Research article

Effects of light on the resistivity of chemical vapor deposited graphene films

Yudong Mo 1, Jose M. Perez 1,* Zhou Ye 2, Lei Zhao 3, Shizhong Yang 3, Liuxi Tan 3, Zhaodong Li 2, Feng Gao 2, and Guanglin Zhao 2,*

1 Department of Physics, University of North Texas, Denton, Texas 76203
2 Department of Physics, Southern University and A & M College, Baton Rouge, LA 70813
3 Department of Computer Science/LONI, Southern University and A & M College, Baton Rouge, LA 70813

* Correspondence: Email: jperez@unt.edu; guang-lin_zhao@subr.edu.

Abstract: We report that the resistance of a chemical vapor deposition (CVD) grown graphene film transferred onto an SiO₂ substrate increases to higher saturation values upon exposure to light of decreasing wavelength from the visible to ultraviolet. Light in the visible range causes a slight increase of up to 10% in saturation resistance. A significant increase in resistance is found starting at about 400 nm. The saturation resistance approaches up to 3 times the original resistance at 254 nm after 5 min. When the light is removed, the resistance falls to its original value with a time constant of several days. The effect is not observed for samples of CVD-grown graphene films on SiO₂ that have been heated in vacuum at 600 °C, nor single-crystal graphene mechanically exfoliated onto SiO₂. We attribute the effect to photo dissociation of interfacial molecules such as H₂O adsorbed between the CVD-grown film and SiO₂ substrate at grain boundaries in the film.

Keywords: graphene; electronic properties; defects; light exposure; water adsorbates
1. Introduction

Graphene, a truly two-dimensional material with a carbon honeycomb planar structure, has attracted tremendous attention since its first realization by exfoliation in 2004 largely due to its unique electronic properties that make it a promising candidate in next generation electronic devices and sensors [1–7]. In graphene, all the carbon atoms are surface atoms, which is different from bulk materials where the number of surface atoms is only a small fraction of the total. As a result, all carbon atoms in graphene are exposed to the environment, which can make the electronic properties very sensitive to its surroundings. Many studies have been reported on the effect of adsorbates on the electronic transport properties of graphene [8–15]. Hydrogenation and oxidation, which are accompanied by a sp² to sp³ transition of the carbon bond, can convert graphene from a conductor to an insulator [16–20]. Chemical doping using NO₂ adsorbates can cause slight but detectable changes in the electronic properties [11]. Physisorption of H₂, O₂, N₂, CO, CO₂, and NH₃ does not significantly affect the electronic properties [12,13]. One of the main goals of these studies was to find a reliable way of changing graphene from a conductor to semiconductor, for electronic applications. The effects of H₂O molecules, one of the main components of the environment, on the electronic properties of graphene have also been reported. Yavari et al. observed a reduction in the conductivity of chemical vapor deposition (CVD) grown graphene in different humidity environments, and proposed that a band gap of up to 0.2 eV was opened [14]. Theoretical studies found that H₂O molecules play the role of electron acceptor when adsorbed on graphene, and this effect is enhanced by a silicon dioxide substrate [15]. Recently, there have been reports [21–24] suggesting that adatoms on graphene can be ionized by applying a gate voltage, and the ionization causes a sharp change in the electrostatic potential.

In this paper, we report that the resistance of a CVD-grown graphene film, which is transferred from deionized (DI) water to an SiO₂ substrate, increases as the wavelength of light incident on the film decreases from the visible to ultraviolet (UV). We attribute this phenomenon to photo dissociation of adsorbates such as H₂O between the graphene film and SiO₂ substrate that are adsorbed at grain boundaries in the film. Our results may be useful in electronic devices that utilize large-area CVD-grown graphene films. For example, in transparent conducting windows for flat panel displays, it may be desirable to have the conductivity of the CVD film constant while it is exposed to light, which may be accomplished by removing adsorbates from the interface. In addition, our results may provide a convenient method for tuning the resistivity of CVD-grown graphene films by varying the wavelength of incident light, and sensing the presence of interfacial adsorbates at grain boundaries and other defects.

