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Time-resolved THz Conductivity of an Intermediate Band Semiconductor

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Abstract

Intermediate band materials have promising applications as affordable, highly efficient solar materials. However, intermediate band solar cells exhibit low efficiency to date. Carrier recombination is a critical process that limits efficiency. If electrons relax to the valence band before they can be collected, their energy is lost. To help understand the recombination dynamics and physical properties of intermediate band semiconductors, we obtain time-resolved THz conductivity measurements of the intermediate band semiconductor, GaPAsN, at various temperatures. From our results, we build a model that provides insight to the recombination dynamics of GaPAsN.

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1. Introduction

As evidence supporting the negative effects of global climate change continues to grow, the use of renewable energy sources becomes increasingly vital. Solar cells allow us to harvest energy from one of the most powerful sources of renewable energy: sunlight. In standard solar cells, one side of the cell is made of a p-type semiconductor that has a low concentration of electrons and the other side is an n-type material with a high electron concentration. The boundary between these two regions of the solar cell is known as the p-n junction. When sunlight hits the solar cell, electrons move from the n-type to the p-type region. Conventional single junction photovoltaic cells have a well-known efficiency limit of only 41%, a limit established in 1961 by Shockley and Queisser [1]. One way to increase this efficiency is to create solar cells using intermediate band semiconductors. Previous studies have shown that intermediate band solar cells have a theoretical efficiency limit of 63% [2]. However, intermediate band solar cells exhibit very low efficiency to date, achieving an efficiency in labs of only 2.9% [3]. Carrier recombination is a critical process that limits solar cell efficiency; if electrons relax to valence band before they can be collected, their energy is lost. Thus, to create efficient intermediate band solar cells, we must fully understand the recombination dynamics of intermediate band materials.

In this study, we investigate the recombination mechanism of $GaP_{0.49}As_{0.474}N_{0.036}$, a previously studied intermediate band semiconductor shown to have nearly optimum band structure for producing solar energy [4,5]. We examine carrier lifetimes (the length of time electrons remain in the conduction band) and recombination dynamics at various temperatures ranging from 77K-300K by optically measuring time-resolved THz conductivity. From our experimental data, we build a model that accurately describes (both qualitatively and quantitatively) the temperature-dependent recombination mechanism of GaPAsN. We show that

there are two temperature-dependent processes that occur during carrier recombination: trap-assisted bimolecular recombination and electron localization. Our model provides insight to the carrier recombination process of an intermediate band material.

2. Methodology

Time-resolved THz conductivity of $GaP_{0.49}As_{0.474}N_{0.036}$ (sample S376B) is measured optically with a laser system (Figure 1) based on a Ti:Sapphire High Power Oscillator (FemtoLasers XL-500). A 50-femtosecond laser pulse with a wavelength of either 800nm or 400nm excites electrons to the intermediate band, increasing the conductivity of the sample. A delayed pulse of THz radiation then probes the sample and the amount of radiation that is transmitted through the sample is measured. The precise timing that the THz radiation probes the sample is controlled by adjusting the mirrors along the THz delay stage. Moving these mirrors 0.3mm backwards along the stage creates a longer beam path, resulting in a 1.0ps delay in the time at which the THz radiation probes the sample. The change in transmission due to the excitement of electrons in the material is measured as a function of the delay between when the laser pulse excites the sample and when the THz radiation probes the sample. The change in transmission is directly related to the change in the material's conductivity by equation 1 below:

$$\Delta\sigma = -\frac{1}{\alpha}\Delta t, \quad\quad\quad (1)$$

where σ is the conductivity, α is a constant, and t is transmission. Since we are only interested in relative values to investigate behavior, we negate our transmission measurements and normalize them to a maximum value of 1, resulting in conductivity measurements for our sample. An optical cryostat pumped with liquid nitrogen is used to access sample temperatures between

77K-300K. Thus, our system allows us to obtain time-resolved optical THz conductivity measurements of our sample at controlled temperatures ranging from 77K-300K.

3. Results & Discussion

3.1 Temperature Dependence

Figure 2 shows the change in conductivity of GaPAsN as a function of time at temperatures of 77K and 300K. Our results show that the recombination dynamics of this intermediate band semiconductor is temperature dependent. While both temperatures display a rapid initial decay in conductivity at short delay times, at long delay times conductivity decreases much faster at high temperature. In other words, GaPAsN has a much longer carrier lifetime at low temperature.

