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The Effects of Hydrazine Monohydrate Surface Doping on Graphene

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Cover Page Footnote
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I. Introduction

Transparent conductors are conductors that are characterized by being highly transparent, meaning optical light passes through the material, having high electron mobility, and having high conductivity. These conductors are used for many different electronic applications such as photovoltaics, LCD screens, touchscreen, field effect transistors, and many other electronics [1]. Two of the most commonly used transparent conductors are indium tin oxide (ITO) and cadmium stannate [1]. These materials work well in electronics, but have a couple of downsides. Indium is a precious metal, which causes the production of ITO to be fairly expensive, while cadmium is poisonous, which tends to be an undesirable quality in different products. These are a couple of reasons for the sparked interest in graphene. In this experiment, we use chemical vapor deposition (CVD) graphene on substrate that consisted of SiO_2 on silicon. CVD is a process of producing graphene that allows large sheets of the material to be produced on a substrate. Our samples were grown and provided to us by Dr. Jeremy Robinson at the Naval Research Laboratory.

Graphene is a transparent conductor with many interesting properties. It is a single-atom, thick, two-dimensional carbon structure. Since it is made of carbon, it has the potential to be a relatively cheap and safe alternative to ITO and cadmium stannate. Graphene does have high mobility and transparency, but does not intrinsically have high conductivity like other transparent conductors due to low charge carrier concentration, but this carrier concentration can be easily manipulated through a process called chemical surface doping [2].

Chemical surface doping is a process in which a chemical solution or vapor is added to the surface of a film or material in order to raise or lower the concentration of electrons.

Hydrazine Monohydrate ($N_2H_4 \bullet H_2O$) is an n-type dopant (otherwise known as a donor) that adds electrons and raises the fermi level [3]. This reversible process can be used to change the carrier concentration and increase the conductivity. Hydrazine Monohydrate degrades in air and electrical properties return to their pristine conditions when left in air. Our experiment investigates the effects that hydrazine monohydrate has on CVD graphene. More specifically, we planned to investigate the effect that exposure to hydrazine monohydrate has on the scattering time and carrier concentration of CVD graphene.

II. Methodology

Overview

We began by annealing (heating the material to remove impurities) samples at 150°C for one hour. We then took Hall effect measurements to measure the mobility (μ) and the carrier concentration (n) of the samples. Immediately afterward, we took Fourier transform infrared (FTIR) spectroscopy measurements to measure the conductivity (σ), carrier concentration, and scattering time (τ) of the charge carriers. We then doped the samples with hydrazine monohydrate and repeated our measurements on these newly-doped samples to see if there was any noticeable difference.

Doping Process

CVD graphene samples are commonly doped using two different methods. One of these methods involves immersion in a hydrazine monohydrate solution, then immersion in water to rinse off excess solution. We originally chose this method in order to control the concentration of the hydrazine monohydrate used to dope the sample. We found this process tended to exfoliate the graphene from the SiO_2/Si substrate and we found that an experiment performed by Pinto that confirmed water can get between SiO_2 and graphene and cause this delamination. For this reason, we chose a vapor deposition process to dope our samples.

The vapor deposition is a process performed by bubbling nitrogen gas in a 16.5% hydrazine monohydrate solution in distilled water. This creates a hydrazine monohydrate vapor, which we then used to coat our graphene samples, which eliminated the need to immerse our sample in water. A single hydrazine monohydrate doping treatment consists of performing this process once for two minutes.

Hall Effect

We performed Hall effect measurements after annealing as well as after each doping treatment. In order to reduce the degradation of hydrazine monohydrate in air, we performed these measurements in a nitrogen purge chamber. This purge chamber is a chamber that is filled with nitrogen rather than air. We used four-wire measurements in a magnetic field to probe the electrical characteristics of our graphene samples. We used these measurements to measure the longitudinal voltage (V_L) created by a DC current (i) going through our CVD graphene. We used these to calculate the conductivity (σ) using Equation 1:

$$V_L = i\frac{1}{\sigma}\frac{L}{dt} \tag{1}$$

where L is the length of the sample, d is the width the the sample, and t is the thickness of the sample. We then measured the Hall voltage (V_H) caused by the introduction of a magnetic field. We used this to calculate the mobility of the charge carriers (μ) in our sample using Equation 2:

$$V_H = \frac{\mu d V_L B}{L} \tag{2}$$

where B is the strength of the magnetic field. Once we have values for σ and μ, we then calculated the charge carrier concentration (n) using Equation 3 where e is the charge of an electron.

