Macalester Journal of Physics and Astronomy

Volume 5
Issue 1 *Spring 2017*

Article 2

May 2017

Transient Photoconductivity of a Thermoelectric Nanomaterial PEDOT:PSS with TeCu nanowires

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Abstract

Thermoelectric materials are able to transfer heat energy into electrical energy. They have many important applications, and an increased understanding of them would allow the scientific community to develop more efficient thermoelectrics. We provide here transient photoconductivity measurements of a thermoelectric nanomaterial - PEDOT:PSS with TeCu nanowires on quartz substrate. Increased copper concentration in nanowires decreases photoconductivity in both transmission and reflectance measurements. Fermi blocking provides a reasonable explanation for this decrease in photoconductivity, which occurs when total nanowire mass approaches ~15% copper concentration.

Keywords

thermoelectric nanomaterial photoconductivity

Cover Page Footnote

We would like to thank Eddy Zaia at the Lawrence Berkeley Laboratory for providing us with these samples.

I. Introduction

Thermoelectric materials are able to convert heat energy into electrical energy through a process known as the Seebeck Effect. The maximum efficiency of a thermoelectric material is governed by the following equation

$$ZT = \frac{S^2 \sigma T}{\kappa}, \quad (1)$$

where ZT is the figure of merit, S is the Seebeck coefficient (a property intrinsic to the material), σ is the material's electrical conductivity, T is the temperature of the material, and κ is the material's thermal conductivity. As ZT approaches infinity, the efficiency of the thermoelectric material (or, in other terms, the heat engine) approaches Carnot efficiency, which is the maximum efficiency the thermoelectric can operate at without violating the second law of thermodynamics. Thus, a common technique for increasing the efficiency of thermoelectrics is to increase the electrical conductivity of the material while lowering its thermal conductivity.

The positive qualities of thermoelectric materials include lack of moving parts, simplicity of design and creation, and a robust nature (that is, they do not break down easily because they do not contain any moving parts). It is of great interest to scientists to develop thermoelectric materials with high efficiencies because they have numerous applications including but not limited to recycling heat waste energy in technological devices and increased fuel efficiency in automobiles. However, the current state of thermoelectrics is rather bleak, as thermoelectric engines remain too inefficient and too expensive to be worth developing for everyday use. This is why thermoelectrics are currently only being used in remote locations or space missions, where cost is a lesser concern.

Our research involved characterizing a specific thermoelectric nanomaterial using photoconductivity measurements. The materials we researched were PEDOT:PSS (an abbreviation for poly(3,4-ethylenedioxythiophene) polystyrene sulfonate) on quartz substratum embedded with tellurium nanowires doped with varying concentrations of copper. We received these samples from Eddy Zaia at the Lawrence Berkeley Laboratory. All research was performed at Macalester College.

Photoconductivity is increased electrical conductivity by the presence of light. In general, conductors (i.e. copper) have a large number of charge carriers available to them in the conduction band. However, semiconductors (i.e. tellurium and PEDOT:PSS) have a limited number of charge carriers available to them in the conduction band. In theory, incident photon energy on conductors and semiconductors will produce different effects: photoexcitation will vastly increase the number of charge carriers in semiconductors, while it will only minutely increase the amount of charge carriers in conductors. Thus, we would expect to see a larger jump in the photoconductivity of samples with little to no copper concentration and a smaller jump in the photoconductivity of samples with large concentrations of copper in the nanowires.

II. Methodology

In order to engage our samples in photoexcitation, we utilized the 5.1 MHz XL-500 Ti-S laser system at Macalester College, equipped with 50 fs laser pulses with an energy of 500 nJ per pulse. (See Figure 1 for a diagram of the laser system.) We performed photoconductivity measurements in two modes: transmission mode and reflectance mode. Transmission mode involved measuring the THz radiation transmitted through the sample, while reflectance mode involved measuring the THz radiation reflected by the sample at an incidence angle of 45° relative to the incoming THz radiation.

