Carrier Lifetime and Carrier Mobility of GaAsN with Changing Nitrogen Concentration

Sun Gyu Park
Macalester College, spark2@macalester.edu

MACALESTER COLLEGE

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Abstract

In this work, we conducted Ultrafast Conductivity Measurements, using THz Spectroscopy to characterize the carrier mobility and the carrier lifetime of gallium arsenide nitride (GaAsN) thin films with a range of Nitrogen concentrations. The photoexcitation of semiconductor samples excites free charges by promoting electrons from the valence band to the conduction band. We then measure the change in conductivity by measuring the transmission of a THz electromagnetic pulse after photoexcitation and comparing with the signal that was measured without photoexcitation. The values of transmission are then converted into conductivity, from which we derive the carrier concentration and scattering time of the electrons. We found that the GaAsN samples we have investigated had carrier mobilities comparable to pure GaAs under photoexcitation by 400-nm and 800-nm photons. We suspect that these results are biased by photoelectrons being generated in the GaAs substrates.

Keywords

gallium arsenide nitride, ultrafast conductivity measurements, Time-Resolved THz spectroscopy, carrier mobility, carrier lifetime

Cover Page Footnote

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Sun Gyu Park

Department of Physics and Astronomy,

Macalester College, Saint Paul, MN 55105

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In this work, we conducted Ultrafast Conductivity Measurements, using THz Spectroscopy to characterize the carrier mobility and the carrier lifetime of gallium arsenide nitride (GaAsN) thin films with a range of Nitrogen concentrations. The photoexcitation of semiconductor samples excites free charges by promoting electrons from the valence band to the conduction band. We then measure the change in conductivity by measuring the transmission of a THz electromagnetic pulse after photoexcitation and comparing with the signal that was measured without photoexcitation. The values of transmission are then converted into conductivity, from which we derive the carrier concentration and scattering time of the electrons. We found that the GaAsN samples we have investigated had carrier mobilities comparable to pure GaAs under photoexcitation by 400-nm and 800-nm photons. We suspect that these results are biased by photoelectrons being generated in the GaAs substrates.

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I. Introduction

Photovoltaic cells are composed of semiconductors. The semiconductors have a band-gap between occupied and unoccupied electron states so that when the materials are struck by photons from the Sun, the valence electrons inside the materials move to the conduction band, creating a free electron and a free "hole." Photons that have lower energy than the band-gap of the material are transmitted through, while the parts of the spectrum equal or greater than the band-gap are absorbed. In a solar cell, light absorption occurs at a PN junction. The net effect is to pump electrons from the valence band in the P-region to the conduction band of the N-region, producing an electric current at a voltage determined by the band-gap. If the cell absorbs photons of energy greater than the band-gap, the extra energy is released as heat, decreasing the total energy that could be gained by the electrons.

Many new materials have been found that produce more efficient solar cells with one type of material which is known as single-junction solar cells. The most common material used to produce these solar cells was silicon with a band-gap of approximately 1.1eV. Photons with energy that are less than 1.1eV will not be absorbed, whereas all levels greater or equal to 1.1eV will be absorbed but excess energy will be released as heat. The Shockley-Queisser Efficiency Limit indicates that the maximum efficiency in capturing the solar spectrum is 41 % at maximum for any possible single-junction solar cell [1]. Multi-junction solar cells have been developed to resolve the problem of energy loss and to expand the absorption spectrum of a solar cell. An example of a multi-junction cell is a combination of gallium indium phosphide (GaInP) with a band-gap of 1.9eV, gallium arsenide (GaAs) with 1.4eV, and germanium (Ge) with 0.7eV in order. Photons would hit the material with the largest band-gap, GaInP, first. All photons with energy 1.9eV or above will be absorbed, while any with lower energy will pass through. The remaining energy levels of the photons will move to GaAs and lastly, Ge. The multi-junction solar cells can reach higher efficiencies than single junction cells. The Shockley-Queisser Efficiency Limit for a triple junction cell is 61% [1]. According the Best Research-Cell Efficiency Chart by National Renewable Energy Laboratory, the most efficient actual multi-junction cell to date has an efficiency of

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46%, much larger than the most efficient silicon single junction (around 25%) [2]. Unfortunately, multi-junction solar cells are very costly. This work is part of a research effort to characterize materials that might minimize the cost of the production of multi-junction solar cells.