$$n = \frac{\sigma}{e\mu} \tag{3}$$

FTIR

Immediately after performing Hall effect measurements on each sample, we performed FTIR measurements on each sample. We also performed these measurements in a nitrogen rich environment in order to reduce the degradation of the hydrazine monohydrate doping. We used a Thermo-Nicolet IS-50 FTIR machine to perform these measurements. We measured the infrared frequency range from 50 to 10,000 wavenumbers. We used a bolometer cooled to 4.2 K using liquid helium in order to detect the range from 50 to 300 wavenumbers, a far infrared (FIR) detector at room temperature in order to detect the range from 200 to 600 wavenumbers, a mid-infrared (MIR) detector cooled to 77 K using liquid nitrogen in order to detect the range from 500 to 4,000 wavenumbers, and a near infrared (NIR) detector also cooled to 77 K using liquid nitrogen in order to detect the range from 2,000 to 10,000 wavenumbers.

We used the Drude model to create a fit for our transmission data. The Drude model assumes that charge carriers are independent, meaning that they do not interact with each other. It also assumes that the charge carriers and have an isotropic scattering rate, meaning that the average scattering rate across the whole sheet is constant. This model also assumes that the average momentum of charge carriers is zero after scattering. This means that the charge carriers scatter in random directions after scattering events. The equation used to perform a fit on our transmission (T) data is given by Equation 4 where ω is frequency. α is given by Equation 5 where μ_0 is the permeability of a vacuum, c is the speed of light, and n_s is the index of refraction. σ_0 is given by Equation 6:

$$\frac{1}{T} = 1 + \frac{2\alpha\sigma_0}{1+\omega^2\tau^2} + \frac{\alpha^2\sigma_0^2}{1+\omega^2\tau^2} \tag{4}$$

$$\alpha = \frac{\mu_0 c}{n_s+1} \tag{5}$$

$$\sigma_0 = \frac{2e^2 v_f \tau\sqrt{\pi n}}{h} \tag{6}$$

where v_f is the fermi velocity.

III. Results and Discussion

We observe a clear absorption feature due to CVD graphene around zero wavenumbers in our annealed samples. We then find the line of best fit using Equation 4 and determine values for the scattering time and carrier concentration of our samples. An example of this absorption feature is given on a linear scale in Figure 1 and on a logarithmic scale in Figure 2. Table 1 displays an example of both Hall effect measurements and FTIR measurements measured for one of our samples. The measurements portrayed in this table show that the carrier concentration measurements are fairly similar between the two measurement techniques. The Hall effect measurements have slightly lower values of both carrier concentration and mobility due to differences in the measurement techniques, which is an expected occurrence.

The data in Table 1 also shows a large difference between the scattering time measured using FTIR and the scattering time calculated from the Hall effect measurements. We calculated the scattering time using Equations 3 and 6. The differences in scattering time measurements are due to the fact that the Hall effect measurements are not entirely reliable in this case. Our samples are actually not homogeneous films as the Hall effect and four-wire measurements assume. After treating with hydrazine monohydrate, we do notice some features such as scratches or cracks in our CVD graphene samples. CVD graphene is also not quite a homogeneous film. The sheet produced by the CVD process actually consists of many smaller sheets conglomerated together to form one larger sheet. These inhomogeneities produce stray resistances that the Hall effect measurements does not account for, causing the scattering time measurements found using Hall measurements to be unreliable and not reflect the true scattering time of the charge carriers. Hall effect measurements can however be used to determine carrier type, which makes this technique useful despite the unreliability of the scattering time measurements. We also know that our FTIR measurements are reliable, because there are no reasonable processes that could produce the absorption feature caused by the intrinsic properties of graphene we observe in Figures 1 and 2.

