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Low-temperature formation of epitaxial graphene on 6H-SiC induced by continuous electron beam irradiation

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It is observed that epitaxial graphene forms on the surface of a 6H-SiC substrate by irradiating electron beam directly on the sample surface in high vacuum at relatively low temperature (~670°C). The symmetric shape and full width at half maximum of 2D peak in the Raman spectra indicate that the formed epitaxial graphene is turbostratic. The gradual change of the Raman spectra with electron beam irradiation time increasing suggests that randomly distributed small grains of epitaxial graphene form first and grow laterally to cover the entire irradiated area. The sheet resistance of epitaxial graphene film is measured to be ~6.7 kΩ/sq.

Graphene, a single layer of carbon atoms arranged in a honeycomb lattice, is a zero band gap semiconductor that can hold an ultimate two dimensional (2D) electron system.1,2 It exhibits many fantastic material properties outperforming other semiconductor materials. Especially, its remarkable transport properties3–5 make it a prominent candidate for future micro- and nano-electronic applications that can replace the current Si-based technologies. Typically, graphene can be produced by mechanical exfoliation of graphite,6 epitaxially on SiC utilizing surface graphitization.6–9 or chemical vapor deposition (CVD)10,11 and/or solid source deposition12,13 on transition metals. Very recently, it was reported that graphene could be grown also on SiC by CVD.14 Following the isolation of graphene from graphite,5 there has been an enormous amount of research activities for fabricating high-quality graphene on a large scale. The epitaxial graphene formed on SiC by surface graphitization has an essential benefit in terms of uniform large-scale growth, since it can be induced just by heating an entire SiC wafer to high temperature in ultra high vacuum (UHV) or Ar atmosphere. In this Letter, we report a relatively simple and well-controllable method to induce a large-scale turbostratic epitaxial graphene with affordable electrical properties by directly radiating continuous electron beam (e-beam) on a 6H-SiC substrate in high vacuum environment (~10⁻⁶ Torr).

Previously, Huang et al.15 reported that epitaxial graphene within three monolayers was induced by the pulsed e-beam irradiated on a 4H-SiC substrate. They pointed out that the pulsed e-beam irradiation has its distinction from the common thermal annealing in the sense that the energy transfer to sublimated atoms from the bombarded electrons is expected to occur less than ~10 nm from the surface at an acceleration voltage of 8 kV and atoms sublimation is localized very near the surface. In the common thermal annealing, the entire SiC substrate is heated up to a high temperature around 1200–1600°C. Hence atoms sublimation could occur further deeper into the substrate from the surface. Differently from Huang et al.,15 we irradiated a continuous e-beam directly on a single-crystalline, on-axis, Si-terminated n-type 6H-SiC wafer purchased from Cree, Inc. by using a commercial e-beam evaporator (Woosung Hi-Vac, South Korea, WC4000). The sample was dipped in diluted HF (1:10) to remove the surface native oxide and rinsed with methanol before being put into the vacuum chamber.16 The e-beam irradiation was performed in high vacuum environment (~10⁻⁶ Torr) at an acceleration voltage of 8 kV. The e-beam irradiated area was ~5 mm × 5 mm and the total current was fixed to be ~2 mA. The only experimental variable was the irradiation time that determined electron fluency (number of electrons per unit area). The four different irradiation times (corresponding electron fluencies) were 0.5 h (9 × 10¹⁹ e/cm²), 1.0 h (1.8 × 10²⁰ e/cm²), 1.5 h (2.7 × 10²⁰ e/cm²), and 2.0 h (3.6 × 10²⁰ e/cm²). The sample temperature was not adjusted intentionally and left at room temperature in the beginning. However, the temperature of sample surface was found to rise up to ~670°C in the IR pyrometer reading during e-beam irradiation. After the e-beam irradiation was completed, the sample was cooled down to room temperature in vacuum.