3.2 Qualitative Model

To explain the temperature dependent recombination mechanism, we built an original model (Figure 3). Fluctuations in the energy level of the intermediate band are due to fluctuations in the nitrogen concentration across our sample. These nitrogen inconsistencies exist because when nitrogen is deposited onto the sample, there is no process that controls how the atoms distribute across the sample. Thus, there exist shallow wells in the intermediate band.

When photons hit the sample, they increase the energy of the electrons in the valence band, exciting them into the intermediate band and leaving electron holes behind in the valence band. Due to the high recombination rate, we conclude that deep traps between the intermediate band and valence band serve as recombination centers for free electrons in the intermediate band and free holes in the valence band.

At high temperature, after electrons are excited into the intermediate band, they remain free to move around. The deep traps first attract the free holes in the valence band and then the free electrons from the intermediate band. The electrons and holes recombine and then relax back down to the valence band. The rate of recombination is dependent on the number of free electrons and free holes. This process is displayed in Figure 4.

At low temperature, after electrons are excited into the intermediate band they are quickly localized in shallow wells in the intermediate band (Figure 5). Once electrons are localized they are no longer free to move and no longer contribute to the material's conductivity. They are physically separated from the recombination centers, and recombine with free holes at a very slow rate. The holes in the valence band remain free and thus contribute to the material's conductivity.

3.3 Quantitative Model

From our qualitative model, we built a mathematical model to quantitatively show the temperature dependent recombination process that we suggest occurs. This model incorporates three processes: free electrons recombine with free holes at a high rate, free electrons become localized in the intermediate band, and localized electrons recombine with free holes at a low rate. Thus, we model the conductivity with respect to time as follows:

$$\sigma(t) = \frac{1}{1+a}[n_F(t) + aP(t)], \tag{2}$$

where a is a constant equal to the effective mass of a hole divided the effective mass of an electron, $n_F(t)$ is the number of free electrons at time t, and $P(t)$ is the number of free holes at time t. To mathematically define $n_F(t)$ and $P(t)$, we must first define the rate at which free electrons recombine with free holes:

$$R_1 = r_1 n_F P, \tag{3}$$

as well as the rate at which localized electrons recombine with free holes:

$$R_2 = r_2(P - n_F), \tag{4}$$

where both r_1 and r_2 are constants. We can also model the number of free electrons at equilibrium as follows:

$$n_F^{eq} = {}^P\!\!/_{(g * e^{\varepsilon T} + 1)}, \tag{5}$$

where g is the volume fraction of localized electrons divided by the volume fraction of non-localized electrons, ε is a constant representing the characteristic trap depth divided by the Boltzmann constant, and T is the temperature. Now we can model change in number of free electrons as:

$$\dot{n_F} = -\left[R_1 + r_3\left(n_F - n_F^{eq}\right)\right], \tag{6}$$

where r_3 is the rate at which the free electron population approaches equilibrium. From this, we can then calculate $n_F(t)$ with the initial condition $n_F(0) = 1$:

$$n_F(t + dt) = n_F(t) + \dot{n_F} dt. \tag{7}$$

Similarly, we can model the number of free holes by first defining the change in free holes as:

$$\dot{P} = -[R_1 + R_2] \tag{8}$$

and thus,

$$P(t + dt) = P(t) + \dot{P} dt \tag{9}$$

with the initial condition $P(0) = 1$. Inserting the results from equations 7 and 9 into equation 2 gives us a quantitative model for conductivity as a function of time, based on temperature and six free parameters ($r_1, r_2, r_3, a, \varepsilon, g$).

3.4 Model Accuracy

The quantitative juxtaposition between our model and our experimental data is displayed in Figure 6 and Figure 7. In both the high and low temperature limits, we see that the model predicts the change in conductivity as a function of time accurately. While our model is not perfect, it does a very good job predicting the general behavior. The free parameters used to find the theoretical values were estimated and adjusted manually per the "eye test," so it is almost certain that these values are not fully optimized. This imperfect method of choosing free parameters may account for some discrepancies between our experimental data and model. While the model may not be perfect, it accurately describes the general temperature dependence of conductivity as a function of time.