The laser system is responsible for subjecting our samples to photoexcitation via a pump beam incident on the sample. Then THz radiation, generated by a THz emitter, is focused on the sample. The change in the electric field of the THz radiation after contact with the sample is measured using a detector. This measurement allows us to calculate the change in the film's conductivity in transmission mode and reflectance mode, depending on the experimental setup. The electrical conductivity of the film is related to the transmission and reflectance of waves in the following equations:

$$\boxed{t = \frac{1}{1+\beta\sigma}} \quad , \qquad (2)$$

$$\beta = \mu_0 c/(1+n_s)$$

$$\boxed{r = -\frac{\gamma - \alpha}{\gamma + \alpha}} \quad , \qquad (3)$$

$$\gamma = n_s + \mu_0 c \cos(\theta_t)\sigma$$

$$\alpha = \cos(\theta_t)/\cos(\theta_i)$$

where t is transmission, μ_0 is the vacuum permittivity constant, c is the speed of light, n_s is the index of refraction of the substrate (which is 2.1 for quartz), r is reflectance, θ_i is the incidence angle of the electric field, and θ_t is the angle of the transmitted electric field (which is 0 degrees). According to these equations, increasing the conductivity of the sample results in decreased transmission and increased reflectance. Using THz conductivity measurements, sample film conductivity was also measured as a function of the THz frequency using the FEMTO Compact laser system at Macalester College.

III. Results and Discussion

Graphs 1 and 2 depict sample change in reflectance and transmission measurements as a function of THz delay, respectively. At some delay = 0fs, charge carriers are excited from the valence band into the conduction band, resulting in an increase in the reflectance of the sample and a decrease of the transmission for the same sample, following equations (2) and (3). Then, as time passes, these electrons fall back into the conduction band, and the sample's conductivity falls back to its value before photoexcitation.

By analyzing the peaks on these graphs (which depict the maximum change in reflectance and change in transmission), we can graph how the samples' copper concentration affect the photoconductivity of the samples. This relationship is depicted in Graph 3. An analysis of Graph 3 shows that as copper concentration increases, change in both the reflectance and transmission measurements decrease. These results mirror our predictions; samples with higher copper concentrations resulted in smaller changes in photoconductivity compared to those with little-to-no copper present. We considered two possible explanations for this data trend: sample measurement sensitivity and fermi blocking.

We can provide a theoretical, mathematical model of the expected trend in our data by considering the change in sensitivity for our signal measurements as a function of the sheet conductivity of our samples. If we assume our sample film is significantly thin by utilizing a thin film approximation, by considering the change in the sample's conductivity due to photoexcitation in the small signal limit, we can derive equations for the change in transmission and change in reflectance of the samples. This transforms equations (2) and (3) into the following equations:

$$\Delta t / t_0 = \frac{-\mu_0 c \sigma}{1 + n_s} \quad , \tag{4}$$

$$\Delta r / r_0 = \frac{2\alpha\sigma}{n_s^2 - \alpha^2} \mu_0 c(cos(\theta_t)) \quad , \tag{5}$$

where Δt is the change in transmission, t_0 is the transmission before photoexcitation, Δr is the change in reflectance, and r_0 is the reflectance before photoexcitation. We can then use equations (4) and (5) to develop sensitivity models describing the relationship between the change in the film's conductivity and the change in the signal produced by this conductivity change. These sensitivity equations are as follows:

$$\Delta T = \frac{\Delta t - t_0}{t_0} \frac{1}{\Delta\sigma_s} \quad , \tag{6}$$

$$\Delta R = \frac{\Delta r - r_0}{r_0} \frac{1}{\Delta\sigma_s} \quad , \tag{7}$$

where ΔT is transmission sensitivity, ΔR is reflectance sensitivity, and $\Delta\sigma_s$ is the change in the film's conductivity due to photoexcitation.

Using equations (6) and (7) we can produce a model for the sensitivity of transmission and reflectance measurements as a function of the change in the film's conductivity. This is depicted by Graph 4. The dashed lines represent the theoretical sensitivity model for transmission and reflectance measurements. As the sheet conductivity of the film increases, the model predicts that transmission and reflectance measurements decrease in sensitivity. In other words, while sheet conductivity remains very low, measurements are highly sensitive to small changes in the film's conductivity. However, as the conductivity of the film increases, measurements are only slightly sensitive to small changes in the film's conductivity.

