Abstract

We have measured carrier relaxation times and nonlinear optical properties in three functionalized epitaxial graphene layers grown on SiC wafers by using ultrafast optical pump-probe spectroscopy and open aperture z-scan at 780 nm. The results demonstrate that after different functionalization, the ratios of the slower relaxation in the range of 3.1-4.6 ps (related to carrier-phonon intraband and interband scattering) increase about 2-6 times compared to original graphene. These changes of relaxation obviously improved the nonlinear optical properties, making functionalized epitaxial graphene can be used as a tuneable saturable absorber.

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Keywords: Epitaxial graphene; saturable absorption; carrier dynamics

1. Introduction

Graphene has received great interest in recent years as a two-dimensional carbon nanomaterial. It has various remarkable properties and applications in modern electronics and photonics. [1,2] The single and multilayer epitaxial [3] or exfoliated graphenes [4] deposited on a substrate display two kinds of the carries relaxation time using the ultrafast dynamics investigation. A fast lifetime corresponds to the carrier-carrier intraband scattering whose order is about fs and a slow lifetime corresponds to the rates for
electron-hole recombination whose order is about ps. [5] Some paper reported the lifetime of Epitaxial Graphene (EG) in the different atmosphere [6], but little paper discussed the influence of the different functionalization on EG.

Since graphene is usually made as a single layer, it is highly sensitive to changes to its surface which is easy affected by the functionalization. Through chemical reactions or charge transfer or even van der Waal’s interactions due to molecular adsorbates, the carriers relaxation time could be adjusted as the transport properties and electron-phonon interactions. Now there is little investigation on the decay process of carriers on functionalized graphene.

2. Experiments

In this paper, our aim is to investigate the effects of functionalization on the optical properties of graphene using ultrafast optical pump-probe spectroscopy and open aperture z-scan at 780 nm. The epitaxial graphene (EG) with 1-3 layers were grown on the silicon face of semi-insulating 4H-SiC wafers according to details given in a previous report [7]. Three functionalization methods have been applied on the EG. For non-covalent functionalization, the chemicals used: tetrasodium 1,3,6,8-pyrenetetrasulphonic acid (TPA) and 1,5-Naphthalenediamine (NaNH₂) were dissolved in ultra-pure water and absolute ethanol respectively (0.01 mol/L), which were purchased from Sigma-Aldrich and used without further purification. In order to avoid errors caused by uniformity, the original EG was first measured as a reference and never be moved. We drop-casted one test solution onto the edge of the sample directly and test it after the solvent had been evaporated. When the measure was finished, the sample was washed with the corresponding solvent and tested again to prove no test solution left. Then we began another test solution and repeated these steps. So, all the data about the non-covalent functionalization were come from the same spots of the un-functionalized sample. For the covalent grafting of aryl groups to the basal plane, the chemical modification of EG is performed in a similar fashion as that reported by Bekyarova et. al. [8]. This test of covalent functionalized EG was repeated at several positions within the same sample for avoiding errors.

A full set of Spectra-Physics laser system with 1 kHz pulse repetition rate, 780 nm centre wavelength, and <50 fs pulse width was used for the excited source in the time-resolved pump-probe spectroscopy test and Z-scan of the graphene samples. Pump pulses with energies of 19 mW were used to generate photon-excited carriers, while the pulses with energies of 0.02 mW were used to measure the changes in the transmittivity of the samples at various delays of the probe pulses. The pump and the probe were focused to a spot size of about ~100 μm and their angles were 0° and 15°, respectively. The probe polarization was rotated by 90° with respect to the pump. Polarizers were used to eliminate scattered pump light going in the direction of the probe beam. The pump beams was modulated at a frequencies near 0.5 kHz. The changes in the intensity of the probe pulses were measured with a lock-in amplifier.