In a multi-junction solar cell, a sub-cell with a bandgap of around 1eV is required to improve the efficiency [3]. The III-V Nitrides have been gaining interest to be those sub-cells. These dilute III-V Nitrides have a special property of decreasing bandgap with additional Nitrogen [4].

Gallium arsenide nitride (GaAs$_{1-x}$N$_x$ or GaAsN), a III-V Nitride, is a material receiving interest as a sub-cell in the multi-junction solar cell (x is the fraction of nitrogen concentration). As a dilute III-V Nitride, GaAsN has a property of decreasing band-gap in respect to increasing concentration of the nitrogen according to Figure 1[5]. The goal of our project was to characterize carrier lifetime and carrier mobility of GaAsN, important parameters for solar energy applications. While the carrier lifetime is normally defined as the time over which the electron in the conduction band recombines with the hole in the valence band of the material, we measured the free carrier lifetime, which is the time constant for the decay of photoconductivity in our thin-film GaAsN on GaAs substrate, whether it be by carrier trapping at defects or by recombination. In a solar cell, the photoexcited electrons must be extracted from the device in a shorter time than the carrier lifetime. The carrier mobility (μ) determines how fast the charges are carried by an electric field. The mobility is determined by the carrier scattering time.

$$\mu = \frac{e\tau}{m^*} \tag{1}$$

where e is the charge of electron, $m*$ is the effective mass of the bulk GaAs electron ($0.067m_e$)[6] and τ is the scattering time. The relation between the scattering time and the mobility is based on the Drude Model of conduction, where we assume that the electrons in the conduction band randomly scatter and the average time between scattering events is the scattering time. The free carrier lifetime and the mobility determine the diffusion length, which is the average distance photoelectrons can travel before recombining with holes or being trapped. Efficient solar cells require diffusion lengths which are much larger than the thickness of the cell.

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II. Experimental Setup

Samples for this study were provided by Dr. Kristin Alberi at the National Renewable Energy Laboratory in Colorado. These consisted of 100nm-300nm thick films of GaAsN grown on GaAs substrates by Molecular Beam Epitaxy. The samples had nitrogen concentration in the range of 0.1%<[N]≤ 2.3%. Because GaAsN was deposited on GaAs substrates, it was important to be able to distinguish between the characteristics of the two materials in the measurement. We sought to do this by photoexciting our samples with 400nm wavelength radiation. At this wavelength, the optical absorption depth was predicted to be less than 20nm, meaning that all the radiation would be absorbed in the GaAsN layers, and the response we observed would be characteristic of GaAsN alone.

The general experimental setup is illustrated in Figure 2. A Titanium-sapphire (Ti-S) laser laser produces 50 femtosecond laser pulses at a wavelength of 800nm and pulse energy of 0.5 microJ/pulse. The laser pulses go through the beam splitter at first where the beam is split into a pump beam which is used to photoexcite the sample and a probe beam which is used for THz spectroscopy. The experiment was conducted with 800-nm photoexcitation. Later, a BBO crystal was used as the medium for Second-Harmonic Generation to generate 400-nm photons from the 800-nm source. To prevent any 800-nm photons from passing, we placed a filter between the BBO crystal and the container that only allowed 400-nm photons to pass. We expected the 400-nm photons to be strongly absorbed by the epilayer, GaAsN, allowing us to isolate the GaAs from photoexcitation.

The probe beam was further divided into a THz excitation beam and a THz probe beam. The THz excitation beam drives a biased semiconductor. The laser excites and accelerates charge carriers in the semiconductor, leading to a THz pulse. The THz pulses are focused onto the sample and then refocused onto a THz electro-optic detector. In the detector, the electric field of the THz pulse changes the polarization of the THz probe beam via the electro-optic effect in a non-linear crystal. Measuring the signal as a function of the delay between the THz pulse and the THz probe beam pulse allows us to map the electric field of the pulse as a function of time. The measured pulse waveform undergoes Fourier

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Transform to be displayed in the frequency domain. The goal of the setup was to measure the transmission of the THz pulse signal through the sample after a certain period during the photoexcitation. We then compared the THz transmission with photoexcitation to the THz transmission when the samples were not excited. Note that the energy of the THz pulse ranges from 0.004eV to 0.04eV, which is much smaller than the band-gaps of our samples in nitrogen concentration from 0.1 %< [N] ≤ 2.3 % according to Figure 1, so free carriers are only excited by the pump pulse. Transmission of THz can then be converted to conductivity with the given relationship (2).

$$t \approx 1\text{-}\alpha\sigma \tag{2}$$

where t is the transmission, σ is the conductivity, and α is the absorption coefficient of the sample. We measured the photo-induced conductivity as a function of the delay between the pump pulse and the THz pulse. The time for the photoconductivity to decay by a factor of exponential e was what we considered as the carrier lifetime.

