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Conductive stability of graphene on PET and glass substrates under blue light irradiation

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ABSTRACT

Electrical properties of graphene transparent conductive film under visible light irradiation are investigated. The CVD-grown graphene on Polyethylene Terephthalate (PET) and glass substrates for flexible and rigid touch screen display application are chosen for research. The resistances of graphene with and without gold trichloride (AuCl₃) doping are measured in vacuum and atmosphere environment under blue light irradiation. Results show that the conductivities of all samples change slowly under light irradiation. The change rate and degree are related to the substrate material, doping, environment and lighting power. Graphene on flexible PET substrate is more stable than that on rigid glass substrate. Doping can improve the electrical conductivity but induce instability under light irradiation. Finally, the main reason resulting in the graphene resistance slowly increasing under blue light irradiation is analyzed.

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1. Introduction

Graphene is an excellent material of transparent conductive films (TCFs) for its good conductivity, high transmittance and great flexibility. It has shown high potential as the replacement material of ITO (Indium tin oxide) in various optoelectronic devices, such as touch screen display, electronic paper [1,2], etc. TCFs work under visible light irradiation in most cases. There were many reports about the electrical conductivity changes of the graphene when irradiated under ultraviolet light [3–7], which was not the actual working environment. Some work under visible light irradiation has also been presented about the graphene modified by the photochromic molecules [8], which was not applied as TCF for touch screen displays. So far less work has addressed the electrical stability under visible light radiation for large area graphene, which should be concerned for TCF applications. In addition, Although AuCl₃ doping can improve the electrical conductivity [9], its impacts on the conductive stability of graphene under blue light irradiation had not been reported.

In this paper, the electric conduction properties of chemical vapor deposition (CVD) single layer graphene under visible light radiation are presented. The graphene films should be attached on a substrate in application. Polyethylene Terephthalate (PET) and glass are the most common materials representing the flexible and rigid transparent substrate respectively. For touch screen of LED-backlit LCD, the graphene TCF mounted on the LCD panel is irradiated by LED backlight. Blue light with the largest photon energy occupies a large proportion in the emission spectrum of LED backlight [10]. Therefore, we focus on the electrical stability of graphene on the two substrates under blue light radiation.

2. Experimental details

2.1. Sample preparation

The samples used in the experiment were a large-scale CVD monolayer graphene grown on Cu foil and transferred onto the PET/glass substrate with polymethyl methacrylate (PMMA) film by etching the Cu foil. AuCl₃ solution was used to dope the graphene films to improve the electrical conductivity. The specific process steps were as follows: (1) PMMA was need to spread on the graphene grown on Cu foil and then the PMMA-graphene-Cu was put in the copper etching solution to get the PMMA-graphene film by drying. (2) PMMA-graphene film needed to be washed with deionized water. (For doped samples, when this step was completed, the PMMA-graphene film would be immersed in AuCl₃ aqueous solution for 3 min and washed with deionized water and then the AuCl₃ doped PMMA-graphene film had been got.) Afterwards PMMA-graphene films were picked up by the substrate materials including glass and PET and then heated to 140°C for forty minutes. In addition, PMMA could be removed by acetone. Finally, the required graphene samples on PET/glass substrate had been obtained. In order to facilitate subsequent measurement, the PET-based graphene samples were cut into 3 × 15 mm rectangle strip. For glass-based samples, the graphene patterns with the same size were defined by photolithography and oxygen plasma etching of graphene layers on the glass. Both ends of the samples were smeared with silver paste as extraction electrodes. The sheet resistances of the graphene films on the PET and glass