Our model shows that at room temperature localization does not occur-- trap-assisted bimolecular recombination is the dominant process. We can model this process in a much simpler manner displayed below, knowing conductivity is solely related to the number of free electrons:

$$\Delta\sigma = \frac{dn_F}{dt} = -rn_F P = -rn_F{}^2 \tag{10}$$

which can be rewritten as

$$\frac{\sigma}{\sigma_0} = \frac{1}{1+\sigma_0 rt} \tag{11}$$

where the initial conductivity σ_0 is equal to 1. We fit equation 11 to our experimental data and find the value r to be 2.7×10^{-8} cm^3/s. This value agrees with previous research conducted in which r was determined to be 2.3×10^{-8} cm^3/s based on transient-absorption measurements taken of GaPAsN using a different system [4].

4. Summary & Conclusions

Our measurements clearly display a recombination mechanism that is temperature dependent in GaPAsN. At high temperature, this material has a short carrier lifetime, limiting the efficiency of intermediate band solar cells made from this material. However, it has been previously shown that carrier lifetime can be elongated and the efficiency of intermediate band solar cells can be significantly improved by optimizing the material synthesis and device structure [6-8]. Compared to high temperature, GaPAsN has a significantly longer carrier lifetime at low temperature.

From these measurements, we built a model that provides a plausible explanation for this temperature dependence. The model shows that free electrons and free holes contribute to conductivity, and electron occupation of shallow wells is determined by temperature. At high temperature, trap-assisted bimolecular recombination is the dominant process in conductivity as a function of time. At low temperature, electron localization in wells is the dominant process. We do not have concrete evidence that our model is correct, but the qualitative and quantitative evidence supporting it leads us to believe that our model is very plausible. Furthermore, our model agrees with previous studies done on GaPAsN at room temperature.

Further analysis of the recombination and further experimentation must be done before we can conduct a deeper evaluation of the accuracy of our model. Further analysis can be done on intermediate temperatures to provide better insight as to the precise temperature dependence of electron localization and bimolecular recombination. Additionally, the six free parameters of the quantitative model could be optimized further, providing a more accurate estimation of the change conductivity as a function of the delay between the laser pulse exciting the sample and THz radiation probing the sample.

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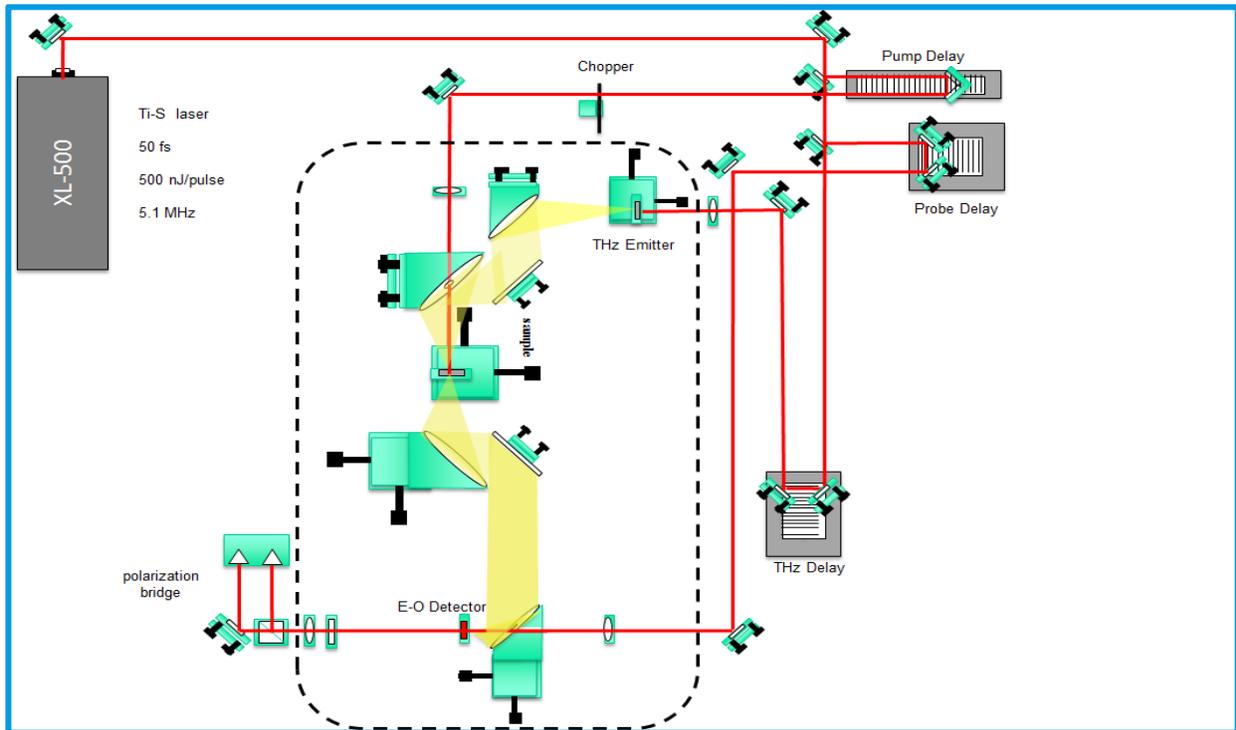
Figures

