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Raman and morphology visualization in epitaxial graphene on 4H-SiC by Nitrogen or Argon ion irradiation

Jin-Hua Zhao [a,*], Xi-Feng Qin [a], Feng-Xiang Wang [a], Gang Fu [a], Xue-Lin Wang [b]

[a] School of Science, Shandong Jianzhu University, Jinan 250101, China
[b] School of Physics, Key Laboratory of Particle Physics and Particle Irradiation, Ministry of Education, and State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, China

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ABSTRACT

Graphene is a one-atom-thick planar sheet of carbon atoms that are densely packed into a honeycomb crystal lattice and is attracting tremendous interest since being discovered in 2004. Epitaxial growth of graphene on silicon carbide (SiC) is an effective method to obtain high quality layers. In this work, the effects of irradiation on epitaxial SiC/graphene were studied. The samples were irradiated with Nitrogen and Argon ions at an energy of 200 keV and different fluence with 4×10^{12} ions/cm^2 to 1×10^{13} ions/cm^2. The results of Raman measurements indicate that ion beam irradiation causes defects and disorder in the graphene crystal structure, and the level of defects increases with increasing ion fluence. Surface morphology images are obtained by atomic force microscope (AFM). This work is valuable for the potential application of epitaxial graphene on SiC in the field of optoelectronics devices.

1. Introduction

Graphene is a single layer of carbon atoms organized into a honeycomb crystal lattice structure. It is attracting tremendous interest and has demonstrated uses in a number of applications since it was fabricated by mechanical cleavage of graphite [1]. Graphene research developed rapidly because of its prominent properties such as peculiar electron transport, ultra-strong chemical and mechanical stability, potential applications and research value as a low dimensional carbon-based material [2–4]. A large proportion of graphene research has gone into high-speed optoelectronic devices and semiconductor devices [5–7]. Epitaxial growth on silicon carbide (SiC) is one of the methods used to obtain graphene [8,9]. Compared to the graphene flakes fabricated by conventional micromechanical cleaving, epitaxial graphene on SiC has some specific advantages and properties [8–11]. Firstly, it can overcome the size limitation grown on SiC and offers realistic prospects for large-scale graphene samples. Secondly, the layer number of graphene can be easily controlled by adjusting the growth conditions. Thirdly, it has an inherent band gap near the K points and this is a property that is crucial for its use in electronic devices. The existence of a gap attributed to the mismatch between the graphene and the SiC substrate can have profound effects on the physical and electronic properties of epitaxial graphene.

Traditionally, ion irradiation has been used to dope semiconductor materials and recent research indicates that it is now a mature tool for surface modification of materials. Hundreds of materials have used ion irradiation in this way. The main advantage of the method is the fact that a number of process variables such as energy and fluence can be used in order to control the bombardment [12–16]. In addition to the detrimental effects on the properties of target materials, ion irradiation can also have beneficial effects on material modification. For example, ion beams may serve as tools to form waveguide structures [13]. Similarly, in graphene it is possible that it may change the morphology in a controllable manner, and tailor its mechanical, electronic, or even magnetic properties according the requirement. To realize enormous applications in electronic devices, it is necessary to be able to adjust the electronic properties. Therefore, research on the irradiation of solids with energetic particles is necessary to understand irradiation-induced modification of materials. Contrary to bulk solids, graphene can be an ideal system for studying effects of ion irradiation on solid targets in various regimes corresponding to the nuclear and electronic stopping due to its well-controlled structure. Thus, from the viewpoint of fundamental aspects of ion–solid interactions, graphene is an extremely interesting target, especially on the degradation of nuclear components.

Based on these advantages, ion irradiation has become an outstanding alternative way to modify graphene samples and has been performed on graphene in numerous studies [14,17–23]. Al-Harthi et al. [19] investigated the changes of surface morphology

* Corresponding author. Fax: +86 531 88363350.
E-mail address: zhaojinhuazjh@gmail.com (J.-H. Zhao).

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Table 1
The irradiation conditions used in our experiments.

Ions	Energy (keV)	Fluence (ions/cm^2)
Nitrogen	200	$(4, 6, 8, 10) \times 10^{12}$
Argon	200	$(6, 10) \times 10^{12}$

and structural transformation through low energy (0.25–5 keV) Argon ions irradiated on few layer peeling graphene They found a ripple structure formation and sp^2 to sp^3 bonding transformation. Ochedowski et al. [20] showed how single layer peeling graphene could be utilized to study swift heavy ion (SHI) modifications on various substrates. Compagnini et al. [21] reported on the defect formation by 500 keV C ions irradiated on single layer peeling graphene. Kalbac et al. [22] studied the effects of ion irradiation by 100 keV Argon ions on isotopically labeled single and bi-layer graphene sheets fabricated by CVD. Prével et al. [23] produced organized arrays of nanodefects using a finely focused gallium (Ga^+) ion beam on epitaxial graphene grown on 6H-SiC substrates. At present, very little research has focused on the use of ion irradiation upon epitaxial graphene, especially those grown on 4H-SiC substrates. The aim of this work is to study the structural modifications of the local properties of graphene layers grown on a 4H-SiC substrate subjected to local ion irradiation.

2. Experimental details

Epitaxial graphene on silicon carbon (EG) used in the experiments were provided by the Institute of Crystal Materials of Shandong University of China. The graphene used in this work is epitaxial graphene on the Si face (0001) grown by thermal decomposition on a SiC surface. The SiC substrates used in this work were 4H-SiC wafers. By using this technique, the number of layers in the graphene could be controlled from 1 to 10. However, the number of graphene layers used in this experiment was 2–3.

