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Abstract

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Keywords

graphene

Cover Page Footnote

Editors of MJPA, Please accept this final revision of my manuscript. Small changes have been made that only fix small errors, and do not change the scientific content of the paper. Andrew Banman

MID-IR EXCITATION OF GRAPHENE

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Abstract. In this research we investigate how the conductivity of graphene changes in response to mid-infrared photoexcitation. Our p-type sample was formed through chemical vapor deposition. Pump/probe methodology produced the time-resolved Terahertz transmission, from which the photoconductivity was calculated. We probed the sample with energies above and below the Fermi energy, which was determined by Fourier transform infrared spectroscopy. Our results support a model in which heating of the electron gas, leading to high carrier scattering rates, is responsible for a decrease in conductivity. We observe this negative photoconductivity at all pump energies, allowing us to rule out the possibility of population inversion to explain the results.

1. Introduction

Graphene has many remarkable properties that make it a fascinating subject for research. Graphene is a single layer of covalent bonded sp^2 carbon atoms arranged in a 2D hexagonal, or 'honeycomb,' lattice. At only one atom thick, it is the thinnest material ever discovered. The strength of the carbon bonds at the microscale translate into a tensile strength up to 1000 times that of steel. Graphene is a zero-gap semiconductor with incredibly high carrier mobility; near the Dirac point electrons and holes move as though massless with velocity $v_f \approx 10^6$ m/s [1]. These and other features make graphene an exciting material for applications in electronics and optics. In particular, understanding how the conductivity of graphene changes in response to photoexcitation, the *photoconductivity*, is of concern for electro-optical applications.

Ultrafast pump probe measurements are a popular method to measure the time-resolved photoconductivity of conducting films. George et. al. used an optical pump and THz probe to find that the conductivity of epitaxial graphene rapidly increased following photoexcitation, indicating *positive* photoconductivity [2]. They explain their results by applying a dynamical model in which the charge carriers of the sample are heated by the pump and cool by optical phonon scattering. In contrast, Boubanga-Tombet found the opposite behavior. Using similar measurements, they found their graphene sample showed *negative* photoconductivity due transmission gain, caused by a population inversion of the charge carriers [3].

In this paper we investigate the photoconductivity of CVD graphene in response to infrared excitation. We use methods of time-resolved THz pump-probe to determine the photoconductivity by measuring the change in THz transmission. We find that THz transmission *increases* following photoexcitation, indicating a *decrease* in conductivity. One possible explanation for this negative photoconductivity is that the interband conductivity becomes negative following excitation due to carrier

population inversion. However, we observe negative photoconductivity for pump energies below the threshold for interband transitions (Figure 1). Instead, our results fit a carrier-heating model, in which the decrease in conductivity is explained by increased scattering rates due to heating of the electron gas.

2. Experiment

The graphene sample was fabricated by chemical vapor deposition. A 1cm^2 graphene film was grown via epitaxial growth on copper foil. The copper was then dissolved and the graphene film was placed on a sapphire substrate. Hall effect and electrical resistivity measurements performed by Heyman et. al. determined the sample to be p-type with carrier concentrations $p = 2 \cdot 10^{12}\text{cm}^{-2}$ - $2 \cdot 10^{13}\text{cm}^{-2}$ with DC mobility $\mu = 1500\text{cm}^2/\text{Vs}$ - $2000\text{cm}^2/\text{Vs}$ [4].

A Thermo-Nicolet IS-50 FTIR was used to calculate the infrared transmission spectrum of the graphene sample over the range 1μm to 200μm (0.001eV to 1.2eV). The FTIR used optics for generating and detecting radiation in the near-, mid-, and far-infrared regions. An IR Labs 4K Si bolometer was used to measure transmission over far-IR wavelengths.

The photoconductivity of the sample was measured according to time-resolved THz pump-probe methods using the University of Minnesota's MULE (Multi-User Laser Experiment) system (Figure 2). An amplified Ti-Sapphire laser with a repetition rate of 1KHz produced optical 120fs pulses at $\lambda = 800$nm. This optical beam was split using a polarized beam splitter and a half-wave plate. The more intense segment powered an optical parametric amplifier (OPA) to produce the tunable frequency pump pulse. The less intense segment was further split into the probe pulse and what would become the THz pulse. The THz pulse was generated by electro-optical rectification in a ZnTe crystal, in which a difference-frequency process resulted in an elongated THz pulse. The pump pulse met the THz pulse at the sample, where photoexcitation due to the pump modified the conductivity of the sample. This change in conductivity results in a change in the transmission of the THz through the sample, as explained in detail below. The modified THz beam met the probe beam at a second ZnTe crystal, where the electric field of the THz beam changed the birefringent properties of the crystal, thereby changing the polarization elipticity of the probe beam [5]. This change is measured as net current in an autobalance detector, which is proportional to the electric field of the THz pulse.