Figure 1. Laser system based on a Ti:Sapphire High Power Oscillator (Femtolasers XL-500). 50fs laser pulse of either 800nm or 400nm is split into three beams. Alternate pulses of one beam are chopped before exciting sample. Another beam travels through THz emitter, after which it probes the sample as THz radiation. Third beam assists in measuring THz transmission through the sample. System measures time-resolved optical THz conductivity of sample.
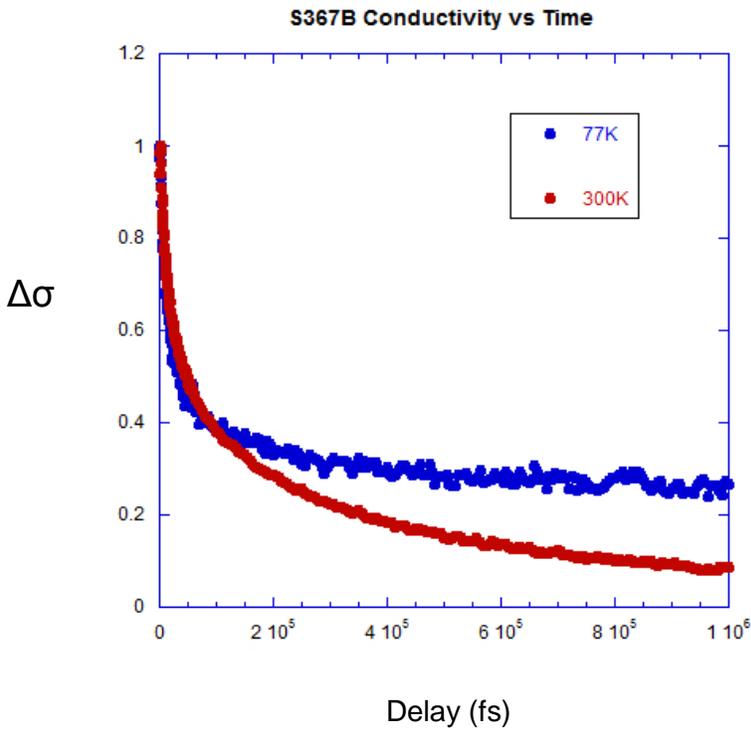
Figure 2. Graph of change in conductivity in $GaP_{0.49}As_{0.474}N_{0.036}$ as a function of the delay between laser pulse exciting sample and THz radiation probing sample. Red line represents data collected at 300K, blue line represents data collected at 77K. Conductivity was normalized to a maximum value of 1, and shifted such that the maximum occurs along the vertical axis. Carrier lifetime at low temperature is longer than at high temperature.
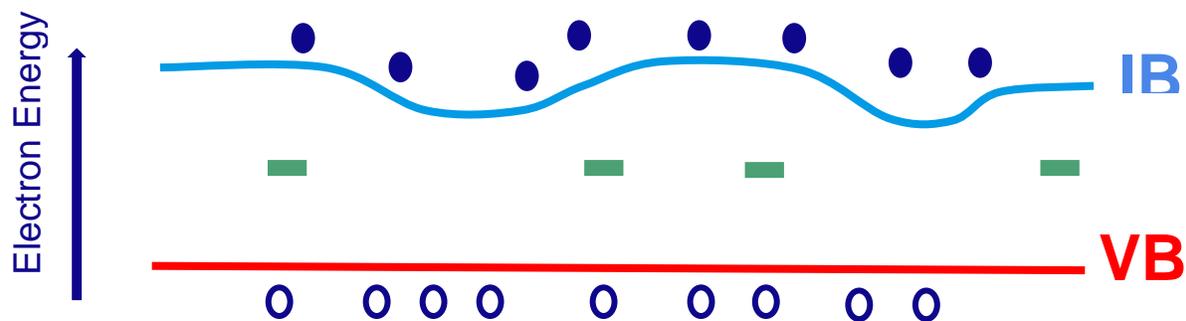
Figure 3. Energy band model of our sample after electrons are excited into the intermediate band, leaving behind holes in the valence band. Fluctuations in intermediate band energy level due to fluctuations in nitrogen concentration across sample. Deep traps exist in between intermediate band and valence band.
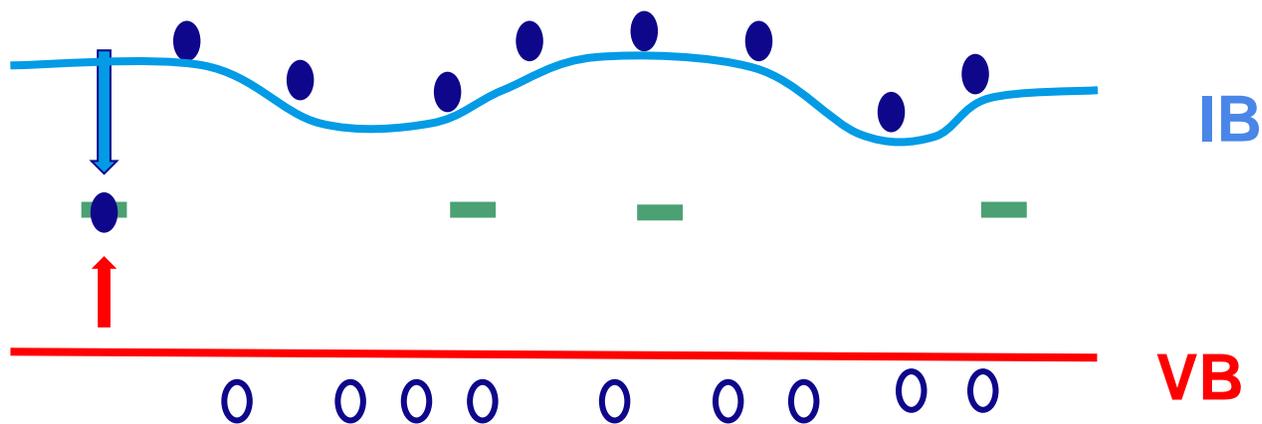