3. Results and Discussion

The time dependent change ΔT/T of the as-prepared EG sample, EG coated with NaNH₂ or TPA and EG grafted with nitro-phenyl groups modified samples were shown in the Fig. 1. T is the transmittivity of samples without the pump pulse. As a reference, the measured transmittivity curve of as-prepared EG sample was shown in Fig. 1 (a), fitted using a simple second order exponential decay as refer. [5]. The values of an initial fast relaxation time constant τ₁ and a slower relaxation time constant τ₂ are obtained. The order of magnitude of the fast lifetime τ₁ agrees with theoretically predicted rates for the carrier-carrier intraband scattering, [9] while that of the slow lifetime τ₂ corresponds to the rates for electron-hole recombination [10]. What is different between our results and other’s published data is that the ratio of
the slow lifetime $\tau_2$ is smaller than other report [5]. According to the paper [5], the slow lifetime $\tau_2$ also be influenced by the thermalization of the carriers with the lattice through carrier-phonon scattering that is the dominant mechanism. $\tau_2$ is proportional to the coherence length of the crystal parameter $I_G/I_D$. But little paper has investigated about the ratios. In this EG sample, $I_G/I_D$ is small (near 2).

Fig. 1. Measured transmittivity transients for the as-prepared EG sample, EG coated with NaNH$_2$, EG coated with TPA and EG grafted with nitro-phenyl groups. The pump power was 19 mW on all the samples.

The dynamics of photo-excited carriers in graphene can be affected by the carrier density that can be adjusted by the molecular doping. In refer. [11], two aromatic molecules: 1,5-naphthalenediamine (NaNH$_2$) and tetrasodium 1,3,6,8-pyrenetetrasulphonic acid (TPA) were chosen to non-covalent functionalize the graphene. So, Fig. 1 (b) and (c) were given to show the measured transmittivity curves of the same EG sample functionalized by TPA and NaNH$_2$, respectively. The interactions between the adsorbates and the graphene surface have been displayed through the changes in the decay process. From Fig. 1 (b), the faster lifetime $\tau_1$ increases twice and the ratios of slower lifetime $\tau_2$ increase almost 6 times, meaning the carries density decreases much. But the changes of FG coated with TPA are very different shown in Fig. 1 (c). Both the faster lifetime $\tau_1$ and the slower lifetime $\tau_2$ decrease little. It is due to that the graphene is already p-doped under atmospheric conditions whose majority carriers are the hole. The NaNH$_2$ which is an n-doped molecule will cause a lager decrease in the majority carrier concentration. It induced the obvious increase of $\tau_1$ and the ratio of $\tau_2$. Because the faster lifetime $\tau_1$ which is related to the carrier-carrier intra-band scattering is dependent on the concentration of the majority carriers as mentioned above. While the adsorption of TPA is a p-doped molecule, it will increase the hole concentration and results in shorter lifetimes for the photo-generated carriers. The changes caused by NaNH$_2$ is more obvious than TPA, because addition of a n-doped molecule in the n-doped conditions is likely to induce a larger change in its carrier concentration as compared to that of a p-doped molecule added one.

But the proportion of slower lifetime $\tau_2$ increases twice after coated with TPA. It may be explained by an increase in crystal disorder which may also be due to band gap opening. In refer. [5], the lifetime $\tau_2$ is mainly influenced by the crystal disorder. In refer. [12], ionic solutions on graphene can screen the
charged impurities between the graphene and substrate. TPA contains four sodium ions per molecule that can screen the charged impurities, leading to a longer coherence lengths and a reduction in carrier mobilities. As a result, scattering due to these charges is reduced and the carrier mobilities of graphene are increased. Although the increase carries density will reduce \( \tau_2 \), but as mentioned above, the influence of TPA (n-doped molecule) in the n-doped conditions is little, the improvement in crystal disorder will be the main factor acting as an opposing effect. For the NaNH\(_2\), after the adsorption, the gradient of the I-V curve decreased significantly, indicating a reduction in carrier mobilities [11]. It may be another reason for the obvious change of EG sample functionalized by NaNH\(_2\). Non-covalent functionalization is an easy and versatile method for adjusting the properties of graphene.