We observe a dramatic change in carrier concentration between samples when they are purely annealed compared to when they receive their first hydrazine monohydrate doping treatments. An example of the difference in transmission data between annealed and doped graphene is given in Figure 3.

While the measurement of carrier concentration goes down by a significant amount between untreated samples and samples treated with hydrazine monohydrate, we know that the concentration of electrons is greatly increased, which is a very desirable in electronic applications. This increased electron concentration is due to the fact that our CVD graphene sample started out heavily p-type (Figure 4), but when the hydrazine monohydrate is introduced, the sample's Fermi level rises and our measurement of carrier concentration decreases. Some of our samples also exhibited a change from p-type to n-type as seen in Figure 5. This is further evidence that hydrazine monohydrate exhibits donor qualities and raises the concentration of electrons in CVD graphene.

We also observed that scattering time was nearly unaffected. There is only a difference in about 20%, which is a fairly insignificant change. This result is shown in Figure 4. An increase in scattering time of charge carriers would cause decreased performance in electronic applications, so the fact that the scattering time was nearly unaffected was a desirable finding.

We also observed that a second treatment of hydrazine monohydrate does not have a significant effect on either the carrier concentration or the scattering time (Figures 4 & 5). This is likely due to saturation of our graphene sample's surface after the first doping treatment with hydrazine monohydrate. Figure 4 also shows the reversibility of this process through the degradation of the hydrazine monohydrate in air as described above.

IV. Conclusions

We conclude from our research that after doping the surface of CVD graphene using a vapor deposition process, the concentration of electrons increased greatly while the scattering time of the charge carriers is nearly unaffected. These are both desirable qualities for various electronic applications. One possibility for future research would be to investigate a process that reduces the delamination (stripping off of the substrate) of graphene from a SiO2 substrate during the immersion process. This would help to control the concentration of the hydrazine monohydrate applied to the CVD graphene more easily.