2. Materials and Methods

Graphene was grown on a 25 µm thick copper foil by the CVD method in a tube furnace. The growth conditions were temperature of 950 ºC, flow rates of 50 sccm for H₂ and 100 sccm for CH₄, and total pressure of 30 Torr for 10 minutes. The copper foil was placed on a flat quartz block. After growth and cool down, the copper foil was placed in a 1 M Fe(NO₃)₃ solution with the growth side facing up. After the copper was etched, the graphene floated to the surface and was then transferred...
to DI water for cleaning purposes. Finally, the graphene was transferred from the DI water onto a SiO2/Si substrate consisting of a highly p-doped Si wafer covered with a thermally grown 300 nm SiO2 layer. The sample was not back gated.

Four electrodes were made on the sample by thermally evaporating 10 nm of Ti, 200 nm of Ag and 30 nm of Au consecutively on the sample at a pressure of 5 × 10⁻⁶ torr. The distance between opposite electrodes is approximately 3 mm. Four gold-coated copper probes were used to contact the electrodes. The I-V characteristics of the sample were measured using a Keithley 485 Picoameter and Keithley 487 Voltage Source programmed with Labview. The micro-Raman system used was a Nicolet Almega XR spectrometer with a spot size of 0.6 μm², a laser wavelength and power of 532 nm and 6 mW, respectively, and a spectral resolution of 2 cm⁻¹.

We used the above device structure to investigate the resistance of the graphene sample as a function of time while under exposure to light of different wavelengths. In the measurements, the output voltage between two of the electrodes is fixed at 1 V, while the current is recorded every 2 seconds as the sample is exposed to light. The light sources are light-emitting diodes (LEDs) of different peak wavelengths (630–380 nm) or a Xenon gas lamp (365 and 254 nm with filters) at a distance of 2 cm from the sample. The exposures are made in the following order: red (630 nm), orange (605 nm), yellow (595 nm), green (525 nm), aqua (507 nm), blue (472 nm), pink (440 nm), violet (420 nm) and UV (400 nm, 380 nm, 365 nm, and 254 nm). The exposures at different wavelengths are made by removing one light source from the enclosure and replacing it with another one. The intensity of the light at each wavelength is carefully calibrated and monitored by an optometer to ensure that light at each wavelength has the same incident intensity of 2 mW/cm².

3. Results and Discussion

Transmission electron microscopy (TEM) images of the CVD-grown graphene films were obtained using copper grids, as shown in Figures 1(a) and 1(b); the films have typical folds and few amorphous particles. A close view of the sample holder with four gold-coated copper probes for electrical contact is shown in Figure 1(c). Micro-Raman spectroscopy at different steps of the process was carried out. Graphene grew only on the side of the copper foil facing the gases as determined using Raman spectroscopy. No Raman signal corresponding to carbon was observed on the lower surface of the foil. After transfer to the SiO2 substrate, as shown in Figure 1(d), the 17 cm⁻¹ full-width-at-half-maximum (FWHM) of the 2D Raman peak at about 2700 cm⁻¹ demonstrates that the sample is monolayer graphene. The Raman spectrum of low-defect density monolayer graphene is also characterized by a ratio between the 2D and G peaks of about 4. In our samples, the ratio is about 1. We attribute this to defects in the film. The Raman spectra in Figure 1 show a slight D peak at about 1330 cm⁻¹ that is due to defects. Figure 1(e) shows the I-V characteristics of the graphene device and demonstrates that the device has good Ohmic contacts.
Figure 1. (a) and (b) TEM images of a typical CVD graphene sample with scale bars of 1 µm and 100 nm, respectively. (c) Photograph of our device. (d) Micro-Raman spectra of a graphene sample. Black: before 254 nm UV light exposure, Red: after 10 minutes of exposure to 254 nm UV light, Blue: after subsequent heating at 600 °C for 10 minutes. (e) I-V characteristics of a graphene sample measured in air at room temperature.

