γ radiation caused graphene defects and increased carrier density*

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We report on a micro-Raman investigation of inducing defects in mono-layer, bi-layer and tri-layer graphene by γ ray radiation. It is found that the radiation exposure results in two-dimensional (2D) and G band position evolution with the layer number increasing and D and D′ bands rising, suggesting the presence of defects and related crystal lattice deformation in graphene. Bi-layer graphene is more stable than mono- and tri-layer graphene, indicating that the former is a better candidate in the application of radiation environments. Also, the DC electrical property of the mono-layer graphene device shows that the defects increase the carrier density.

Keywords: graphene, γ ray radiation, Raman spectrum, defects

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1. Introduction

Recently, with the development of science and technology, researchers are becoming more and more interested in the exploration of the universe, and have begun to detect the Moon, Mars, and so on. In these detection processes, equipment that is small with fast properties is required to record the data. The smaller the device and the higher the speed, the more beneficial such exploration is, and thus it is rather a challenge to materials suited for these devices.

Meanwhile, graphene has attracted much attention since the discovery of its existence.[1−3] It is considered as an ideal candidate for high speed devices and circuits because of its extremely high carrier mobility and rather high saturation velocity.[4,5] However, the presence of defects and disorder in the material degrades these properties to a large extent. Defects and lattice distortion in graphene can easily be introduced by charged particles, such as electrons.[6−9] For devices used in the aerospace or nuclear industry, where the radiation characteristics may be a major concern, it is essential to ascertain the radiation effect on the properties of graphene. In this paper, our attention focuses on the γ ray radiation effects on mono-, bi- and tri-layer graphene samples. It is observed that γ ray radiation results in defect formation in mono-, bi- and tri-layer graphene samples. However, bi-layer graphene exhibits greater stability in the radiation environment, indicating that it might be used in high speed devices in the aerospace or nuclear industry. In addition, we fabricate a graphene field effect device and measure the dc electrical properties before and after γ radiation. Through these analyses, we find that the defects can increase the carrier density and form n-type doping.

2. Methods

Samples used in our experiment were prepared by micromechanical cleavage of highly oriented pyrolytic graphite (HOPG), as described in Ref. [1]. Initially, the mono-layer, bi-layer and tri-layer graphene were identified through optical microscopy and registered. The samples were further confirmed by analysing the corresponding Raman two-dimensional (2D) band.[10] The Raman measurements were performed at room temperature with a Renishaw inVia Raman system at a wavelength of 532 nm. As for the radiation exper-

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iment, cobalt-60 (Co-60) γ ray, which is popular for radiation tests, was used as a radiation source for a total ionizing dose (TID) radiation test. The registered samples were transferred into a Co-60 radiation chamber at room temperature and irradiated with a rate of 50 rad/s radiation adsorbed dose for 180 min. The samples were characterized by Raman spectroscopy before and after radiation. Furthermore, we fabricated a mono-layer graphene field effect transistor and performed the TID radiation test on it.

3. Results and discussion

Figure 1 shows a typical graphene flake fabricated by the micromechanical cleavage method. It can be seen that the flake is composed of several regions marked with different colour contrasts that relate to different layers of graphene (i.e., (i) the lightest region (mono-layer), (ii) the darker region (bi-layer), and (iii) the darkest region (tri-layer)).

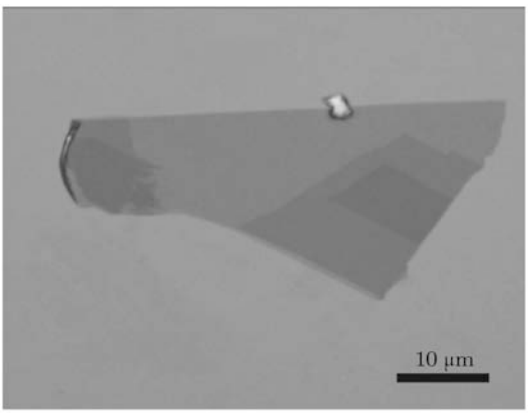


Fig. 1. A typical graphene flake fabricated by the micromechanical cleavage method. The different contrasts correspond to different layer numbers in the graphene.