III. Analysis

The attained transmissions of the THz pulses were then converted to conductivity as the following equation:

$$\sigma = \frac{\sigma_0}{1+i\omega\tau} \tag{3}$$

where σ_0 is the DC conductivity of sample, ω is the frequency and τ is the carrier scattering time. In this treatment the conductivity is a complex quantity. The real part of the conductivity is associated with the resistance of the sample and the imaginary part is associated with the reactance. The real and the imaginary conductivity curves were fit to the AC Drude Model with σ_0 and τ as adjustable parameters. The scattering time found in (3) was then applied to (1) to compute the carrier mobility of the sample after photoexcitation.

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The fit in Figure 3 is a fit for the AC Drude Model through the conductivity values for the GaAsN sample with 1.3% nitrogen concentration. We only considered the THz domain, as there was no signal outside of the THz domain in our experimental setup. The blue points are the real part from (3) and the black points represent the imaginary part from (3). To get the best fit, we adjusted the DC conductivity and carrier scattering time. The set of values for DC conductivity and carrier scattering time that make the best fit is what we considered as the output.

IV. Results and Discussion

The results for GaAsN-GaAs using 800nm in photoexcitation showed responses very similar to GaAs. The carrier lifetimes were also all longer than 1ns (1000 ps) The pump delays were commonly measured until approximately 1200 ps. The carrier mobilities were all approaching 5000 cm^2/(V·s) at greater delays, a value of carrier mobility that is suspected to resemble more of GaAs than GaAsN because it is much greater than 1000 cm^2/(V·s)[6]. We predicted that responses by GaAs would be dominant because of the penetration depth. The penetration depth, which is the distance that the intensity of light falls by one factor of exponential e), is approximately 500nm for 800-nm radiation but the epilayers were 100nm-400nm thick. So, it makes sense that the GaAs is dominant in the results for 800-nm photoexcitation. With 400-nm radiation, our expectation was that the penetration depth was approximately 20nm, which is significantly smaller than the range of given thickness of GaAsN epilayers, and isolate the GaAs from GaAsN.

Unlike how the carrier lifetimes under 800-nm photoexcitation were in order of hundred picoseconds, the samples under photoexcitation with 400-nm radiation can be measured in the order of ten picoseconds as seen in Figure 4. According to Figure 4, the photoconductivity of GaAsN samples drops at a greater rate than it does with GaAs with 400-nm photoexcitation in the beginning. After the drop, the photoconductivity of each sample starts to decay in a similar manner as GaAs. With longer pump delay, we are given more characteristics of GaAs over GaAsN. Then the times that have

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conductivity decay to 30% of the maximum for each sample is given at Figure 5. Note that there is no explicit pattern that could be observed to describe the change of conductivity in respect to nitrogen concentration. The results suggested that the results might be biased by the photoexcitation of GaAs substrate.

Moving to carrier mobility, Figure 6 is a plot of carrier mobility in respect to nitrogen concentration after 10 ps of 400-nm photoexcitation. We do see an increase in carrier mobility from samples above 0.5% but starts decreasing near 1.3% without a noticeable pattern. Then let us look at Figure 7 closely with the sample with nitrogen concentration 1.3%. We can see that the carrier mobility computed in 400-nm falls closely in the trend of the carrier mobility of 800-nm photoexcitation for this sample, another indication for a possible bias from the GaAs substrate.

D.G. Cooke performed similar experiments on GaAs and GaAsN samples. According Table 1, his experiment measured a carrier mobility to be 920 ± 80 cm^2/(V·s) for GaAsN ([N]=0.84%) and 3300 ± 100 cm^2/(V·s) for GaAs [6]. While our results are also in this range, many of our measured mobilities of GaAsN were larger and fell in the range between 1000-3000cm^2/(V·s). We believe that we have essentially measured the characteristics of GaAs substrate, as if there was an absence of the GaAsN epilayer. Since we used similar techniques as Cooke, our result also casts doubt on the validity of those measurements. For future work, the experiment should be further adjusted that the energy of photons used to excite GaAsN should be greater than the band-gap of GaAsN, but smaller than the band-gap of the GaAs to ensure isolation of the epilayer.