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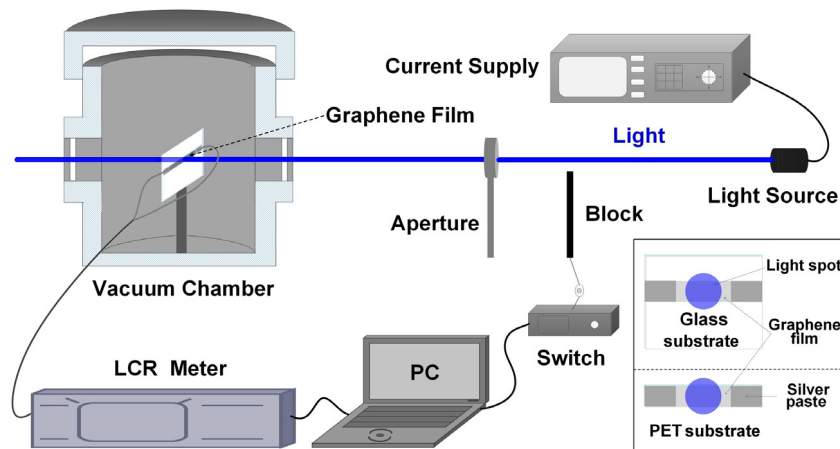


Fig. 1. Schematic diagram of experimental system.

substrates without doping were 1265 Ω/sq and 304 Ω/sq respectively. After doping, the corresponding sheet resistances were reduced to 668 Ω/sq and 102 Ω/sq .

2.2. Experimental system

The experimental system is shown in Fig. 1. For the electrical measurements, the samples were placed inside a vacuum chamber which can provide the minimum pressure of 0.1 Pa. Experiments were performed before and after the air is extracted, corresponding to the atmosphere and vacuum environment respectively. All of the electrical measurements were conducted at room temperature using an impedance analyzer (WK4100 LCR METER) interfaced to a computer. The light source was a power adjustable blue light laser diode with the center wavelength of 450 nm. On the sample surface, the beam diameter was controlled approximately 5 mm by an aperture and the light power were

4, 8, 12 and 16 mW. The corresponding power densities were 20–80 mW/cm^2 . Measurements were carried out in a standard light–dark cycle of 300 s light followed by 300 s total darkness, after the resistance values were stable.

3. Results and discussion

The relative rate of resistance change $\Delta R = (R - R_0)/R_0 \times 100\%$ is utilized to investigate the influence of the light on the samples, where R_0 is the average resistance in the first 300 s without light irradiation. For the PET-based graphene after lighting, the resistance decreases immediately at the very beginning and then increases slowly (Fig. 2). The rapid decrease is obvious for undoped sample especially in atmosphere with limit relative change less than 0.25%. The resistance changes for doped sample are larger than that of the undoped sample.