The probe pulse was delayed relative to the THz pulse such that it sampled the THz waveform at its greatest amplitude, and the pump was modulated using a chopper connected to a lock-in amplifier that recovered the THz signal. The time evolution of the change in THz transmission was found by variably delaying the pump pulse via changing its path length with a translation stage. In this way we were able to measure the change in peak THz transmission, ΔT_E, in response to photoexcitation by the pump as a function of time. Furthermore, the path of the THz beam was purged to limit absorption due to water. Pump energies from 0.35eV to 1.55eV were investigated, where each pump energy varied in intensity according to the emission spectrum of the OPA.

3. Results

We used FTIR spectroscopy to directly measure how graphene absorbs infrared radiation. The transmission spectrum from the FTIR shows typical Drude (intraband) absorption (Figure 3). The Drude model assumes electrons behave as free carriers which scatter at a well defined rate. As a classical model it is not without its limits, but it does predict the electrical conductivity of metals with some accuracy. The gap in the spectrum around 0.1eV is explained by the opacity of the sapphire substrate in that region. The step feature at $2\epsilon_F$, representing a transmission decrease - conductivity increase, is clear evidence for interband absorption. This mechanism is blocked at lower energies as expected.

However, our ultrafast pump/probe measurements show a decrease in THz transmission at all pump energies investigated, notably above and below twice the Fermi level, $2\epsilon_F$. The transmission of THz radiation, T_E through the graphene sample is given by Equation 1:

$$T_E = \left(1 + \frac{\mu_0 c \sigma}{n_s + 1}\right)^{-1} \tag{1}$$

where σ is the conductivity, μ_0 is the magnetic permeability, c is the speed of light, and n_s is the substrate index of refraction [4]. Hence a positive change in transmission corresponds to a negative change in conductivity. The pump-probe measurements show a transient increase in THz transmission following excitation from all pump energies investigated (Figure 4). In each case, the transmission change takes place over the first 1ps, followed by a relaxation period over the next 4ps-5ps. We observe an additional transient increase in transmission following the relaxation period that we attribute to the echo caused by the THz pulse reflecting off the back of the sample. The transmission curves were normalized since we are primarily concerned with the sign of ΔT_E. Notably, there is no qualitative difference between pump energies above and below $2\epsilon_f$. We do not observe any dependence in ΔT_E on the pump energy, with the exceptions of 1.55eV and 0.35eV that show a smaller change in transmission. We attribute this discrepency to the fact that measured pump beam intensities for these energies were an order of magnitude less than the others. This is consistent with the theoretical model discussed below.

4. Discussion

We clearly observe an increase in T_E corresponding to a transient decrease in conductivity σ at pump energies above and below the $2\epsilon_F$ from our time-resolved transmission data, suggesting that intraband, rather than interband, transistions are the driving mechanism. Semiconductors typically exhibit the opposite behavior: interband conductivity *increases* in response to photoexcitation. When a semiconductor absorbs a photon with $\hbar\omega > 2\epsilon_E$, an electron is promoted from the valence band to the conduction band, resulting in the creation of two new carriers: an electron in the conduction band and a hole in the valence band. This increase in carrier concentrations results in an increase in conductivity, as described by the basic model

$$\sigma = (n\mu_n + p\mu_p)e$$

where n is the electron concentration, p is the hole concentration, and μ_n and μ_p are the carrier mobilities.

However, the mobilities are inversely proportional to the carrier scattering rates, which themselves depend on temperature. Conductivity only increases if the increase in carrier concentration dominates the decrease in carrier mobility due to increased temperature. In our graphene sample we observe intraband absorption resulting in a decrease in conductivity, presumably due to heating of the electron gas that leads to increased scattering rates, and therefore lower carrier mobility. An alternate explanation for negative photoconductivity is that the portion of the conductivity due to interband absorption becomes negative. This happens when the electron and hole populations become inverted, meaning there are more carriers in excited states than in lower energy states. Since this process is driven by interband transitions, it should not be observed for pump energies below $2\epsilon_F$. Our results contradict this possibility because we observe negative photoconductivity both above *and* below this threshold.

We found that, by controlling for the power absorbed by the sample at each pump energy, ΔT_E depended only on the total absorbed energy (Figure 3). This result is consistent with the carrier-heating model described developed by Rhyan Foo Kune, in which carriers thermalize within 100fs and cool by optical phonon scattering. Importantly, the model predicts that ΔT_E depends on the amount of energy absorbed by the graphene rather than the energy of the exciting photons. This prediction is well supported by our data, where it can be seen that ΔT_E at each pump energy lies on an absorbed energy contour. The data fall on the $400\mu\text{J/cm}^2$ contour for energies 0.52eV - 1.03eV and the $40\mu\text{J/cm}^2$ contour for 0.35eV and 1.55eV. Presumably, the graphene sample is fully saturated at $400\mu\text{J/cm}^2$, so pump beams with sufficiently high intensity will excite the sample to this point.