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References

[1]   J. N. Heyman, A. M. Schwartzberg, K. M. Yu, A. V. Luce, O. D. Dubon, Y. J. Kuang, C. W. Tu, and W. Walukiewicz. "Carrier Lifetimes in a III−V−N Intermediate-Band Semiconductor." *Physical Review Applied*, 7(1), 2017.

[2]   NREL. Best Research-Cell Efficiency Chart. *National Renewable Energy Laboratory (NREL).* https://www.nrel.gov/pv/cell-efficiency.html, 2021.

[3]   F. Suarez, T. Liu, A. Sukiasyan, J. Lang, E. Pickett, E. Lucow, T. Bilir, S. Chary, R. Roucka, I. Aeby, L. Zhang, and S. Siala."Advances in Dilute Nitride Multi-Junction Solar Cells for Space Power Applications." *E3S Web of Conferences*, 16, 03006, 2017. (Suarez, et al, 2016)

[4]   Hans Christian Alt, Yuri Gomeniuk, Gerhard Ebbinghaus, Arun Ramakrishnan, and Henning Riechert. "Quantitative spectroscopy of substitutional nitrogen in $GaAs_{1-x}N_x$ epitaxial layers by local vibrational mode absorption," *Semiconductor Science and Technology*, 18(4): 303-306, 2003.

[5]   J. Wu, W. Shan, and W. Walukiewicz. "Band anticrossing in highly mismatched III-V semiconductor alloys," *Semiconductor Science and Technology*, 17(8): 860–869, 2002.

[6]   D. G. Cooke, F. A. Hegmann, E. C. Young, and T. Tiedje. "Electron mobility in dilute GaAs bismide and nitride alloys measured by time-resolved terahertz spectroscopy," *Applied Physics Letters*, 89(12), 122103, 2006.
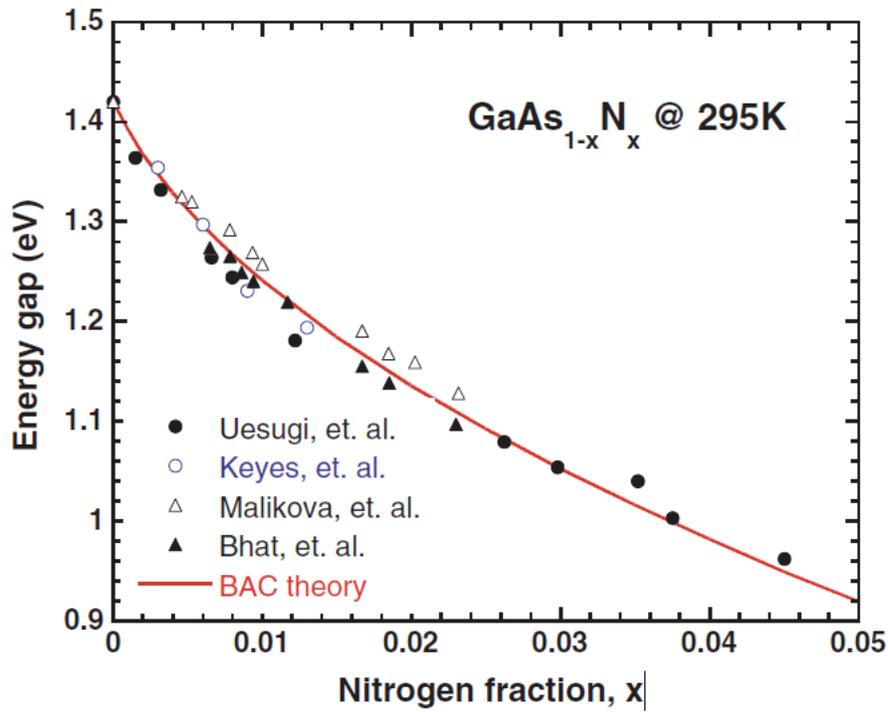
V. Figures and Tables