Nevertheless the sensitivity model is not compatible with the transient photoconductivity measurements in both transmission mode and reflectance mode, as depicted by the dots depicted in Graph 4. These data points do not line up with the theoretical sensitivity model, so we have concluded that the sensitivity model alone is not complex enough to describe the behavior we are seeing in our samples. We cannot thereby conclude what relationship the change in transmission and reflectance has with the sheet conductivity of the material.

Instead, a more plausible explanation for the trend we see in Graph 3 is fermi blocking. Fermi blocking is a physical phenomenon which occurs when electrons in the conduction band block transitions from electrons in the valence band. When electrons make the transition from the valence band to the conduction band, the energy imparted to these particles is equal to the band gap energy. However, when electrons start filling up states in the conduction band, in order for electrons from the valence band to make the transition, additional energy is required. This is so because these electrons must transition to states with higher energies than the band gap energy, which have been filled up by already photoexcited electrons. Because the XL-500 laser system operates at a fixed energy, and imparts a fixed photon energy to electrons in the valence band, electrons already present in the conduction band block these transitions.

The energy required to make the transition from the valence band to the conduction band after electrons have filled up a significant number of states in the conduction band is given by

$$E = E_G + E_F \quad , \tag{8}$$

where E_G is the band gap energy for tellurium (approximately 0.35eV), and E_F is the fermi energy of the electrons in the conduction band given by

$$E_F = \frac{\hbar^2}{2m^*}(3\pi^2 n)^{2/3} \quad , \tag{9}$$

where $\hbar$ is the Planck constant divided by 2π, m^* is the effective electron mass, and n is the electron concentration required for fermi blocking.

If we assume E_F = 1eV, equation (9) can be rearranged to solve for n. Dividing the density of atoms in tellurium by this value of n yields an atomic electron concentration of ~15%. That is, when the nanowires are composed roughly of 15% copper of their total mass, fermi blocking should occur. This result is not unreasonable. So fermi blocking provides a better explanation for the trend we see in Graph 3 than our sensitivity model.

IV. Summary and Conclusions

In conclusion, thermoelectric materials are of great importance to physicists because of their practical applications in recycling heat waste energy and increased automobile efficiency. An increased understanding of thermoelectrics would allow us to create more efficient thermoelectric materials. Our research attempted to further characterize one specific type of thermoelectric nanomaterial, PEDOT:PSS embedded with tellurium-copper nanowires on quartz substrate, through photoconductivity measurements using an XL-500 Ti-S laser system.

Our hypothesis was that samples with little-to-no copper concentration should experience a larger jump in photoconductivity due to a significantly-increased number of charge carriers in the conduction band. Conversely, samples with high concentrations of copper should experience a smaller jump in photoconductivity. Our limited research confirmed the hypothesis, and an attempt was made to provide an explanation for the data trend in Graph 3.

Our theoretical model predicted that the sensitivity of our measurements should decrease as the sheet conductivity of our samples increased in the small signal limit. However, our data failed to match up with our predicted model in Graph 4, so we cannot definitely conclude what relationship sheet conductivity has with sensitivity in the small signal limit. Thus we formulated another explanation for the decreasing change in photoconductivity due to copper concentration: fermi blocking. A rough estimate predicts that fermi blocking should occur in our samples when approximately 15% of the nanowires are composed of copper. This explanation is much more reasonable.

In order to derive a larger understanding of PEDOT:PSS with tellurium-copper nanowires, more experimentation should be done. In the future we would like to perform the experiments again with a larger sample size and a greater range of copper concentrations. Additionally this experimentation would include Hall-effect measurements to determine DC conductivities as well as THz measurements to determine AC conductivities. PEDOT:PSS provides potential as a cheap, manufacturable thermoelectric for every-day use. More research is required to determine this potentiality, as thermoelectrics have the capacity to reduce fossil fuel emissions and increase efficiency in electrical devices.

