZnSnN₂ is thus the III-V analog to the III-V In₁−ₓNₓ. Zinc and tin are orders of magnitude more abundant, and recycling structures are already in place due to it only recently being synthesized, information on ZnSnN₂ is lacking. Basic electronic properties such as effective mass have yet to be explored in depth.

Sample Preparation

Three samples were provided by Dr. Steve Durbin at Western Michigan University. The samples displayed X-ray diffraction peaks consistent with the expected peaks of ZnSnN₂ and likely have wurtzite structure. ZnSnN₂ exhibits different structural phases and zinc and tin fluxes. These variations produce different purities, carrier concentrations, and different structural phases.

Experimental

The edges were sanded in order to prevent shorting to the backside. Copper wires connected to the sample with indium contacts were used for Hall measurements. The copper-constant thermocouples were used. The wires were sealed in order to prevent shorting to the backside. Lakeshore 370 AC Resistance Bridge and Lakeshore electromagnet operated from -0.7 to +0.7. Testa were used for Hall measurements. Hall and Seebeck measurements were taken at a variety of temperatures ranging from 7-300K using a closed cycle helium cooling system at a vacuum of 10⁻⁶ torr.

A photograph of sample C with thermocouples attached. The heater is seen on the left side.

Transport Properties

**Seebeck Effect**

- These measurements were not corrected for the possible Seebeck effects due to the wires connected to the sample
- A sign change was observed at low temperatures
- Taken with automated LabVIEW program

**Sheet Density and Mobility**

- Sheet density (which equals carrier concentration divided by thickness), and mobility remain relatively constant with temperature
- However, there is more of a temperature evolution for the sample with the higher carrier concentration

**Model Comparison**

- The material is modeled as having a parabolic band gap and a charge carrier scattering time dependent on Eᵣ, where E is the energy and r is the scattering

n(E, T) = 4π(2mₑf₄ eₐ₄ e₄ k₄ B₄ T)⁴/3

- Carrier Concentration mₑ = effective mass

- Temperature T

- Fermi Integral η = Fermi Energy

**Seebeck Coefficient**

r = scattering coefficient

S(r, η) = 10⁴kₑ² e⁴ε⁵

F(η, η) = ∫₀⁺∞ xⁿ⁺¹ exp(−x) dx

Different values of r correspond to different modes of scattering. r = 3/2 corresponds to ionized impurities, r = 0 to neutral impurities, and r = 0.5 to acoustic phonon scattering.

Using the integral form of these coefficients, a plot of Seebeck coefficient as a function of carrier concentration is generated which allows comparison between experimental data and the model.

**Summary**

- Transport measurements were performed on three samples of ZnSnN₂
- All three samples exhibited similar Seebeck coefficients despite one having significantly higher carrier concentration
- The sample with the higher carrier concentration does not fit the model, possibly indicating multiple bands

**Future Work**

- More analysis into why Sample C does not fit the model is needed
- Measuring more samples, particularly those with lower carrier concentrations would help fill in the graph of S vs r
- There are two different structures of this sample: wurtzite, and a more pure, structured orthorhombic structure
- These samples are suspected to be wurtzite, and thus they have more impurities. Studying the other type of ZnSnN₂ may show more promise as a replacement to ln₁−ₓNₓ

**References**


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