Figure 1. This is the relationship of the bandgap of GaAsN in respect to changing nitrogen concentration. Note that the band-gap decreases as the concentration increases. Adapted from *Band anticrossing in highly mismatched III-V semiconductor alloys* by Wu, et. al., 2002, p. 863 Figure 2.
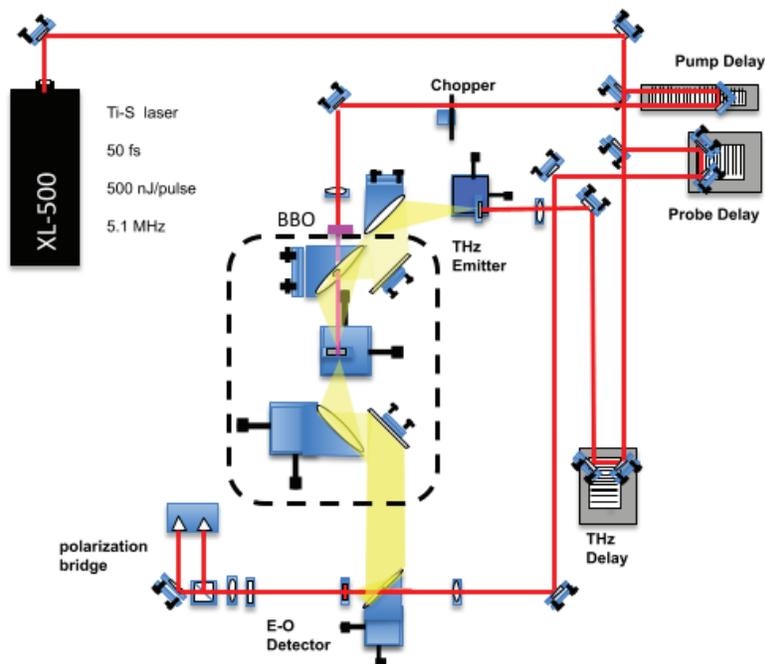
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Figure 2. Above is the setup for time-resolved THz spectroscopy measurement for the carrier lifetime and the carrier mobility using the THz pulse signal through the sample holder in the middle of the dry-air purged container (the dotted box).
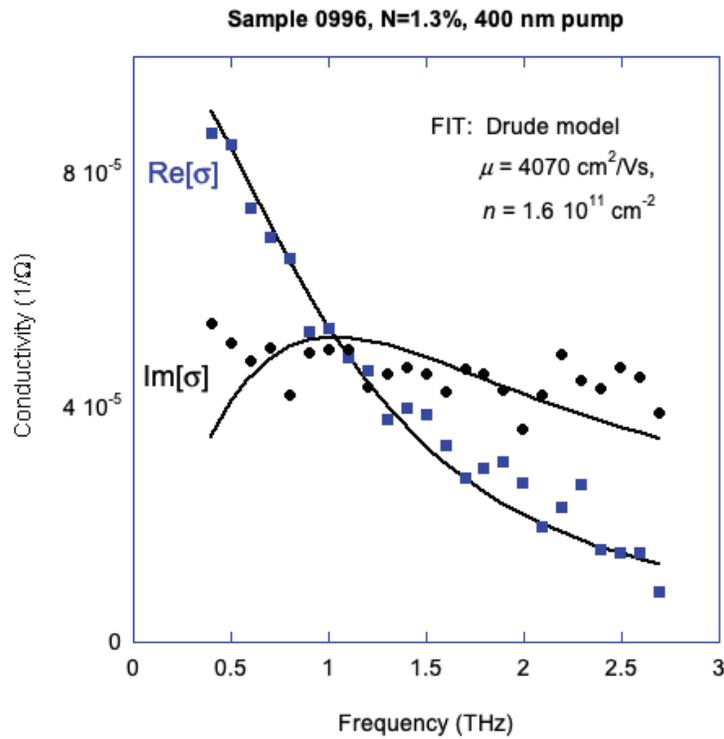
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Figure 3. This is the AC Drude Model fit for GaAsN with 1.3% nitrogen concentration. The blue points represent the real part of the equation (3) and the black points are the imaginary part of (3). We adjusted the carrier scattering time and DC Conductivity to find the best-fit for both imaginary and real parts.
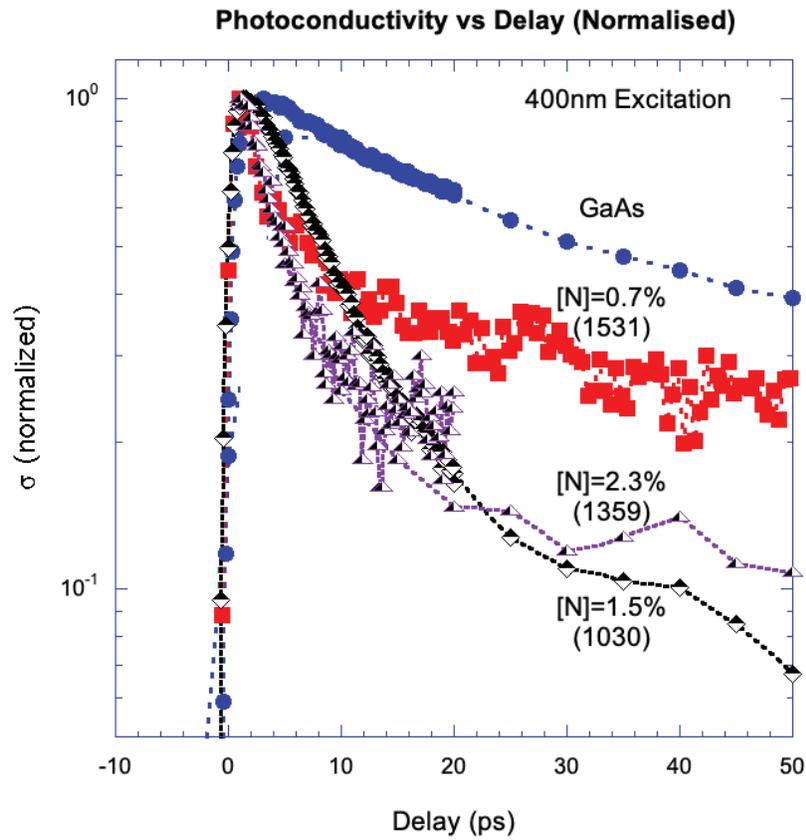