References

1. Bult et al., ACS Nano, **7**, 7251 (2013).

2. Pinto H. and Jones R., School of Physics, University of Exeter (2010).

3. Song et al., Applied Science and Convergence Technology, **23**, 192 (2014).

Tables

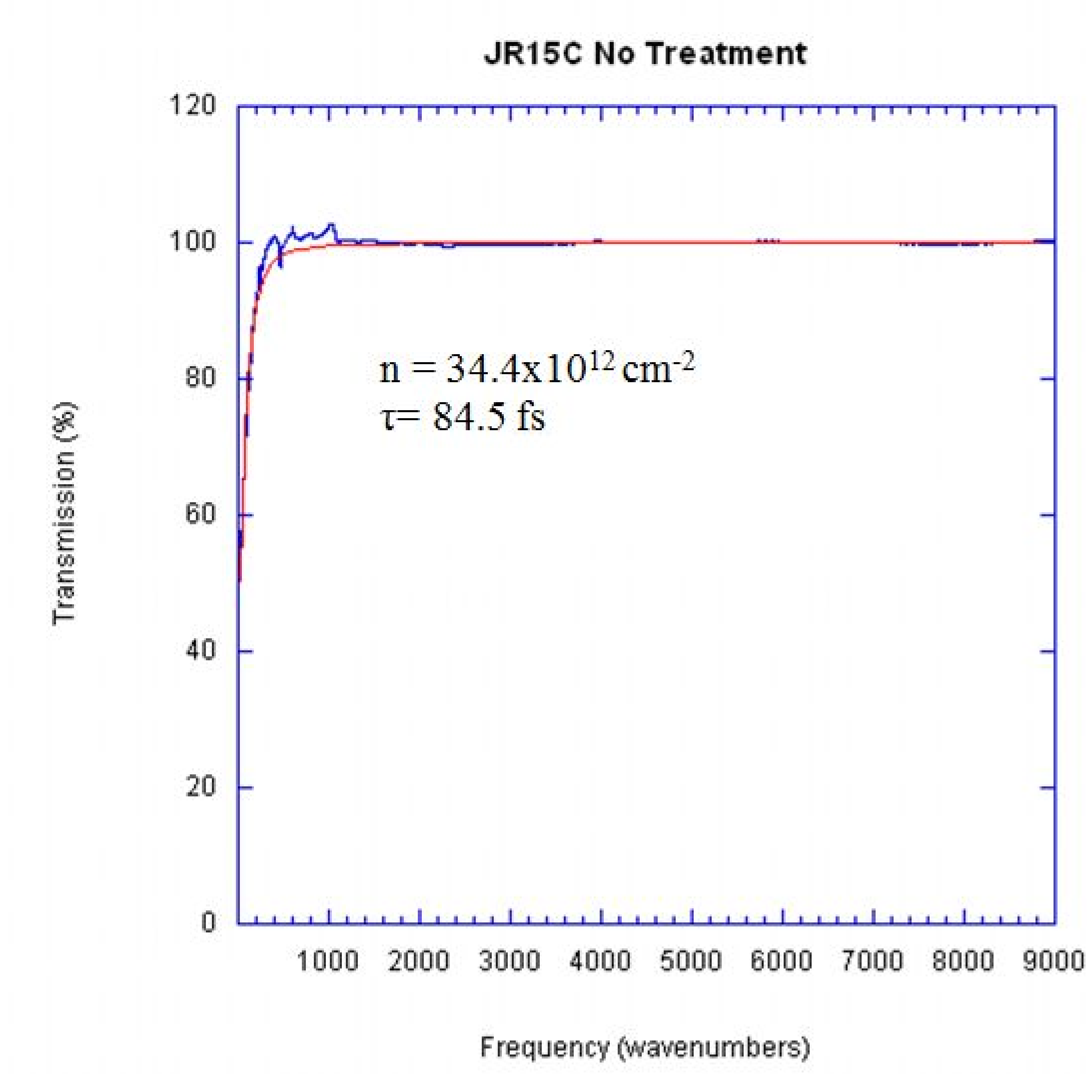
Sample	FTIR		Hall		
	n (x10^{12} cm^{-2})	τ (fs)	n (x10^{12} cm^{-2})	µ	τ (fs)
JR15C (untreated)	34.4	84.5	24.8	535	39
JR15C (1 treatment)	1.9	119.3	0.72	3000	37
JR15C (2 treatments)	4.2	112.3	2.78	589	14
JR15C (24 hours in air)	10.0	103.6	4.94	1020	33

Table 1

This table gives the results from one of our samples (JR15C) over multiple treatments. This gives the results for both Hall effect measurements as well as FTIR measurements. This table displays results for carrier concentration (n) and scattering time (τ) for both measurement techniques as well as the mobility measurements (μ) found through Hall effect measurements.

