Vacuum 116 (2015) 90–95

Contents lists available at ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum

Effects of defects and thermal treatment on the properties of graphene

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ARTICLE INFO

Article history:
Received 13 August 2014
Received in revised form
22 December 2014
Accepted 2 March 2015
Available online 13 March 2015

Keywords:
Graphene
Annealing
Defects
Doping
Strain

ABSTRACT

For graphene films, the change of crystal structure induced by ion bombardment as well as the doping and strain generated in thermal annealing process is addressed in this work. Experimental results show that both the structure and number of defects for graphene depends strongly on the ion dose. Furthermore, it is found that the structure defects caused by ion bombardment in graphene can be healed and the graphene samples are all doped in subsequent thermal annealing. The frequency shift of G and 2D peaks in Raman spectra reveals that compressive strain in graphene results from the thermal annealing treatment and the occurrence of strain is influenced by the thermal annealing and defects in graphene. For graphene, since defects and thermal annealing are unavoidable for the fabrication of graphene-based devices, the systematical investigation on these two aspects in this work is, therefore, of great importance and significance.

1. Introduction

As a kind of 2-dimensional materials with a hexagonally ordered atomic structure, graphene exhibits many impressive properties, including high mobility [1,2], excellent thermal conductivity and stability [3,4]. Especially, its extraordinary electronic properties suggest that graphene may serve as potential material to build next generation electronics [5–9]. However, pristine graphene materials are not always the ideal choices in practical applications and it is necessary to modify its properties by introducing certain intentional process such as: physical adsorption [10,11], chemical modification [12–14], nano-tailor [15–18], ion or electron bombardment [19] and annealing [20–23]. Among them, ion bombardment and annealing are conventional methods to modify the properties of graphene. Due to the fact that process-induced defects and thermal treatment are inevitable in graphene device fabrication, it is therefore necessary to study the effects of defects and thermal annealing on the properties of graphene. In recent years, apart from doping issues [20,23], strain induced in graphene after thermal treatment on patterned substrate is usually discussed [22]. However, such kind of research rarely touched sheet resistance, doping and strain effect of graphene simultaneously handled with ion bombardment and vacuum annealing. In this context, we systematically investigate the effect of ion bombardment process and subsequent annealing on the properties of graphene by means of Raman spectra analysis and sheet resistance measurement.

To clarify the profile of Raman spectra in this paper, symbols e.g. I_D, I_G, $I_{D'}$, and I_{2D} which representing the intensity of D, G, D′ and 2D peak respectively are clearly marked. Applying the same naming rule, a peak with "Pos" in front to it means the frequency of the peak. Meanwhile, intensity ratios of peaks are defined as the form of intensity symbols ratio, such as I_D/I_G denotes the intensity ratio of the D and G peaks.

2. Experiment

The graphene used in this study was synthesized on copper foil by low pressure chemical vapor deposition (LPCVD) [24,25], with methane as carbon source. After synthesis, it was transferred onto heavily doped Si substrate with a 100-nm-thick SiO_2 capping layer. The samples were then bombarded by boron ions to doses ranging from 0 to 5×10^{14} cm^{-2} at a fixed energy of 32 keV. Those boron ions was introduced by an implanter (Varian 350D) which is widely

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http://dx.doi.org/10.1016/j.vacuum.2015.03.003
0042-207X/

used in semiconductor industry. Afterwards bombarded graphene samples were thermally annealed in Ar atmosphere. For both groups (450 and 600 °C), annealing time was 15 min, pressure and flow rate of Ar were 55 Pa and 50 sccm. Graphene samples were characterized by Raman analysis and transport measurements. The Raman analysis was carried out at room temperature by a HORIBA confocal Micro-Raman equipment (LabRAM HR800) with a 100× objective magnification. The spot size is ~1 μm, the incident laser power is kept below 2 mW to avoid self-heating effect and the excitation wavelength is 473 nm.

3. Results and discussion

3.1. Raman spectra and sheet resistance of bombarded graphene

After ion bombardment, the graphene samples were characterized by Raman analysis [26,27]. Raman spectra of bombarded graphene with different ion doses are shown in Fig. 1a. There are two dominant peaks in the Raman spectra of pristine graphene before ion bombardment, i.e. the G peak and 2D peak located at ~1580 and ~2700 cm^{-1}, respectively. The high I_{2D}/I_G ratio, a symmetric 2D profile, and a very weak D peak together indicate that as-synthesized graphene without ion bombardment is single layer with little defects [27,28].

After ion bombardment, some obvious changes can be seen in Raman spectra. The D and D′ peaks appear and the 2D peak is suppressed. The D and D′ peaks originate from single-phonon intervalley and intra-valley scattering processes, respectively. For pristine graphene with perfect crystal structure, these two peaks are always absent but they can be activated by defects. These defects provide the missing momentum in order to satisfy the momentum conservation in the Raman scattering. As a result, the intensities of D and D′ peaks are indicators of defects in graphene.