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Figure 4. Above is the photoconductivity in respect changing pump delay for different samples and GaAs under 400-nm photoexcitation. Note that the photoconductivity decays in the order of 10 ps. Also, there is a great exponential decay for the GaAsN samples but eventually converge to a similar behavior as GaAs.
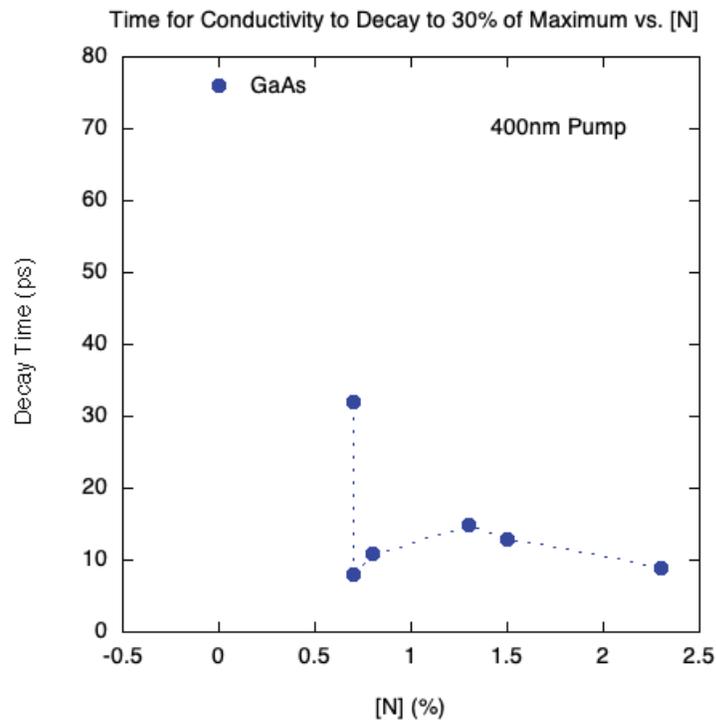
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Figure 5. The given figure is a plot of the time that the samples require to have the conductivity decay to 30% of maximum conductivity in respect to changing nitrogen concentration. From the given domain of 0.5%-2.5%, there is no particular trend to be described. The only significance is that the decay times are much quicker in GaAsN than in GaAs.
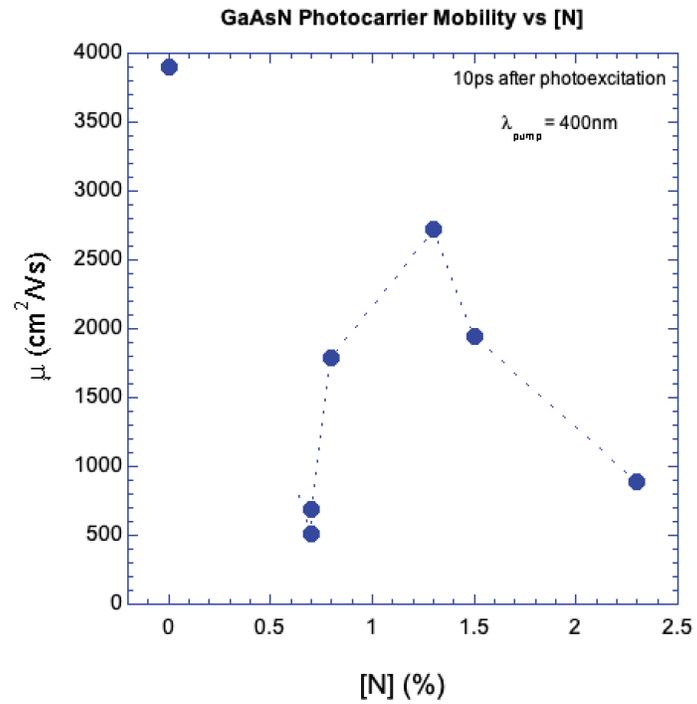
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Figure 6. This plot presents the carrier mobility in respect to nitrogen concentration. Similar to Figure 5, the given plot also does not show a particular pattern.
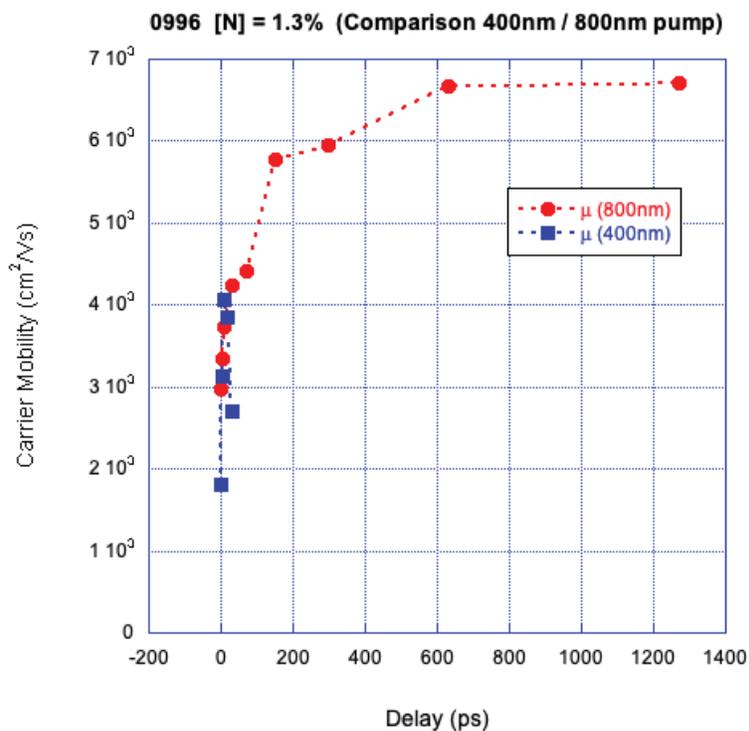