Figures and Graphs

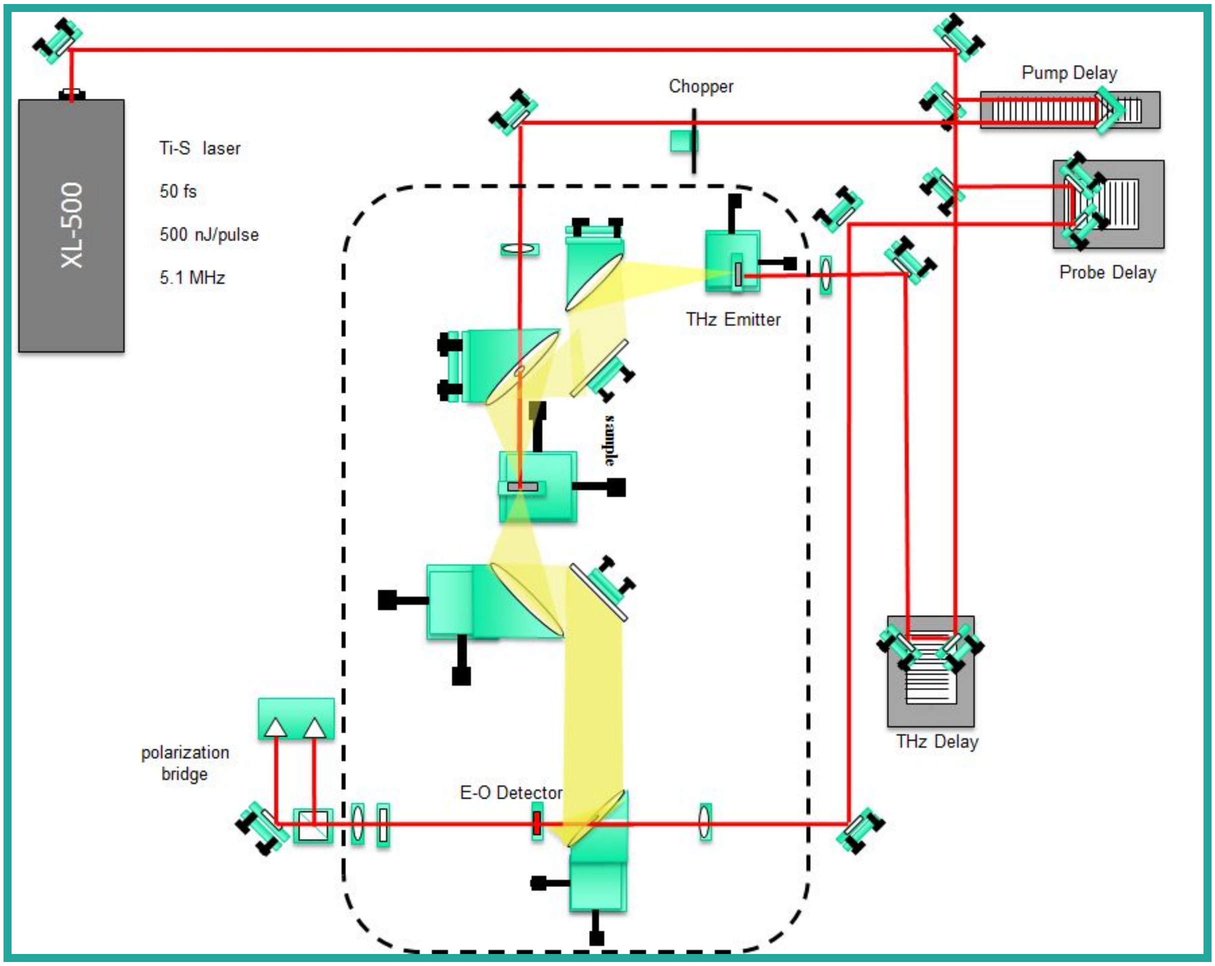