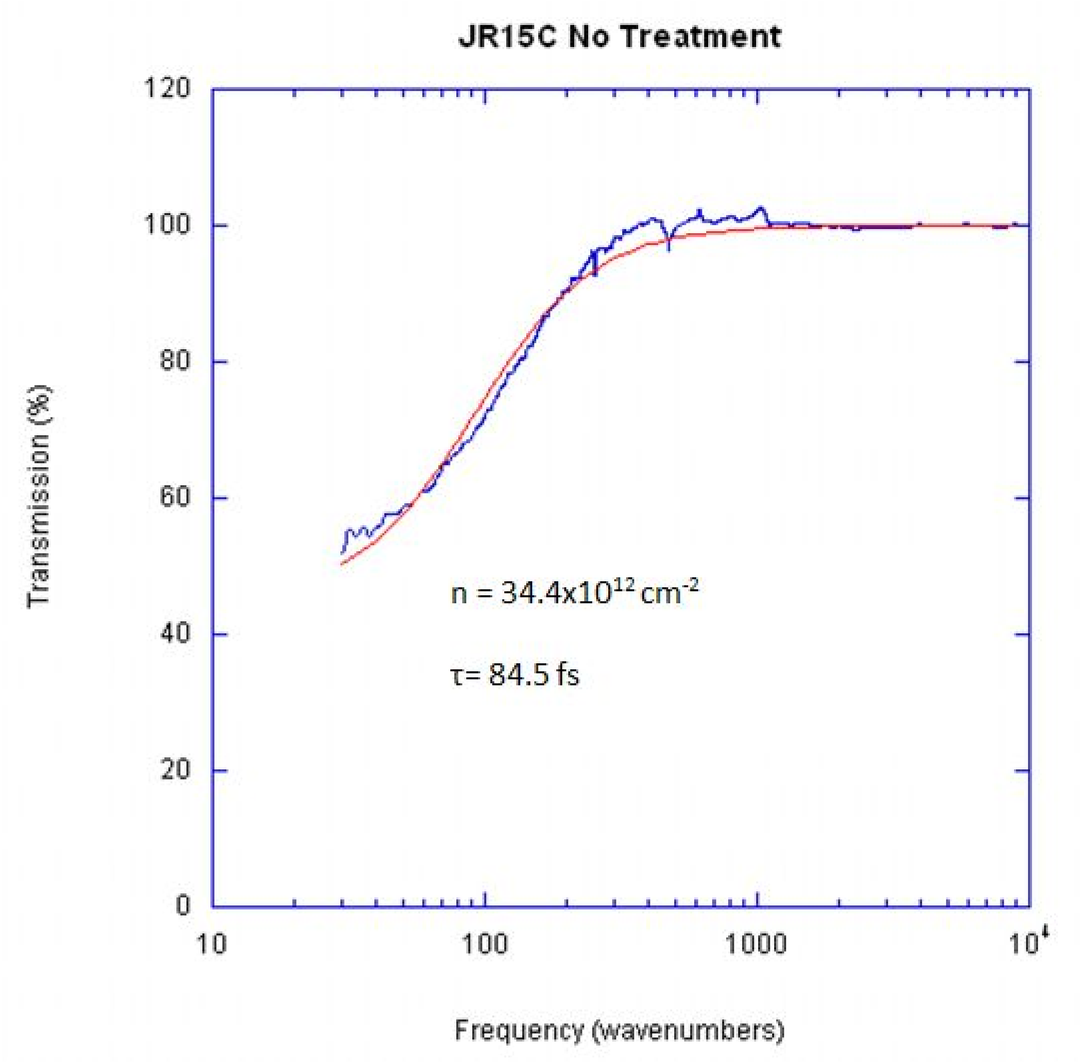
Figures

Figure 1



This figure shows the FTIR results for one of our annealed samples (JR15C). It shows the transmission in percentage versus frequency in wavenumbers with the x-axis on a linear scale. The blue line is our data while the red line is our fit. We also reported the carrier concentration and scattering time we found from our fit.

Figure 2



This figure shows the FTIR results for one of our annealed samples. It shows the transmission in percentage versus frequency in wavenumbers with the x-axis on a logarithmic scale. The blue line is our data while the red line is our fit. We also reported the carrier concentration and scattering time we found from our fit.

