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Investigating change of properties in gallium ion irradiation patterned single-layer graphene

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ABSTRACT

Besides its excellent physical properties, graphene promises to play a significant role in electronics with superior properties, which requires patterning of graphene for device integration. Here, we presented the changes in properties of single-layer graphene before and after patterning using gallium ion beam. Combined with Raman spectra of graphene, the scanning capacitance microscopy (SCM) image confirmed that a metal–insulator transition occurred after large doses of gallium ion irradiation. The changes in work function and Raman spectra of graphene indicated that the defect density increased as increasing the dose and a structural transition occurred during gallium ion irradiation. The patterning width of graphene presented an increasing trend due to the scattering influence of the impurities and the substrate.

1. Introduction

Graphene has many claims to fame: it is the thinnest possible membrane and has unique electronic and excellent mechanical properties [1–3]. The unusual electronic characteristics of graphene have attracted a remarkable interest in potential applications in high performance thin film electronics devices [4,5]. The patterning of graphene is a very important step during the preparation of graphene-based devices. Graphene-based devices are commonly fabricated using electron-beam lithography with subsequent reactive ion etching or plasma etching [6–10]. However, the photoresist processing during the electron-beam lithography will contaminate the graphene and degrade its intrinsic characteristics. Many other methods have been used to pattern graphene for the device applications, such as scanning tunneling microscopy lithography, atomic force microscopy anodic oxidation, chemically derived techniques [11–13]. Recently, graphene nanoribbons have been processed by neutral beam and electron beam, which realize the nano-patterning of graphene [14,15]. Additionally, because of the advantage of achieving well-controlled modification for graphene, ion irradiation has received enormous attention. The modification of graphene for device applications has been obtained by gallium and helium ion beams [16,17].

Since focused ion beam (FIB) has been already employed in semiconductor industry with high spatial resolution, this method could become an alternative approach for cutting and patterning of graphene. The method is based on using a high electric field to accelerate ion source and form ion current. Then, the ion current is focused using focusing lens to obtain ion beam. The ion beam irradiates on surface of graphene sample at different incident angles, and modifies graphene by sputtering carbon atoms.

In this letter, we use gallium ion beam from DualBeam systems equipped with a FIB to irradiate the graphene, and the irradiation doses are changed by varying dwell times. The changes in properties are explored using Raman spectroscopy (RS) and atomic force microscope (AFM). Different modes of AFM are used to simultaneously identify changes of the surface capacitance and the work function after gallium ion irradiation. This, along with the changes in properties, gives promise that FIB patterning of graphene will open the way for the manipulation of materials to be used in the electronic and sensing applications.

2. Experiment

The graphene samples here were grown by chemical vapor deposition (CVD) on copper film [18]. Then, polymethyl methacrylate (PMMA) was used to transfer graphene samples from copper film to the Si substrate with 90 nm thermal oxidation SiO_2. Hot acetone

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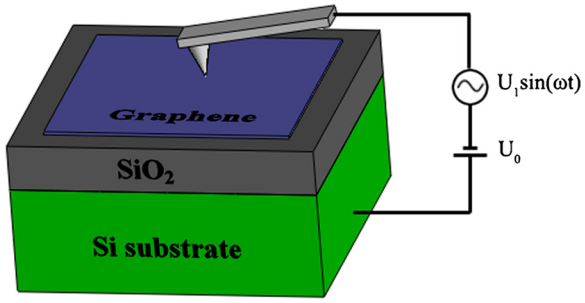

Fig. 1. The measurement setup of AFM used on graphene/SiO_2/Si sample.

solution was utilized to wash the residual PMMA on graphene, and then graphene was annealed to remove impurities and water molecules. RS (Witec Alpha 300, Witec) with a laser excitation wavelength of 532 nm revealed the numbers of layers and surface quality of pristine graphene. The laser power was attenuated below 2 mW to avoid introducing defects for graphene. The 5 μm × 5 μm Raman mapping was obtained by measuring Raman spectrum at every point of selected area.

FIB (Quanta 3D FEC 600, FEI) was employed to introduce gallium ion irradiation for graphene. The pressure of vacuum chamber was maintained at 10^{-6} mbar. The accelerating voltage and constant current of gallium ion beam were kept at 30 kV and 10 pA, respectively. The beam diameter was about 13 nm. The irradiation dose was controlled by varying the dwell time. The dwell times of gallium ion irradiation were 1, 5 and 10 μs. Then, single point Raman spectra of graphene were observed after gallium ion irradiation of different doses.