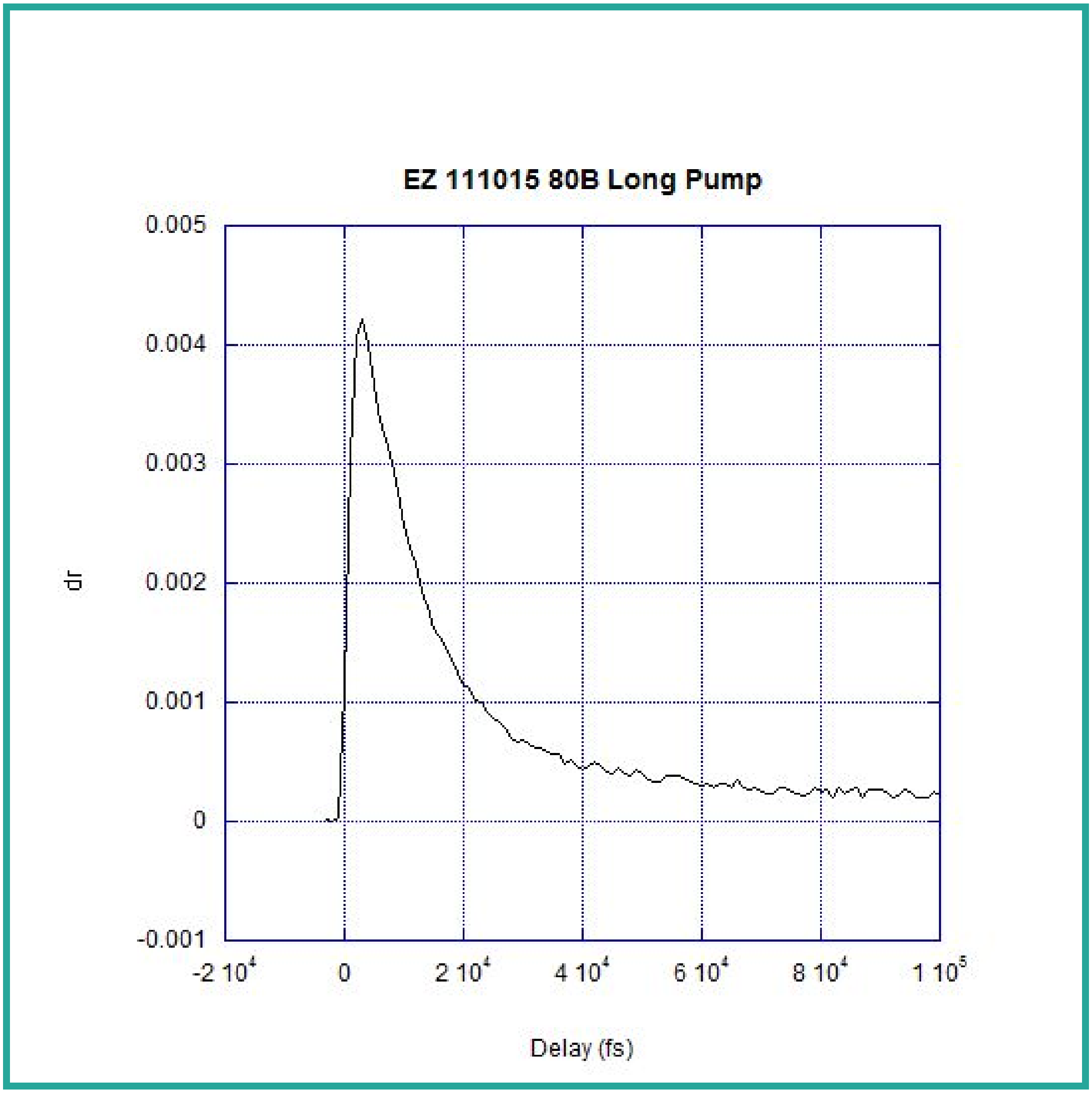