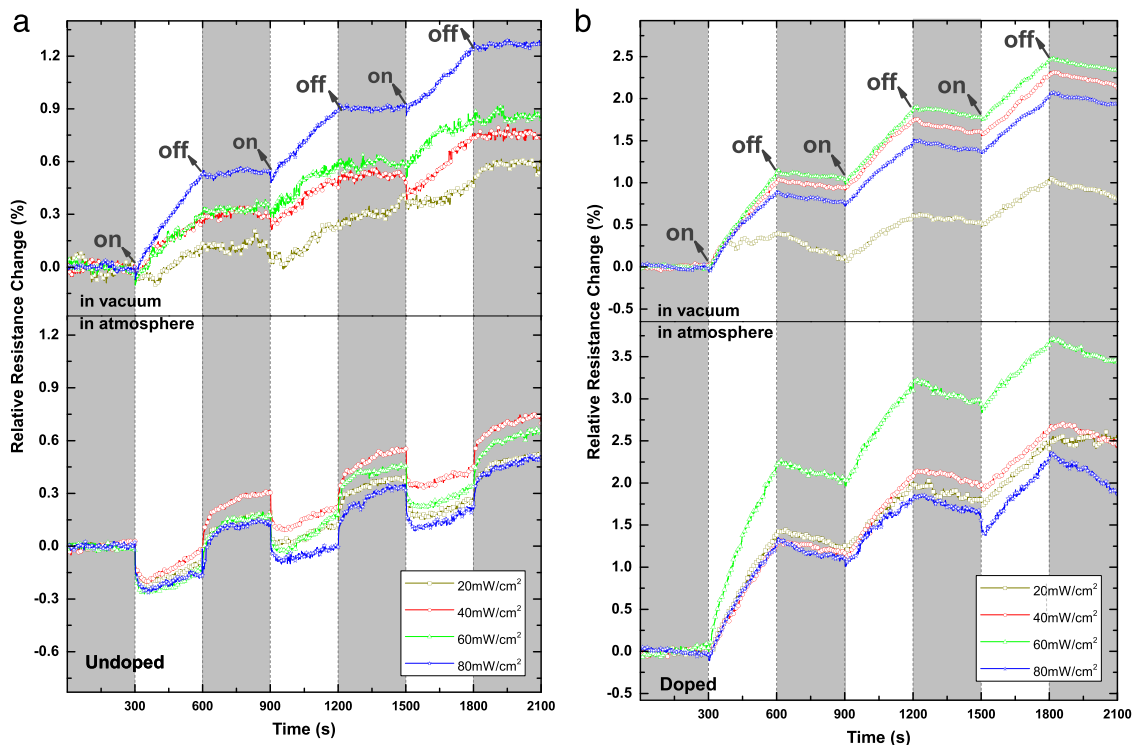


Fig. 2. Time response of the relative rate of resistance change for (a) undoped and (b) doped PET-based graphene in vacuum and atmosphere environment. The on/off arrows represent the light on and off.

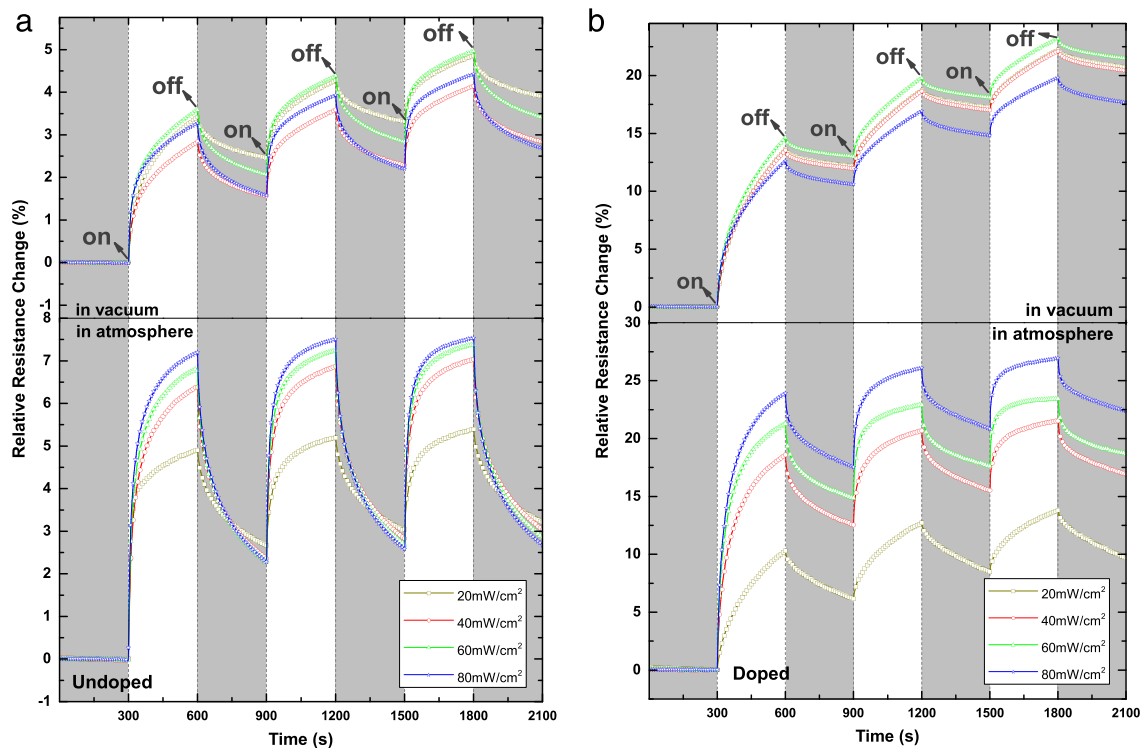


Fig. 3. Time response of the relative rate of resistance change for (a) undoped and (b) doped glass-based graphene in vacuum and atmosphere environment.