As-prepared samples were irradiated with 200 keV Nitrogen (N) ions at four different fluences: 4×10^{12}, 6×10^{12}, 8×10^{12} and 1×10^{13} ions/cm^2. To investigate the effect of different ions on graphene samples, they were irradiated with Argon (Ar) ions at an energy of 200 keV with fluences of 6×10^{12} and 1×10^{13} ions/cm^2 in our experiments. The implantation conditions are shown in Table 1. Ion irradiations were carried out using an implanter based at Beijing Normal University, at room temperature and under high vacuum conditions in order to minimize surface contamination. The graphene samples were loaded into the chamber with an aluminum target. SRIM 2012 (stopping and range of ions in matter) [24] is used to calculate the ion implantation process.

To study the crystal structure of pristine and irradiated graphene samples, Raman spectra were collected under ambient conditions with a laser excitation of 633 nm. The confocal micro-Raman experiments were performed on a JYT64000 measurement system located at the School of Chemistry and Chemical Engineering, Shandong University. The spot diameter of the focused laser beam on the sample was about 1 μm. All Raman measurements were taken at room temperature. Atomic force microscopy (AFM) measurements were performed under ambient conditions both before and after Nitrogen ion irradiation in order to analyze the effect on surface morphology of the graphene samples.

3. Results and discussion

As an effective and powerful tool in describing material structure, Raman spectroscopy has been widely used on carbon-based materials throughout history [25]. Recent studies have demonstrated that it has played an important role in nanometer sized carbon based materials for accurate structural analysis [21,23,25]. Its powerful use in graphene allows it to confirm crystalline size, layer number, spatially resolved disorder information. Raman scattering spectroscopy of experimental samples was obtained by using a confocal micro-Raman method. The Raman measurement results of EG samples irradiated by 200 keV Nitrogen ions with fluences of 4×10^{12}, 6×10^{12}, 8×10^{12} and 1×10^{13} ions/cm^2 are shown in Fig. 1. As depicted in this figure, the Raman spectrum of un-irradiated EG is presented also for comparison. In graphene materials, the areas of interest are the so called D (1350 cm^{-1}), G (1580 cm^{-1}) and 2D (2700 cm^{-1}) bands [25,26]. As shown in Fig. 1, the prominent Raman modes of un-irradiated EG samples are located at 1582 cm^{-1} and 2681 cm^{-1} after subtracting the modes from the SiC substrate. The band at 1582 cm^{-1} is the G band that corresponds to longitudinal optical (LO) phonons. The peak at 2681 cm^{-1} is the 2D band corresponding to second order zone-boundary phonons. The FWHM of the 2D peak is 80 cm^{-1} (unirradiated EG sample), which is broader than a graphene sample grown on top of a Ni surface (about 46 cm^{-1} for monolayer graphene before plasma etching). Let us first note that on the 2D peak, the change of relative intensity and position is not obvious with different irradiation fluences as shown in Fig. 1. We need to pay particular attention to the variation of the D peak with increasing ion fluence. The location of the D peak is about 1327 cm^{-1}. This is a defect peak and it is not present in perfect graphene. Fig. 1 shows that a D peak is not observed in the as grown EG sample, which shows the absence of a significant number of defects. As ion irradiation fluence increases, the D peak becomes more obvious when a fluence value of up to 8×10^{12} ions/cm^2 is reached. This is characteristic of disorder and defects. The intensity of the D peak (I_D) has an upward tendency in the Raman spectrum along with increasing ion fluence.

To investigate the effect of different ions on graphene samples, they were irradiated with Argon ions at the same energy (200 keV) and the same fluences (6×10^{12} and 1×10^{13} ions/cm^2) in our experiments. Fig. 2 shows the Raman spectrum of EG samples irradiated by 200 keV Argon ions with fluences of 6×10^{12}, and 1×10^{13} ions/cm^2. In contrast to Nitrogen ion irradiation, the location of the D peak (about 1340 cm^{-1}) has a blue shift. On the other hand, the intensity of the D peak increases obviously. In addition, the intensity of the 2D peak (I_{2D}) has some variation when compared to Nitrogen ion irradiation. The comparison diagram is shown in the inset of Fig. 2. We will explain this phenomenon in the following section. The I_{2D} has a downward tendency in the Raman spectrum along with increasing ion fluence. The important difference is that the D peak increases up to a ratio I_D/I_G of about 1.0, implying the presence of more disorder or defects. The Raman

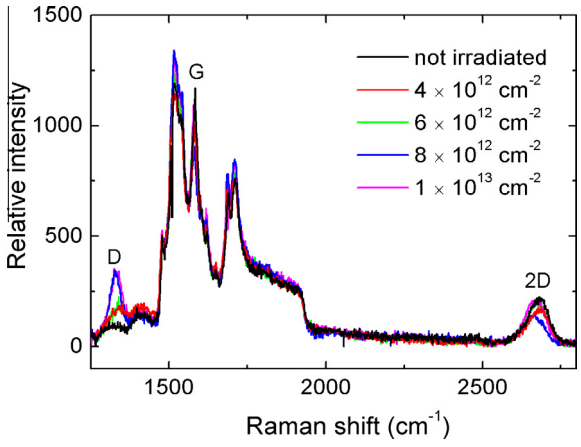

Fig. 1. Raman spectrum of EG with a laser excitation wavelength of 633 nm: a pristine EG; and 200 keV Nitrogen-irradiated EG at fluences of 4×10^{12}, 6×10^{12}, 8×10^{12} and 1×10^{13} ions/cm^2.