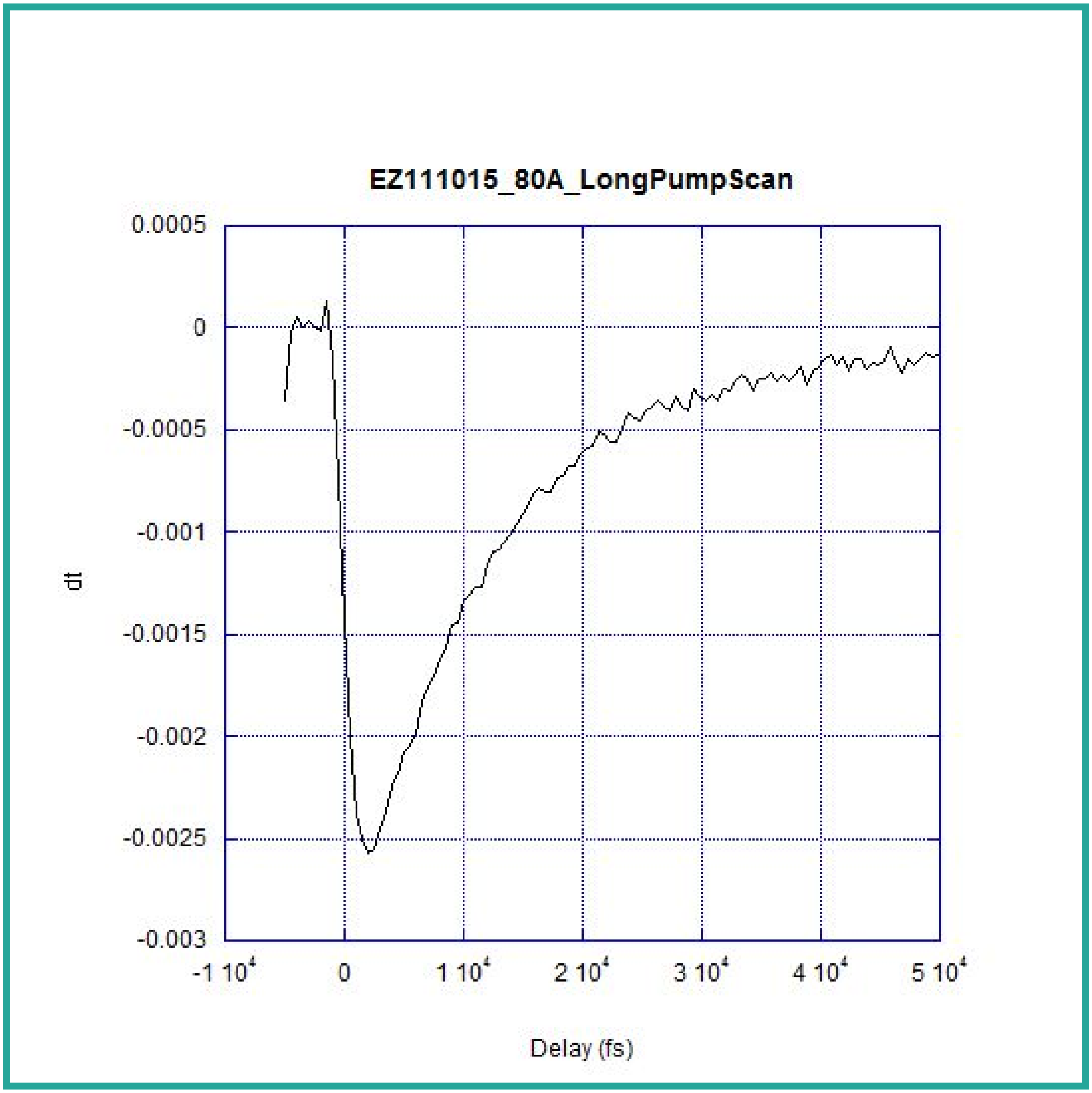