For glass-based graphene as shown in Fig. 3, the resistance change trend is similar to the PET-based graphene. While the photoresponse at the lighting moment is not obvious. The resistance increases exponentially under lighting, while decreases slowly in an exponential form as well after the light is switched off. The rate and degree of change are greater than that of PET-based graphene. For doped sample, the change degrees are as high as 27% and 23% in atmosphere and in vacuum respectively. As well as the PET-based samples, the doped graphene has greater changes than that of undoped graphene.

The transient falling of resistance can be attributed to the photoconductive effect of semiconductor [11]. Different from glass substrate, when exposed to the ambient air, the PET substrate may be doped as weak p-type semiconductor due to the easier physisorption of the oxygen molecules [12–14]. The AuCl_3 doped graphene presents a obviously less transient falling of the resistance because of the contribution of the AuCl_3 doping to the conductivity. The photoconductive effect is relatively quite weak because the doping level is limiting, which may not influence the performance of device based on graphene.

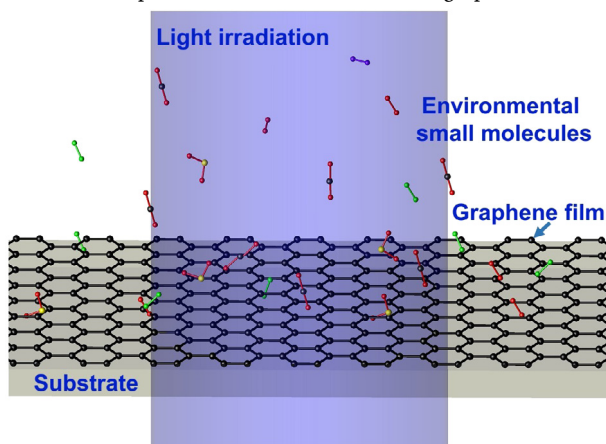


Fig. 4. Graphene film sample under irradiation.

However, the slow increase of resistance might have negative effects on the device. To exclude the thermal effect, we measured the temperature of the substrate under the same light source with laser calorimeter. The temperature rise is less than 10 mK and the photo-thermal effect could be completely ignored. Another possible reason resulting in the slow increase of resistance may be the photo-desorption of the environmental molecules near the surface [15–17]. The small molecules adsorbed physically on the surface may provide carriers and reduce the resistance (see Fig. 4). When the graphene is irradiated, the photo-desorption of small molecules on the graphene surface decreases the carrier concentration, thus increasing the resistance of graphene. When the light is turned off, the re-adsorption of small molecules onto the surface of graphene film increases the carrier concentration again, thus decreasing the resistances. For AuCl_3 doped graphene, more carriers can be provided in the graphene [18]. Thus the resistance variation induced by irradiation is larger than that of undoped sample.

4. Conclusion

This paper presents the experimental results of the conductivity changes of graphene on PET and glass substrates under blue light irradiation of different power, in vacuum and atmosphere environments. Results show that the conductivity of all samples changes slowly under light irradiation. Photo-desorption of small molecules on the graphene surface may be the main reason resulting in the graphene resistance increasing. Graphene on flexible PET substrate is more stable than that on rigid glass substrate. Doping can improve the electrical conductivity but induce instability under light irradiation.

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Appendix A. Supplementary data

Supplementary material related to this article can be found online at <http://dx.doi.org/10.1016/j.optcom.2017.05.006>.

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