Fig. 2 shows a typical Raman spectrum of graphene with various layers before and after γ ray radiation. The main features lie at around 1580 cm^{-1} and 2680 cm^{-1} for visible excitation, which are the so-called G and 2D peaks, respectively. The peak at ~1580 cm^{-1} originates from the G mode of graphene, which is due to the bond stretching of all pairs of sp^2 atoms in both rings and chains. The other peak at ~2680 cm^{-1} is the 2D mode, the features of which are due to the double-band dispersions of bi-layer graphene caused by the interaction of the graphene planes, which is the second-order phonon effect.[11] The 2D mode peak shifts towards a higher position with an increase in layers. The feature of 2D mode is due to the double-band dispersions of bilayer graphene caused by the interaction of the graphene planes. The 2D mode peak of mono-layer graphene is blue shifted about 10 cm^{-1}, from 2672 cm^{-1} to 2682 cm^{-1}, while bilayer graphene is shifted about 4 cm^{-1}, from 2682 to 2686 cm^{-1}.

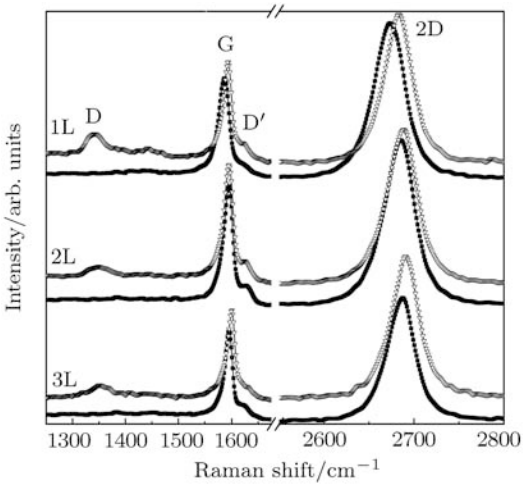


Fig. 2. Typical Raman spectra of graphene before (solid square line) and after (open triangle line) radiation. The D-band is sensitive to disorder/defect generation.

As for mono-layer graphene, there is a significant blue shift of G mode from 1585.4 cm^{-1} to 1592 cm^{-1} after radiation. For bi- and tri-layer graphene, the blue shift is much weaker than that of mono-layer graphene. The blue shift of the Raman peak may be caused by the defects in the lattice, which are caused by radiation and the relevant lattice deformation. For bi- and tri-layer graphene, the carbon atoms are coupled with each layer, making it more stable than mono-layer graphene, and little influence in the radiation environment.[7,12–14]

The appearance of the D mode peak (the peak at ~1350 cm^{-1}) is also observed when graphene is exposed to a radiation environment, which indicates that the defects are formed in graphene by γ ray radiation. D mode is forbidden in perfect graphene and becomes active only in the presence of disorder. The D peak is due to the breathing modes of sp^2 atoms in rings. It originates from intervalley scattering that connects two adjacent K and K' points at the Brillouin zone boundary via a second order process that requires an in-plane transverse optic (iTO) phonon and a symmetry breaking perturbation. These phonons are not Raman-active, owing to the momentum conservation in the scattering. However, they become active in the presence of structural disorder, as described by the

disordered band.[15−17] The black line spectrum (before radiation) indicates the high quality of graphene and its crystalline nature. The emergence of the D band after radiation means that defects are introduced. The D mode is dispersive; it varies with photon excitation energy, even when the G peak is not dispersive. Figure 3(a) shows the variation in the D peak with layer number after γ radiation. In general, the D-peak position will decrease with increasing disorder.[17] Thus, compared with that in mono- and tri-layer graphene, few defects are introduced in bilayer graphene.