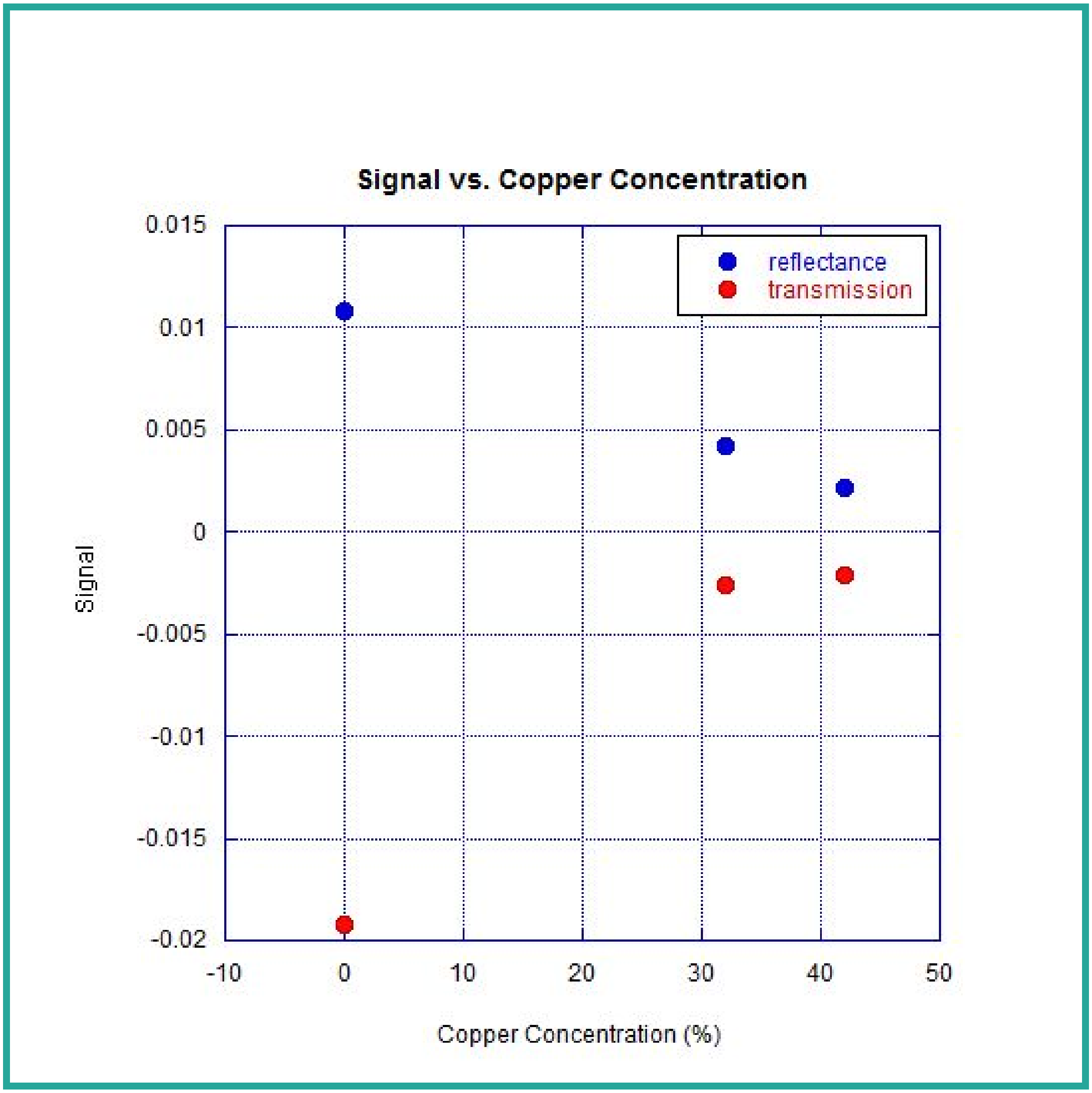
Figure 1. This figure depicts a diagram of the XL-500 Ti-S laser system present at Macalester College. The system is equipped with several mirrors, two beam splitters, pump, probe, and THz delays, a THz emitter, and an E-O detector used in reading out the electric field of the transmitted or reflected THz radiation. A sample is lowered into the laser system and subjected to photoexcitation by the pump beam. THz radiation is focused and transmitted or reflected by the sample, and this transmission or reflectance is measured and used to calculate the change in the film's conductivity.