In order to investigate the formation of epitaxial graphene, Raman spectra measurement was first performed on the e-beam irradiated sample. Fig. 1(a) shows the Raman spectra with electron beam irradiation time increasing suggests that randomly distributed small grains of epitaxial graphene form first and grow laterally to cover the entire irradiated area. The sheet resistance of epitaxial graphene film is measured to be ~6.7 kΩ/sq. © 2012 American Institute of Physics.
spectra measured on the 6H-SiC sample before and after e-beam irradiation by using a Raman microscope (Alpha300R, WITec). The laser excitation energy was \( \sim 2.33 \text{ eV} \) (532 nm), and the laser spot size was \( \sim 1.2 \mu\text{m} \). On the bare 6H-SiC (before e-beam irradiation), the strong Raman peaks of 6H-SiC around 1510 cm\(^{-1}\) and 1710 cm\(^{-1}\) are observed as expected.\(^{17,18}\) When e-beam is irradiated on the 6H-SiC sample, the characteristic Raman peaks of graphene show up clearly around 1350 cm\(^{-1}\) (D peak), 1580 cm\(^{-1}\) (G peak), and 2700 cm\(^{-1}\) (2D peak), indicating the actual formation of epitaxial graphene. As can be seen in Fig. 1(a), the relative intensities of those Raman peaks change somewhat gradually as e-beam irradiation time increases. To manifest the change of the Raman peaks more clearly, the Raman signals coming from the 6H-SiC substrate (background signals) were subtracted as shown in Fig. 1(b) and the relative intensities of the D and 2D peaks compared to the G peak were calculated (Fig. 2(a)). For the relatively short irradiation time (0.5 h), the intensity of the D peak is about twice that of the G peak, and the 2D peak is barely seen (the green curve in Fig. 1(b)). This large D peak indicates that the formed epitaxial graphene contains a large number of defects or its grain size is quite small (maybe nanocrystallites) to bear a significant amount of grain boundaries. As shown in Fig. 2(a), the relative intensity of the D peak decreases while that of the 2D peak increases with e-beam irradiation time increasing. When the irradiation time reaches 2.0 h, the 2D peak intensity now becomes similar to the G peak but the D peak intensity decreases greatly. This observed change of the Raman peaks suggests the following scenario of the growth of epitaxial graphene, shown in Fig. 3. In the early stage of growth, many small graphene islands with a small area-to-circumference ratio form randomly on the sample surface. Here, the area-to-circumference ratio of a graphene island is approximately proportional to its size. As e-beam irradiation time increases, the small graphene islands grow laterally to increase the area-to-circumference ratio and eventually cover the entire area irradiated by e-beam. Since the grain boundary effect is expected to be reduced with larger area-to-circumference ratio, the scenario described above is believed to suggest a reasonable explanation for the dependence of the measured Raman spectra on e-beam irradiation time.

There is some additional important information that we can obtain from the Raman spectra. For the sample irradiated by e-beam for 2.0 h where the formation of epitaxial graphene might get saturated pretty much, the exact positions of G and 2D peaks were found to be \( \sim 1582 \text{ cm}^{-1} \) and \( \sim 2689 \text{ cm}^{-1} \), respectively. These peak positions are only slightly blue-shifted (G peak: \( \sim 2 \text{ cm}^{-1} \) and 2D peak: \( \sim 75 \text{ cm}^{-1} \)).

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**FIG. 1.** (a) The original Raman spectra measured on a 6H-SiC substrate as a function of e-beam irradiation time and (b) the corresponding Raman spectra with the Raman signals coming from the 6H-SiC substrate subtracted.

**FIG. 2.** (a) The relative Raman intensities of the D and 2D peaks compared to the G peak as e-beam irradiation time increases and (b) the zoom-in of the 2D peak measured on the 6H-SiC substrate irradiated by e-beam for 2 h with the curve fitted to the measured data by a single Lorentzian function.

**FIG. 3.** Schematic diagram showing the formation of epitaxial graphene on the 6H-SiC substrate by directly irradiating e-beam on the sample surface: (a) 6H-SiC substrate before e-beam irradiation, (b) the early stage of e-beam irradiation with many small graphene islands distributed randomly on the sample surface, (c) the lateral growth of the formed graphene islands as e-beam irradiation time increases, and (d) the 6H-SiC substrate after e-beam irradiation is completed where epitaxial graphene layers cover most of the e-beam irradiated area.
\(~10 \text{ cm}^{-1}\) in comparison with the freestanding monolayer, indicating that the e-beam induced epitaxial graphene is subject to very little compressive stress differently from the common thermal-annealing-induced one. Another important information from the Raman spectra is that the 2D peak is quite symmetric and can be fitted reasonably well to a single Lorentzian with a full width at half maximum (FWHM) of \(~87 \text{ cm}^{-1}\), larger than the typical value (\(~24 \text{ cm}^{-1}\) for a monolayer graphene (Fig. 2(b)). This suggests that the epitaxial graphene induced by e-beam irradiation is turbostratic, meaning that the stacking of graphene layers is rotationally random with respect to one another along the stacking direction. The random stacking of graphene layers in rotation-wise would be a sign of the adjacent graphene layers being decoupled from each other, which is very likely to be the main reason for the low compressive strain observed in our epitaxial graphene. The mechanism of the e-beam induced epitaxial graphene becoming turbostratic is not clear at this moment. Hence more detailed studies to investigate the physical environments near the surface of SiC substrate supplied by e-beam irradiation and their influence on the formation of epitaxial graphene are necessary.