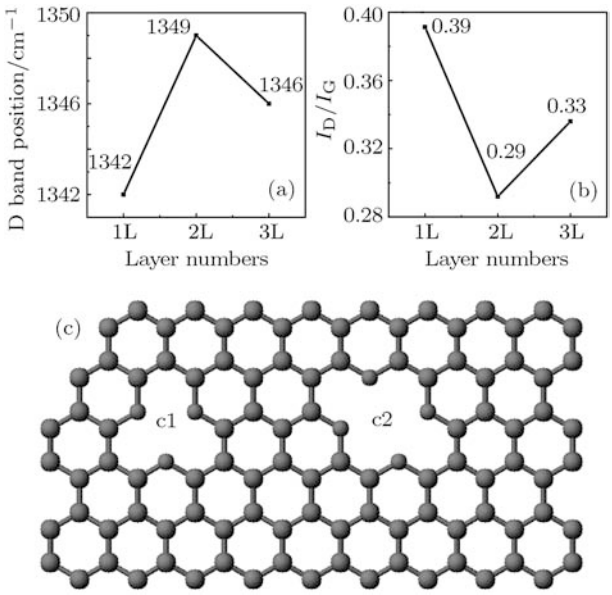


Fig. 3. (a) Evolution of D band intensity with the number of layers after radiation. (b) The evolution of I_D/I_G with the number of layers, I_D and I_G are the intensities of D and G band, respectively. (c) Schematic diagram of defects in graphene after γ ray radiation.

A small peak at $\sim$1620 cm^{-1} is also observed after exposure, which is designated as D$'$ mode. The D$'$ band at the right shoulder of the G mode is a weak intravalley transition that requires one in-plane longitudinal optic (iLO) phonon and a symmetry break, which indicates the degree of the defect.[15,18−20] Judging from the result of our experiment, after radiation, D$'$ band intensities in graphenes of three kinds of layers are enhanced (see Fig. 2), which confirms that the defects are induced by γ radiation.

The intensity ratio of D-band to G-band (I_D/I_G) in the Raman spectrum is very sensitive to the size of crystal (L_a). In carbon material, the I_D/I_G ratio is a linear function of the inverse of the crystallite size of graphene.[17,21−23] While in the graphene material with defect in the film, the intensity ratio (I_D/I_G) varies; at a fixed λ, I_D/I_G increases with increasing disorder, according to

$$\frac{I_D}{I_G} = \frac{C(\lambda)}{L_a}, \tag{1}$$

where C is a variable scaling coefficient and λ is the laser excitation wavelength of the Raman spectrum. Fig. 3(b) shows the evolution of the intensity ratios (I_D/I_G) with the number of layers. It is noted that the ratio of I_D/I_G changes significantly after γ ray radiation, the ratio I_D/I_G is the smallest for the bilayer graphene, but it is the biggest for the monolayer, which indicates that bilayer graphene is much more stable in γ ray radiations environments.

As mentioned above, defects are introduced in the few-layer graphene in the γ ray radiation environment. These results are in agreement with previous computer simulations[24] and the electron-beam radiation conclusions.[6,7] The γ ray bombardment is capable of creating radiation defects at certain points. A schematic diagram of defects in graphene is shown in Fig. 3(c). In order to damage the carbon atoms on the surfaces of nanostructures, the energy transferred to them must exceed a certain threshold value E_d. This value in carbon materials ranges from 15 keV to 90 keV.[25] Assuming that the thresholds of graphenes with different numbers of layers are similar, and taking into account that in our experiments the γ ray energy is about 1.33 MeV, we can conjecture the vacancies due to the knock-on damage to be a possible mechanism for the observed lattice modification, which involves the Compton effect as well as the photoelectric effect with the creation of electron–hole pairs. The electrons ejected from the atoms by γ-photons have high kinetic energy and are the direct cause of the formation of interstitial atoms and other kinds of defects in grapheme.[26] The formation of defects and the relevant lattice deformation are responsible for the spectrum modification.