Figure 4. Bimolecular recombination at high temperature. Both electrons in the intermediate band and holes in the valence band are free. Electrons recombine with holes at high rate in recombination centers (traps), then relax back down to the valence band.
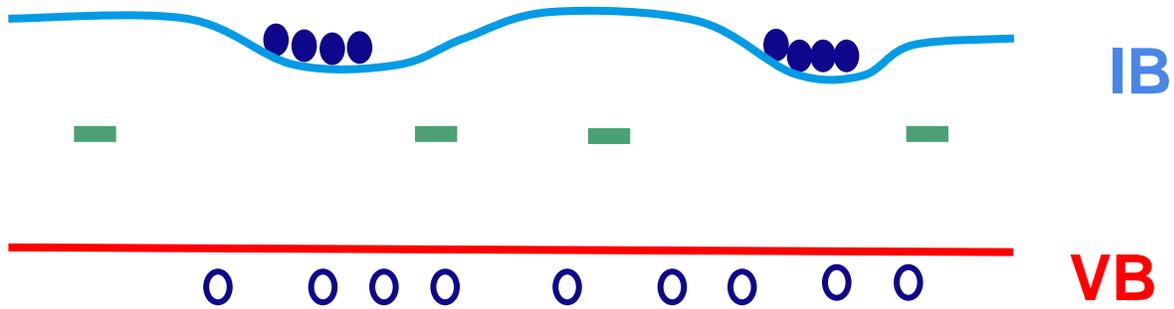
Figure 5. Electron localization at low temperature. Holes in valence band are free, electrons in intermediate band are stuck in shallow wells, unable to move freely. Localized electrons may be physically separated from recombination centers, resulting in recombination occurring at a slow rate.
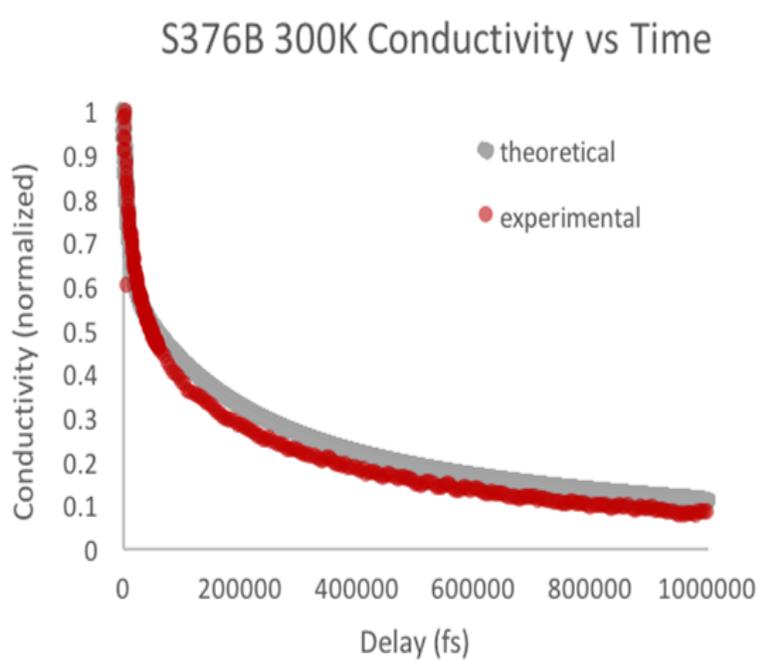