Figure 3

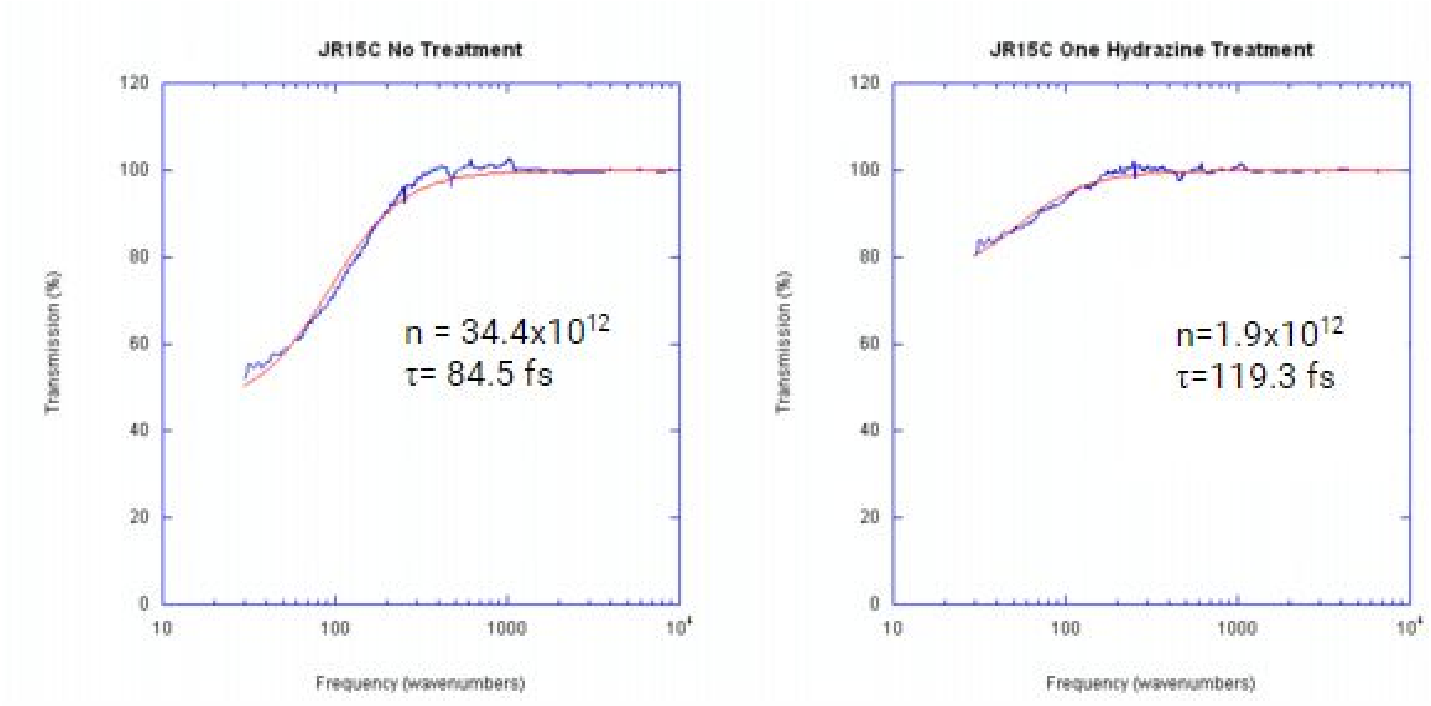
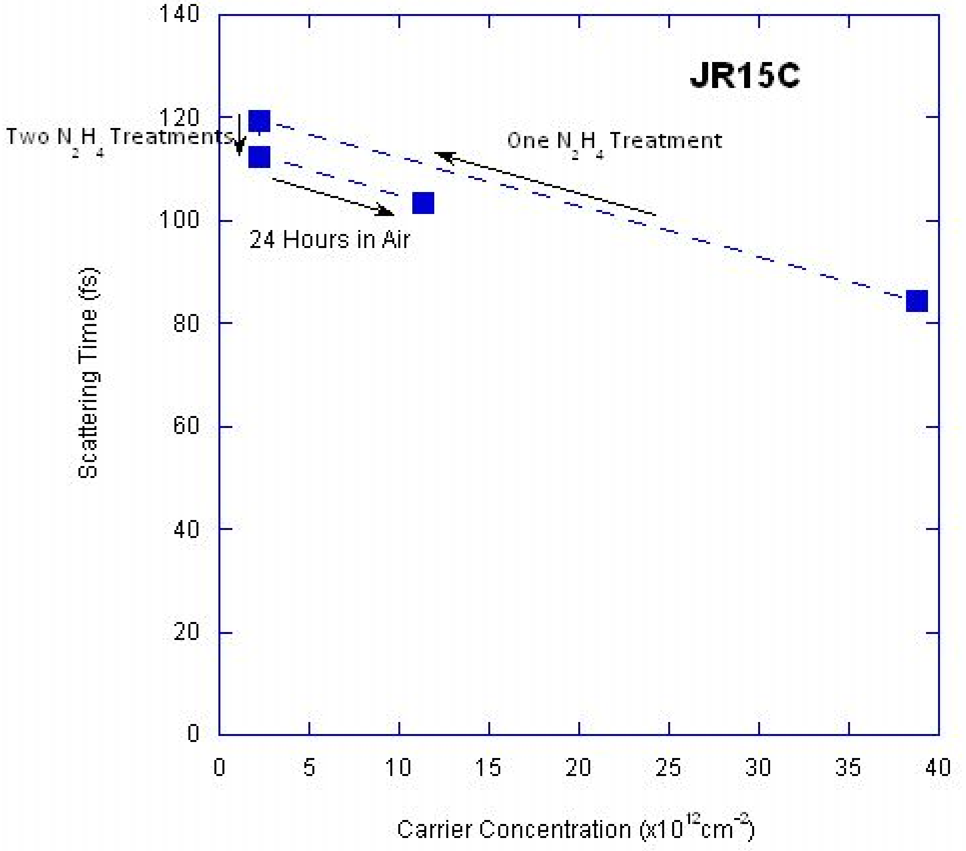