5. Conclusion

In this research we have found that CVD, p-type graphene exhibits negative photoconductivity in response to mid-infrared excitation. We used FTIR spectroscopy in tandem with time-resolved transmission measurements to show that carrier heating is responsible for the decrease in conductivity. The fact that we observe this effect at pump energies below the threshold for interband transitions indicates that population inversion cannot be responsible for the observed negative photoconductivity. Thus, our conclusions do not support the use of graphene as a gain medium for THz lasers.

Figures

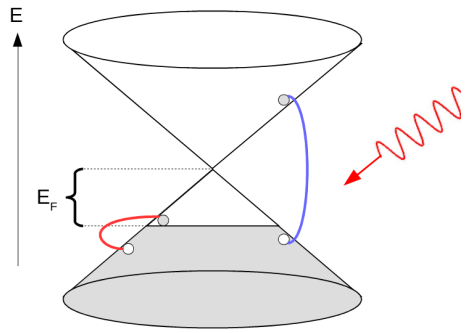

Figure 1. A mock energy-momentum diagram for our p-type graphene samples. The fermi enery E_F is shown, illustrating the fact that interband (blue) transitions are not possible for photon energies below twice the fermi level. A valence band intraband transition (red) is also shown.

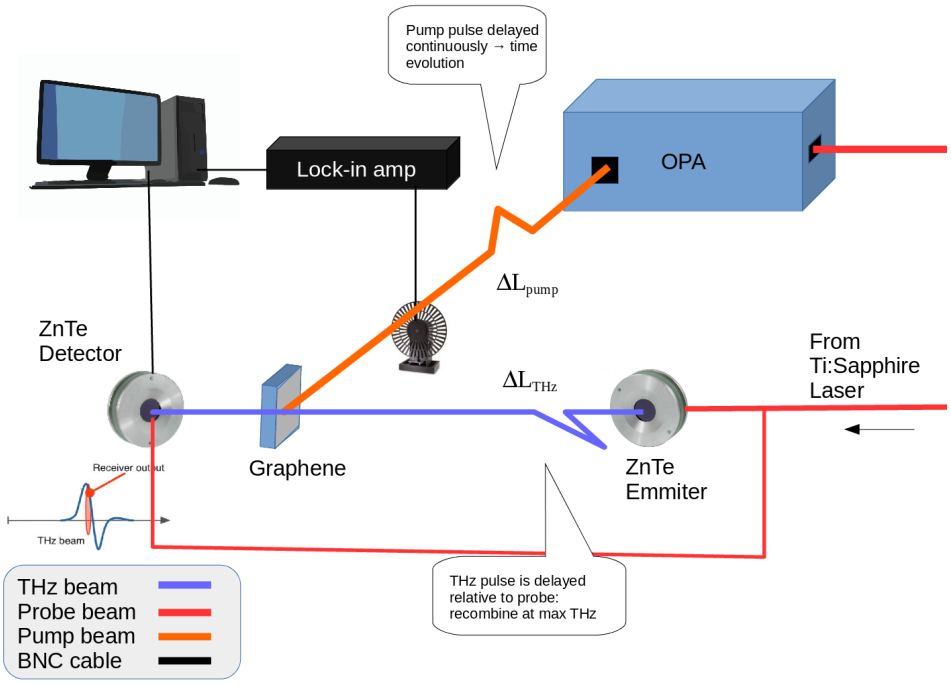

FIGURE 2. A conceptual diagram of the experimental setup. A Ti:Sapphire laser emitting 120fs pulses at $\lambda = 800$nm with a 1KHz repetition rate powered the OPA as well as the THz and probe beams.