In order to extend the understanding, the covalent functionalized EG grafted with nitro-phenyl groups was tested for comparison. The result is shown in the Fig.1 (d). The changes are similar as the effect caused by NaNH\(_2\) that both the fast lifetime \( \tau_1 \) and the ratios of the slow lifetime \( \tau_2 \) increase to 0.20ps and 21%, respectively. Because the nitro-phenyl groups also is an n-doped like NaNH\(_2\). What is different from non-covalent functionalization is that the slow lifetime \( \tau_2 \) increases to 4.60 ps obviously. Because one merit of covalent functionalization is that the defects have been introduced in the form of sp\(^3\) carbon atoms, leading to the disruption of extended conjugation in graphene and the reduction in the carrier density. [13]

Fig.2 (a) give the representative transmittivity curves of EG coated with NaNH\(_2\) at the pump power 13mW, 19mW, and 21mW. The trend and the ratio of lifetimes change little with the increase of excitation intensity as refer. [5], meaning the differences from as-prepared EG sample is caused by the functionalization. Fig. 2(b) shows the normalized peak value of the transmittivity change (\( \Delta T/T \)) plotted as a function of the pump pulse energy for EG and functioned EG. The maximum value of \( \Delta T/T \) is proportional to the pump pulse energy when the pump pulse energies below 17 mW. This result is similar to the study of ref [5]. But when the intensity increased exceeded 18mW, the trend of transmittivity shows a nonlinear increase, so the saturation absorption is observed at the functioned EG, different from the origin EG. The mainly reason is that the low relaxation increased obviously after functioned, whose order is larger than the pump pulse width. This result can be proved by that the ratios of slow relaxation increased greater, the saturation absorption increased more obviously. What is better is that we can choose the ratio of the slow lifetime if we chose the appropriate functional material. Therefore, functioned EG may have the potential value as a tuneable absorber.

![Fig. 2](image_url)

Fig. 2, (a) The representative transmittivity curves of EG coated with NaNH\(_2\) at the pump power 13 mW, 19 mW, and 21 mW. (b) Transmittivity after photon-excitation is plotted for various pump pulse energies for the samples: EG, EG coated with NaNH\(_2\), EG coated with TPA and EG grafted with nitro-phenyl groups.
Because the saturation absorption of modified EG is influenced by the variety of the molecule used to functionalize, the open aperture z-scan was tested to confirm it. Fig. 3 (a) shows the Open Aperture Z-scan data of the origin EG and the functioned EG. The nonlinear optical constant $\beta$ is deduced after fitting the data with the theory given in refer. [14]. The fitting results are given in Fig. 3(b), comparing to the ratios of the slower lifetime $\tau_2$ from the pump-probe data. It was found that the transmittance of functioned EG increases earlier as the positions of samples move to $Z_0$ from Fig. 3 (a). The nonlinear absorption constant $\beta$ was increased linearly after the functionalization, corresponding to the ratio of the slower lifetime $\tau_2$ as shown in Fig. 3 (b). It could be explained that the greater influence of slower lifetime $\tau_2$ leads to an easier saturable absorption and a greater nonlinear absorption. So the appropriate functionalization can adjust the saturation absorption easily. We have checked that the pump-probe and Z-scan experiments carried out on the films of the functionalization materials: NaNH$_2$ and TPA. They did not show any signals under the same conditions.

![Figure 3(a)](image1)
![Figure 3(b)](image2)

Fig. 3 (a) Open aperture Z-scan data of EG, EG coated with NaNH$_2$, EG coated with TPA, and EG with nitro-phenyl group on the power 360 $\mu$W of the 780 nm fs laser. The solid lines are the fits; (b) the nonlinear optical constant $\beta$ increases linearly as the ratio $\tau_2$ increase.

4. Conclusions

In summary, the influences of three functionalization methods for EG on photo-generated carrier relaxation and recombination dynamics have been investigated by pump-probe and z-scan experiments using <50 fs laser pulses centered at 780 nm. The results display that the different modified graphene have obvious different changes both on the fast lifetime and the slow lifetime. The ratios of slow lifetime on the EG coated NaNH$_2$ are increased about 6 times compared to origin EG, leading to an obvious saturation absorption enhancement proved by the z-scan. Therefore, the functioned EG may have the potential value as a tuneable absorber in ultrafast lasers and ultrafast optical switches.

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References