In addition to Raman spectra measurements, high resolution transmission electron microscopy (HR-TEM) images (cross-sectional) were taken to directly observe the formed epitaxial graphene layers. Fig. 4(a) shows the HR-TEM image measured on the 6H-SiC sample irradiated by e-beam for 2 h where 7~8 layers brighter than the others are found on the sample surface as indicated in the figure. According to the profile of TEM signal intensity (Fig. 4(b)), the spacing between two adjacent brighter layers is \(~0.32 \text{ nm}\). This measured spacing is very close to the known spacing of graphene layers. In order to confirm that those brighter layers are graphene layers in actual, Auger electron spectroscopy (AES) measurements were performed to analyze the atomic composition of the e-beam irradiated area. Fig. 4(c) shows the AES spectra of C KLL Auger electrons before and after e-beam irradiation and Fig. 4(d) is the corresponding AES spectra of Si KLL Auger electrons. As shown in the figures, Si atoms disappear almost completely after e-beam irradiation and only C atoms are left near the sample surface. This measured AES spectra strongly indicate that any layers induced on the sample surface by e-beam irradiation should be composed of C atoms and hence the brighter layers observed in the HR-TEM image are really graphene layers.

Once the structural analysis had been completed, the electrical properties of the formed epitaxial graphene were measured. In particular, circular transfer length method (CTLM) structure was used to investigate the sheet resistance \((R_S)\) and specific contact resistance \((\rho_C)\) of the epitaxial graphene induced on the 6H-SiC substrate by 2 h of e-beam irradiation. Since it does not require etching a mesa structure of conducting layer differently from the conventional transfer method (TLM), the CTLM structure is simple to be made just with one patterning step. It can also eliminate any undesirable effects from the patterned edges on measuring the intrinsic electrical properties of conducting layer. By using lift-off processes, the CTLM structure including the inner circular contacts with 50 \(\mu\text{m}\) diameter and outer circular contacts with various contact pad spacing were fabricated. The circular contacts were made with Ni/Au (500 nm/200 nm) thin films, and the electrical properties were measured with a semiconductor parameter analyzer (Agilent Technologies, Inc. B1500A) at room temperature.

Fig. 5 shows the measured resistances (open squares) between the inner and outer circular contacts as the contact pad spacing changes. The red line is the curve fitted to the measured data with the known equation for CTLM structure, \(R_T = (R_S/2\pi)\ln(1+S/r_I) + L_T(1/r_I + 1/(r_I + S))\). Here, \(R_T\) is the total resistance between the inner and outer contacts, \(R_S\) is the sheet resistance of conducting layer, \(r_I\) is the radius of inner circular contact, \(S\) is the contact pad spacing, and \(L_T\) is the transfer length. From data fitting, the sheet resistance of the epitaxial graphene is obtained to be \(R_S = \sim 6.7 \text{ k}\Omega/\text{sq}\) and the transfer length be \(L_T = \sim 1.8 \mu\text{m}\). Then, the specific contact resistance at the interface of Ni
and epitaxial graphene is calculated to be \( \rho_C = R_s L_T^2 \approx 2.2 \times 10^{-7} \, \Omega \, \text{cm}^2 \). The extracted sheet resistance is relatively high compared with those of the common thermal-annealing-induced or CVD-grown graphene layers.\(^{26}\) This implies that our epitaxial graphene layers induced by e-beam irradiation might contain more grain boundaries due to smaller grains or be less continuous than the graphene layers induced by the other two methods.

Hall effect measurements were also performed on the same sample as the one used for the CTLM measurements. The charge carrier type was found to be n-type (electron) and its density be \( \sim 3.0 \times 10^{16} \, \text{cm}^{-2} \). The carrier mobility was measured to be \( \sim 97 \, \text{cm}^2 \, \text{V}^{-1} \, \text{s}^{-1} \), much lower compared with the common thermal-annealing-induced or CVD-grown graphene. This measured low carrier mobility is considered to be due to strong carrier scattering from graphene grain boundaries. Together with the relatively high sheet resistance, it directly implies the imperfection of our e-beam induced graphene layers. Further work to optimize the e-beam irradiation conditions is needed to improve the quality of formed epitaxial graphene layers.

In summary, we report: (1) Epitaxial graphene can be induced on a 6H-SiC substrate by directly irradiating continuous e-beam on the sample surface in high-vacuum at a significantly lower temperature (\( \sim 670^\circ \text{C} \)) than the common thermal-annealing method. (2) The e-beam induced epitaxial graphene is predicted to be turbostratic from the symmetric shape and FWHM of 2D peak in the measured Raman spectra. Also, the gradual change of the Raman spectra with e-beam irradiation time increasing suggests that randomly distributed small grains of epitaxial graphene form first and grow laterally to cover the entire e-beam irradiated area. (3) The sheet resistance of the e-beam induced epitaxial graphene is measured to be \( \sim 6.7 \, \text{k}\Omega/\text{sq} \). This relatively high sheet resistance is believed to be due to small grains or local discontinuity of the formed epitaxial graphene. Our experimental results suggest that it would be possible to directly write epitaxial graphene patterns on a SiC substrate without any additional patterning processes involved if a proper equipment capable of focusing e-beam and adjusting its location in an arbitrary fashion is developed.

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