The electrical properties of graphene before and after gallium ion irradiation were characterized using different modes of AFM (Ntegra Spectra, NT-MDT). Fig. 1 depicts the measurement setup with various modes in this device. Scanning capacitance microscopy (SCM) with a type of conducting probe (the FMG01 probe) was equipped to demonstrate surface capacitance distribution of graphene after gallium ion irradiation. The two-pass measurement scheme was adopted in order to minimize the influence of surface topography features on the measurement results. During the first pass, the tapping mode was utilized to acquire the surface topography. The resonance frequency ω_0 of the cantilever was measured and a positive rotation ac voltage of frequency ω_0 was applied on piezoelectric oscillators under the cantilever to drive the probe to oscillate. The feedback signal was the oscillation amplitude of the cantilever. Then, in the second pass, the probe was lifted above the surface at the height dZ and a positive rotation ac voltage of frequency $\omega_0/2$ was applied between the probe and the sample to enhance second-harmonic oscillation. The feedback signal acquired was proportional to the capacitance between the probe and the sample. All experiments were performed in ambient environment, and every SCM image was acquired under the same measurement conditions, i.e., the probe–sample space dZ = 100 nm, the dc bias voltage $U_0 = 0$ V, the ac voltage $U_1 = 2.5$ V and the resonance frequency of the cantilever $\omega_0 = 50$ kHz. Then, kelvin probe microscopy (KPM) was adopted to characterize distribution of the surface electric potential of graphene In KPM test, alternating electric field with vibration frequency ω_0, which is same as the resonance frequency of the probe, was produced after the voltage had been applied. The appearance of alternating electric field can drive the vibration of probe. The process of the test is similar to the SCM test.

3. Results and discussion

In order to evaluate the distribution of quality of graphene sample, Raman spectrum of pristine graphene was measured. Fig. 2(a) shows a point Raman spectrum of pristine graphene in the test area. Three characteristic peaks of graphene are observed at 1336 cm^{-1} (D-band), 1587 cm^{-1} (G-band) and 2673 cm^{-1} (2D-band). The ratio of 2D peak intensity and G peak intensity (I_{2D}/I_G) is equal to 1.5, and the 2D peak is well fitted by a single Lorentzian peak. These features are consistent with those of single layer graphene. The ratio of D peak intensity and G peak intensity (I_D/I_G) is equal to 0.1, which confirms that there are a small amount of intrinsic defects in pristine graphene. Fig. 2(b) and Fig. 2(c) are the Raman mapping image of pristine graphene on SiO_2/Si substrate which is the randomly selected 5 μm × 5 μm test area. The I_D/I_G ranges from 0.01 to 0.14, and the I_{2D}/I_G is above 1.5, indicating that most of the sample is uniformly high-quality monolayer graphene.

The sample was irradiated using gallium ion beam with different doses. Raman spectra of graphene sample after irradiation are shown in Fig. 3. Pristine graphene presents a sharp and symmetric 2D peak and a little D peak. After irradiation of dwell time of 1 μs, the intensity of D peak increases sharply, while the intensity of 2D peak decreases significantly and G peak and 2D peak start to broaden. At the same time, the D′ peak appears at around 1620 cm^{-1}. The D′ peak and G peak approach each other and become a peak. The I_D/I_G is equal to 2, the corresponding defect density σ of graphene can be approximately calculated using the following equations [19]:

$$I_D/I_G = A/L_D^2 \tag{1}$$

$$L_D = 1/\sqrt{\sigma} \tag{2}$$

where $A = (102 \pm 2)$ nm^2, L_D is the average distance between defects, σ is the defect density. By calculating, the defect density σ of graphene is around 1.9%. After irradiation of dwell time of 5 μs, the intensity of G peak and D peak decrease greatly. The 2D peak

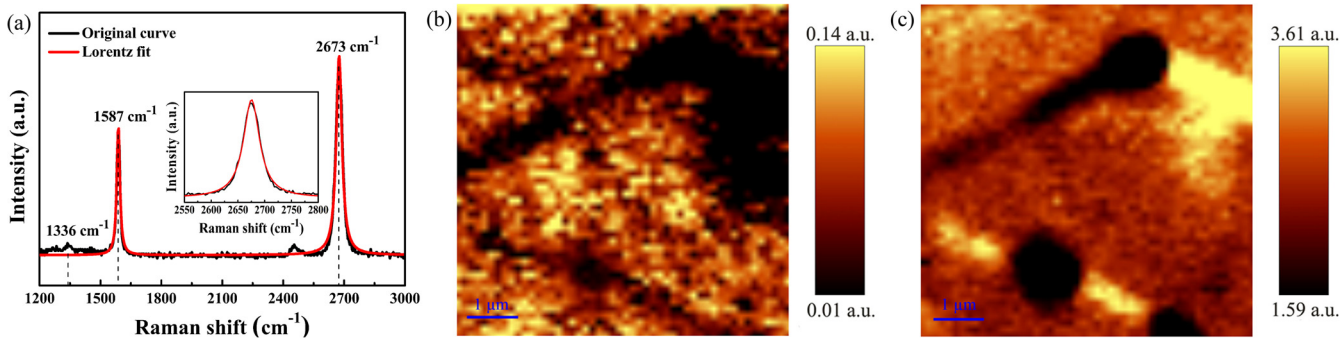

Fig. 2. Raman spectrum of pristine graphene sample on SiO_2/Si substrate. (a) A point Raman spectrum of graphene at random position. The insert is the Lorentz fitting of 2D peak. (b) Raman mapping image of the intensity ratio of D and G peaks (I_D/I_G) at randomly selected 5 μm × 5 μm test area. (c) Raman mapping image of the intensity ratio of 2D and G peaks (I_{2D}/I_G). (For interpretation of the colors in this figure, the reader is referred to the web version of this article.)