We observe that the smaller the wavelength of incident light, the greater the saturation value of the sample’s resistance, as shown in Figure 2. The experiments were carried out by changing the wavelength of the incident light from longer to shorter. The total exposure time at each wavelength was 10 minutes. As shown in Figure 2(a), in the visible light range, incident light only slightly increases the resistance of the sample. When the incident light is in the UV range (starting from about 400 nm), the saturation resistance of the sample increases to a higher value. The largest saturation resistance observed is about 2.5 times the value before light exposure. The small abrupt drop in resistance each time the light source is replaced every 10 minutes observed in Figure 2(b) is due to the fact that the I-V measurement is continuous. During the time period during which the light source is replaced (usually 20–30 seconds), the resistance of the sample decays slightly, although the drop is insignificant in comparison to the saturation value of resistance resulting from the subsequent exposure.

The resistance vs. time curve of the sample shown in Figure 3(a) shows a typical exponential increase with a time constant of several minutes; in this case, 1.6 minutes for 254 nm. When the incident light is turned off, the resistance decays exponentially with a much longer time constant of tens of hours; in this case, 21 hours after 254 nm irradiation, as shown in Figure 3(b).
fluctuations in Figure 3(b) are attributed to uncontrollable humidity changes in the environment during the long decay [15]. After decay, the increase in resistance upon irradiation is repeatable.

Figure 2. Resistance vs. wavelength of incident light. Exposure time for each wavelength is 10 minutes. (a) Resistance vs. wavelength in the range 630 nm to 254 nm as a function of time; (b) An enlarged graph for the visible light range in (a); (c) Saturation value of resistance vs. wavelength of incident light.
Figure 3. (a) Resistance vs. time measured under exposure to 254 nm light; (b) Time decay of resistance after turning off the 254 nm light.

The increase in resistance vs. time is also observed when the sample is placed in vacuum at $1 \times 10^{-5}$ Torr and exposed to 254 nm UV light. This implies that the density of H$_2$O and other molecules in the air is not a significant parameter in the observed phenomenon. Micro-Raman spectroscopy was carried out after the sample was irradiated by 254 nm UV light. No significant changes of the D peak in the Raman spectrum was observed. This excludes the possibility of defect creation or hydrogenation of the graphene sample induced by light exposure, as the appearance of the D peak is an indicator of defects and hydrogenation of graphene [18]. Furthermore, we did not observe a G peak shift, as known in the case of graphene oxidation [25].

We cleaned samples of CVD-grown films on SiO$_2$ substrates by heating them at 600 °C in a vacuum of $1 \times 10^{-7}$ Torr for 10 minutes to remove residual adsorbates such as H$_2$O molecules. After cooling the sample to room temperature (RT), it was removed from the vacuum chamber and micro-Raman spectra were measured in air, as shown in Figure 1(d). The Raman data show that heating did not introduce defects into the sample. We then carried out the electrical measurements under irradiation at 254 nm on cleaned samples that had been subsequently stored in air at RT and a relative humidity of 45% for two days, and did not observe an increase in resistance. We also carried
out the same experiments on monolayer graphene mechanically exfoliated from highly oriented pyrolytic graphite (HOPG) onto an SiO₂ substrate at RT and a relative humidity of 45%, and did not observe an increase in resistance with light exposure. In addition, we carried out electrical measurements under irradiation at 254 nm on CVD-grown films transferred onto mica and glass substrates, and observed an increase in resistance.