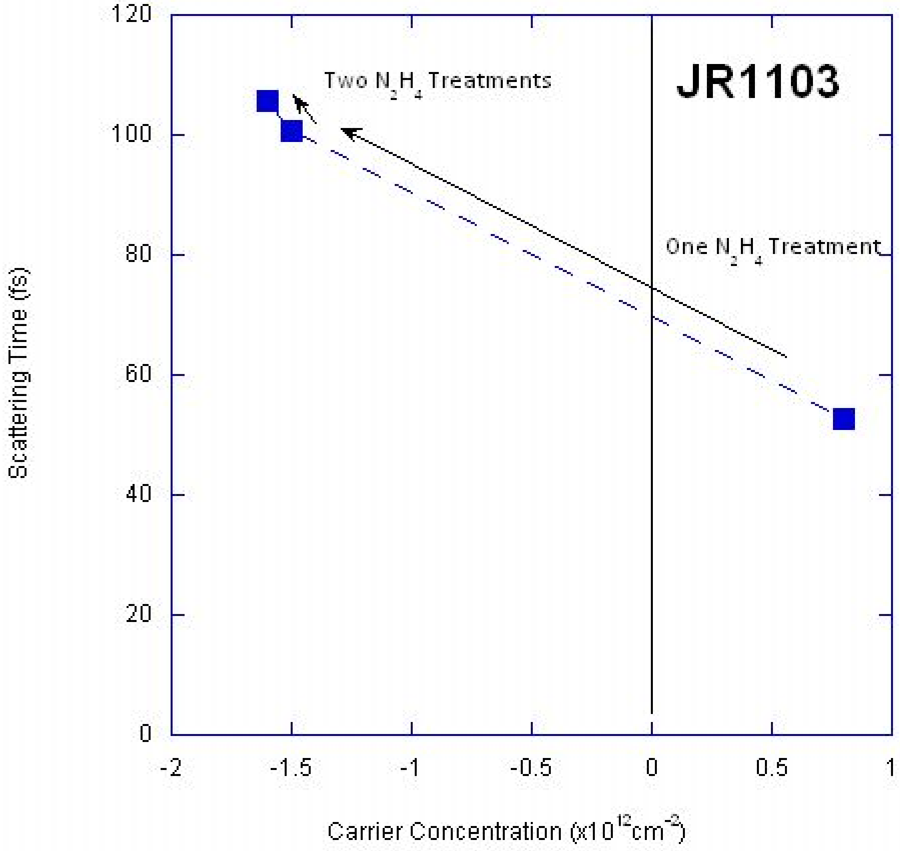
Figure 3 shows the FTIR results for one of our annealed samples (JR15C) next to the results of that same sample after a hydrazine monohydrate doping treatment. This shows the transmission in percentage versus frequency in wavenumbers with the x-axis on a logarithmic scale. The blue line is our data while the red line is our fit. We also reported the carrier concentration and scattering time we found from our fit.

Figure 4



This figure shows the FTIR results for one of our samples (JR15C) after annealing, after one doping treatment, after a second treatment, and after sitting in air for 24 hours. It shows a plot of the scattering time versus the carrier concentration. This is a p-type sample.

Figure 5



This figure shows the FTIR results for one of our samples (JR1103) after annealing, after one doping treatment and after a second doping treatment. This shows a plot of the scattering time versus the carrier concentration. This sample begins as a p-type sample and changes in the doping process to become n-type. A line is present at the zero concentration point to highlight this change.