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Figure 7. The given plot displays the carrier mobility in change of pump delay for both 400-nm and 800-nm photoexcitation for the sample with 1.3% nitrogen concentration. We can notice that the carrier mobility from 400-nm photoexcitation actually follows the trend of the carrier mobility from 800-nm photoexcitation. Such result suggests that the results were still biased from the possible photoexcitation of the GaAs substrate.

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Sample	μ_e (cm^2/V s)
GaAs buffer layer	3300 ± 100
GaAs$_{1-y}$Bi$_y$ (y=0.84%)	2800 ± 100
GaAs$_{1-y}$Bi$_y$ (y=1.0%, AlGaAs barrier)	2800 ± 100
GaAs$_{1-y}$Bi$_y$ (y=1.4%)	2700 ± 100
GaN$_x$As$_{1-x}$ (x=0.84%)	920 ± 80[a]
GaN$_x$As$_{1-x-y}$Bi$_y$ (x=0.85%, y=1.4%)	340 ± 30[a]

Table 1. This is the carrier mobility values measured by D.G. Cooke, et. al. using the similar experimental techniques. Adapted from *Electron mobility in dilute GaAs bismide and nitride alloys measured by time-resolved terahertz spectroscopy* by Cooke, et. al., 2006, p.122103-3, Table I.

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