The profile of I_D/I_G and $I_D/I_{D'}$ is shown in Fig. 1b. It is clear that the ratio I_D/I_G follows a two stage evolution. At the state of low ion dose, I_D/I_G increases quickly with increasing ion dose from 10^{13} to 10^{14} cm^{-2}. However, it starts to decrease at even higher dose ($>2 \times 10^{14}$ cm^{-2}). On the other hand, the ratio which reflects the relationship between the evolution of I_D and $I_{D'}$ is larger than 7 at the state of low dose. Vacancy defects induced by ion bombardment should be ascribed to such a large $I_D/I_{D'}$ ratio [29]. As the dose increases to the highest value (5×10^{14} cm^{-2}), the $I_D/I_{D'}$ ratio keeps decreasing to lower than 4. As the increase of ion doses, the two stage evolution of I_D/I_G and the decreasing trend of $I_D/I_{D'}$ are attributed largely to the nano-crystalline graphene is gradually transformed into amorphous disordered carbon [30,31] since stuffing vacancy defects.

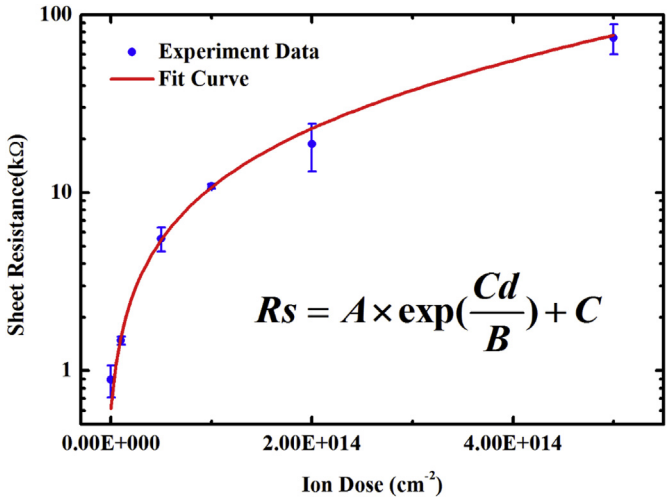

Fig. 2. Graphene sheet resistance test data (blue dots) with error bars indicating the scatter of values measured in five random points per sample, and fit curve (red line) of bombarded-graphene with various ion dose. The function of fit curve has been inserted into the bottom of the picture. In our case A, B and C in the function is 49.24 kΩ, 5.35 × 1014 cm^{-2} and −48.62 kΩ respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

To further investigate the property of graphene with ion bombardment, the sheet resistance of graphene samples was measured using a four-probe electrical measurement station. For a given sample (1.5 × 1.5 cm), measurements were performed at five randomly chosen locations and the average value was calculated as the sheet resistance. In Fig. 2, the sheet resistance as a function of ion dose is displayed. It can be seen that the sheet resistance fits exponentially with ion dose very well (c.f. inset of Fig. 2). The empirical exponential function is inserted in Fig. 2 and the variable named C_d in the function refers to the ion dose. The physical model behind the exponential relationship is not clear now and further work is undergoing to explain this relationship clearly.

3.2. Thermal annealing of bombarded graphene

Next the bombarded graphene samples were thermally annealed at 450 and 600 °C in Ar atmosphere. For both groups, annealing time was 15 min, pressure and flow rate of Ar were 55 Pa and 50 sccm.

Raman spectroscopy studies were further performed for abovementioned annealed graphene samples. Typical results are shown in Fig. 3. The black curves in each group correspond to as-

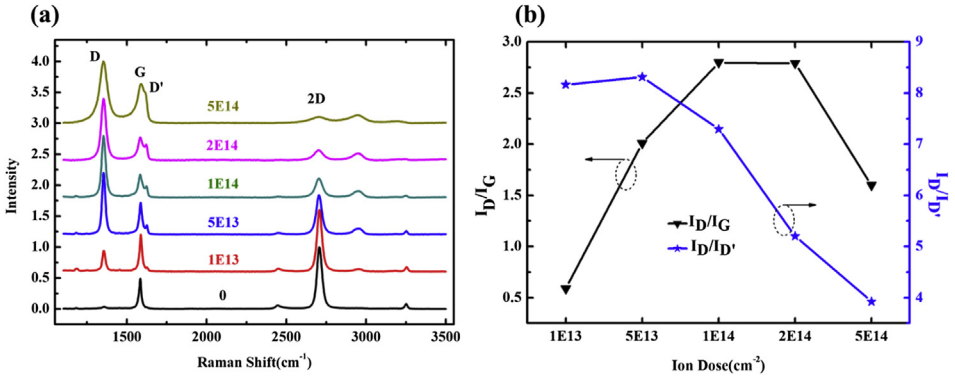

Fig. 1. (a) Raman spectra of bombarded-graphene with different ion does. (b) the trends of I_D/I_G and $I_D/I_{D'}$ versus ion dose.