Figure 6. Graph of change in conductivity in $GaP_{0.49}As_{0.474}N_{0.036}$ as a function of the delay between laser pulse exciting sample and THz radiation probing sample at 300K. The red line shows experimental data and the gray line shows theoretical values predicting by mathematical model. The values of free parameters are $r_1 = 1.2 \times 10^{-5}$, $r_2 = 1 \times 10^{-8}$, $r_3 = 1 \times 10^{-4}$, $a = 0.8$, $\varepsilon = 200$ K, $g = 0.7$.
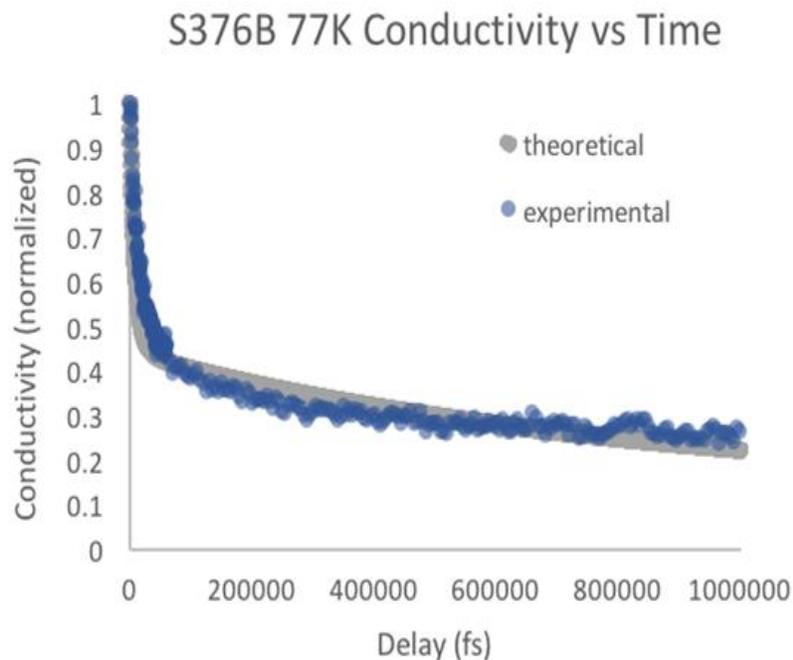
Figure 7. Graph of change in conductivity in $GaP_{0.49}As_{0.474}N_{0.036}$ as a function of the delay between laser pulse exciting sample and THz radiation probing sample at 77K. The blue line shows experimental data and the gray line shows theoretical values predicting by mathematical model. The values of free parameters are $r_1 = 1.2 \times 10^{-5}$, $r_2 = 1 \times 10^{-8}$, $r_3 = 1 \times 10^{-4}$, $a = 0.8$, $\varepsilon = 200$ K, $g = 0.7$.