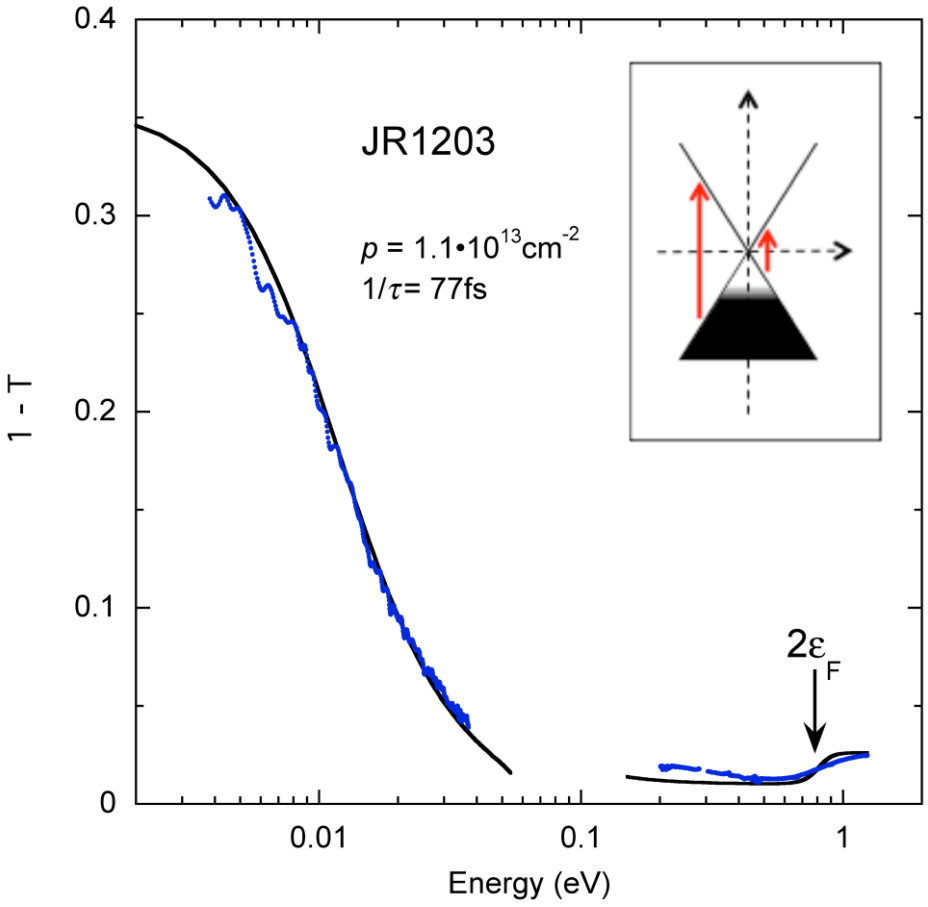

FIGURE 3. Infrared transmission spectrum of CVD graphene sample JR1203. The black line is the Drude model fit and Fermi energy simulation. The gap is due to the opacity of the sapphire substrate for those energies. The step feature at high energies indicates interband transition, as illustrated by the inset. [4]

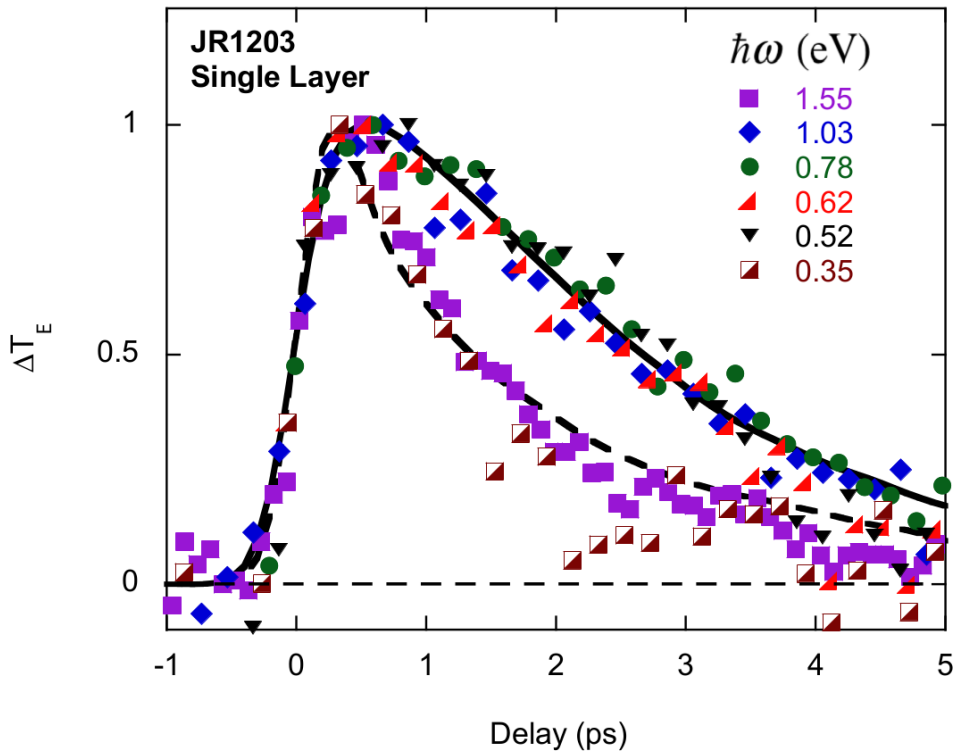

FIGURE 4. Time-resolved change in THz transmission versus delay. Curves are normalized based on long range determination of transmission. Solid lines indicate contours of absorbed pump intensities: 400 μJ/cm^2 (solid) 40 μJ/cm^2 (dashed). [4]

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