Based on these experimental observations, we conclude the following. First, gases in the atmosphere do not directly influence the light induced resistance increase since the effect is observed both in air and vacuum. Second, both CVD-grown and mechanically exfoliated graphene samples have layer(s) of H₂O molecules at the interface between the graphene and SiO₂ substrate from prior exposure of the substrate to air [26]. However, a significant difference between CVD-grown graphene and an exfoliated sample is that the CVD-grown sample is full of defects mainly at grain boundaries [27]. This suggests that the effect is correlated to grain boundaries since the effect is not observed in single-crystal exfoliated graphene but observed in CVD-grown graphene films that contain grain boundaries. Third, CVD-grown graphene has adsorbates on almost all of its grain boundaries [27]. Heating in high vacuum eliminates the effect, which suggests that the effect is due to adsorbates bound on grain boundaries that are desorbed by heating. The specific adsorbates bound at grain boundaries in CVD-grown films are not known [27]. However, since water is used in the etching of the copper foil and transferring of the film to the SiO₂ substrate, it may be one of the adsorbates. Since samples of CVD-grown films on SiO₂ substrates that are heated in vacuum and then exposed to air for two days do not show the effect, we conclude that gases adsorbed during this exposure are not responsible for the effect. Such gases would be mainly adsorbed above the graphene film since gases typically require temperatures greater than 340 ºC to readily intercalate into the graphene/substrate interface [28,29]. In particular, it takes H₂O over 70 days at RT to diffuse on the order of 10 µm into the graphene/SiO₂ interface [26]. This distance is over two orders of magnitude smaller than our sample dimensions and distance between electrodes. This suggests that the effect is due to adsorbates at the graphene/SiO₂ interface.

The increase in saturation resistance with decreasing wavelength suggests that the effect is due to photo-induced processes. It has been reported that photo dissociation of H₂O adsorbed between the basal plane of single-crystal graphene and an SiO₂ substrate occurs at an incident wavelength that exhibits a maximum intensity between 150 and 200 nm [30]; these authors proposed that the dissociation was also facilitated by –OH silanol groups on the SiO₂ surface. In our experiments, a large increase in resistance is observed at about twice the wavelength (400 nm), possibly because the molecules are chemisorbed at grain boundaries and consequently already partially dissociated, requiring less energy to dissociate them further. First principles calculations show that dissociation of H₂O adsorbed on defects in graphene occurs at activation energies lower than half of those of bulk water along many reaction pathways [31]. The chemical species that we propose are produced from water molecule dissociation are hydrogen and hydroxyl radicals, similar to the species produced in Ref. [30]. As discussed in Ref. [30], hydrogen and hydroxyl radicals may react with carbon atoms in the graphene lattice producing sp³ bonds that locally distort the lattice. The hydrogen radicals may produce hydrogenation of carbon atoms that has been reported to increase the resistivity of graphene [16,18]. Hydrogenated graphene has been reported to slowly dehydrogenate and return to its original state over a period of hours to days at room temperature [16,18]. The exact recovery
mechanism is not well understood, but may involve desorption of hydrogen or recombination of hydrogen and hydroxyl species.

4. Conclusions

In summary, we have observed that the resistance of CVD-grown graphene films transferred onto SiO2 substrates increases as the wavelength of incident light decreases from the visible to UV. We attribute this effect to photo dissociation of interfacial adsorbates at grain boundaries in the film. We propose that a possible adsorbate is H2O, based on the large increase in resistance at 400 nm. This is consistent with reports on the dissociation of interfacial H2O between defect-free graphene and SiO2 occurring at 200 nm, and theoretical predictions that the dissociation energy of H2O adsorbed on defects in graphene is less than half that of bulk water. Our results may be useful in the design of electronic devices that utilize large-area CVD-grown graphene films, and as a method for tuning the resistivity of CVD-grown films and sensing interfacial adsorbates on grain boundaries. We believe additional experiments and computer simulations would help us to better understand the quantum behavior of H2O adsorbed between defects in graphene and the SiO2 substrate.

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Conflict of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

References


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