In order to further investigate the influence of γ radiation on conductance, we fabricated a mono-layer graphene field effect device (see the lower right inset in Fig. 4(a)) and measured the output characteristics (see Fig. 4(a)). It was found that the graphene field effect transistor studied here exhibits a nearly linear I_{DS}–V_{DS} dependence up to 0.4 V for the back gate voltage ranges measured. The absence of current saturation is due to the fact that graphene is a zero-gap semiconductor. Due to the same behaviours for all of the back gate voltage, we plot only the output characteristic curves with $V_g = -30$ V before and after

γ radiation (shows in the inset). It is suggested that the slope of the output characteristic curve after γ radiation is greater than that before radiation. The slope of the characteristic curve is the conductance of the graphene field effect transistor. Figure 4(b) shows measured values of conductance G ($G = I_{\rm D}/V_{\rm D}$), each as a function of back-gate voltage ($V_{\rm g}$), of the graphene transistor before and after γ radiation. It is known that $G \propto \sigma$ for the same device, where $\sigma = qn\mu$, with σ being the 2D conductivity, q the electron charge, a constant, and n the 2D carrier density that is controlled by the gate voltage, μ the mobility of material. For this graphene field effect device, G and σ increase after γ radiation, which is shown in Fig. 4(b). Because the defects introduced by γ radiation (mentioned above) can make the scatter increase and the mobility decrease,[27] the enhancement of G and σ after γ radiation may be due to the increase in carrier density. Defects introduced by γ radiation enhance the doping of graphene. It has been reported that doping and defects can enhance the conductivity of graphene films.[28,29]

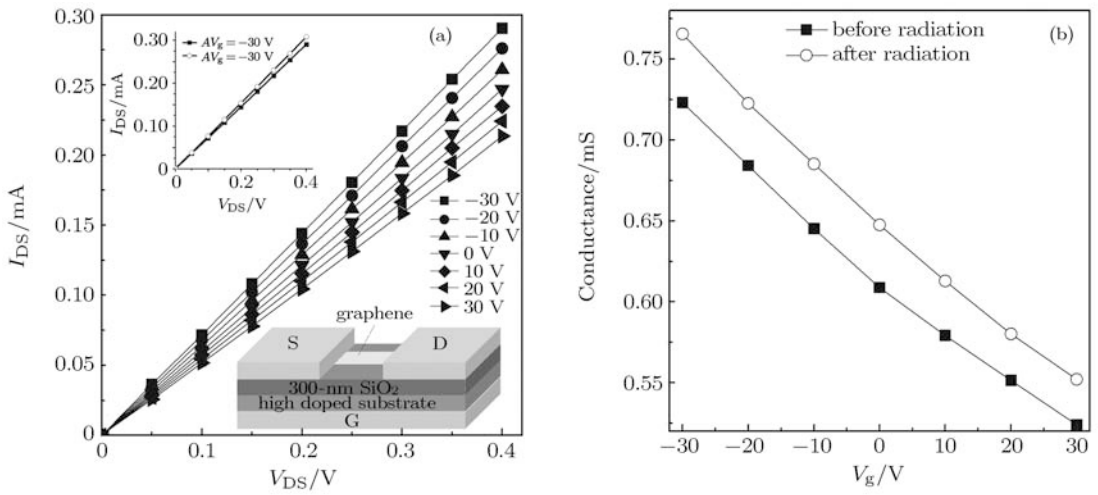


Fig. 4. (a) Measured output characteristics of a mono-layer graphene field effect transistor before γ radiation with the back gate voltage ($V_{\rm g}$) ranging from −30 V to 30 V. $I_{\rm DS}$ is the electric current of the source and drain, and $V_{\rm DS}$ is the voltage between the source and drain. The lower right inset shows a schematic of the device and the above left inset shows the same device before and after γ radiation, at the $V_{\rm g} = -30$ V. The open circle is the result after γ radiation, while the solid square is the result before γ radiation. (b) Measured conductances each as a function of back-gate voltage ($V_{\rm g}$) of the graphene transistor before and after γ radiation. Here the open circle is the conductance after radiation and the solid square is the conductance before radiation.

4. Conclusion

Radiation influence on the few-layer graphene is studied. Defects are produced and induce crystal lattice deformation, which is confirmed by the blue shift of the G band, and the increase in the D and D′ bands after radiation. It is found that bi-layer graphene suffers less influence than mono- and tri-layer graphene, indicating that bi-layer graphene has many more potential applications in radiation environments. The results have important implications for graphene characterization and graphene-based device application, such as in space exploration. Also, the DC electrical property of the mono-layer graphene device shows that the defects increase the carrier density.

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