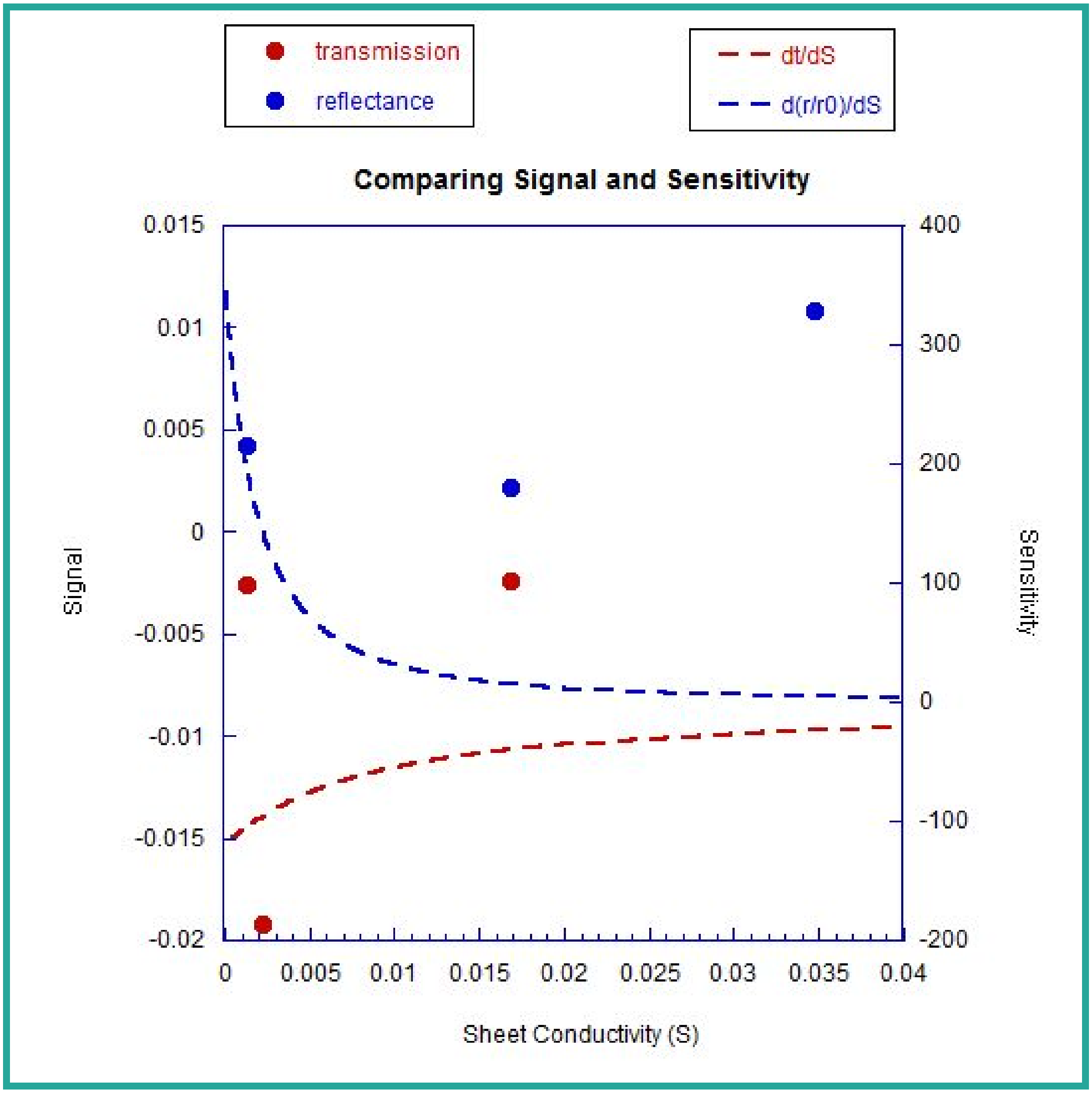
Graph 1. This graph depicts the relationship between change in reflectance (in volts) on the y-axis and THz delay (in femtoseconds) on the x-axis of sample 111015 80B. The graph depicts electrons being excited into the conduction band and falling back down into the valence band over time, causing the sample to become less reflective due to loss of charge carriers. The graph title is simply the name our lab imparted to the sample.



Graph 2. This graph depicts the relationship between change in transmission (in volts) on the y-axis and THz delay (in femtoseconds) on the x-axis of sample 111015 80A. The graph depicts electrons being excited into the conduction band and falling back down into the valence band over time, causing the sample to become more transmittable due to loss of charge carriers. The graph title is simply the name our lab imparted to the sample.



Graph 3. This graph depicts the relationships between the change in signal of the THz beam (in volts) on the y-axis and the copper concentration of the samples (in percent) on the x-axis being photoexcited. Reflectance measurements are depicted with blue dots, and transmission measurements are depicted with red dots. Both modes of measurement depict change in the signal approaching zero as the copper concentration of the nanowires increases.



Graph 4. This graph depicts one theoretical model for signal sensitivity on the y-axis shown in dashed lines and one data set for measurements concerning change in transmission and reflectance (in volts) versus sheet conductivity (in semens) on the x-axis. Reflectance is depicted with the color blue, and transmission is depicted with the color red. The data points do not line up with the sensitivity model, so this model is too simple to explain the trend in our data for change in signal versus copper concentration.