Raman-Scattering Spectroscopy of Epitaxial Graphene Formed on SiC Film on Si Substrate

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(Received 2 December 2008; Accepted 14 January 2009; Published 21 February 2009)

By conducting a 1200°C vacuum annealing of a 3C-SiC(111) ultrathin film preformed on a Si(110) surface, we have succeeded in forming a graphene layer on a Si substrate. Raman-scattering spectrum from this surface presents a distinct 2D band, whose deconvolution into four subcomponents indicates that the film mostly consists of a two-layer graphene. The peak position is blue-shifted from that of a free-standing graphene formed by a mechanical exfoliation method, suggesting a compressive stress in the film. [DOI: 10.1380/ejssnt.2009.107]

Keywords: Silicon carbide; Heteroepitaxy; Organosilane; Gas-source MBE; Graphene

I. INTRODUCTION

By conducting a 1200°C vacuum annealing of a 3C-SiC(111) ultrathin film preformed on a Si(110) surface, we have succeeded in forming a graphene layer on a Si substrate. Raman-scattering spectrum from this surface presents a distinct 2D band, whose deconvolution into four subcomponents indicates that the film mostly consists of a two-layer graphene. The peak position is blue-shifted from that of a free-standing graphene formed by a mechanical exfoliation method, suggesting a compressive stress in the film. In the formation of GOS structure, it is of highest priority to form a qualified SiC film on top of the Si substrate. In this respect, the large lattice mismatch (>20%) between Si and 3C-SiC crystals (Si>SiC) is a big challenge, which might be one of the reasons for the absence of preceding studies on the GOS structure. We have solved the problem by using a unique growth properties of the 3C-SiC/Si hetero-system; a 3C-SiC(111) film grows on the Si(110) substrate. In this combination, the strain in the SiC film is significantly reduced from that in the 3C-SiC(111)/Si(111) system, as evidenced by a factor-of-four reduction in the anisotropy of the lattice constants between in-plane and out-of-plane directions. This orientational rotation in the heteroepitaxy is consistent with a recent potential-energy calculation [11], which accounts for this phenomenon as due to the reduction of the strain energy in the film. This reduction overwhelms the increase in the interfacial energy caused by deviation of the interfacial coordination number from the ideal number of four. The (111)-oriented 3C-SiC surface is desirable to form graphene on it because its Si face has, up to four bilayers from the surface, exactly the identical layer stacking as of the 6H-SiC(0001) Si surface used in conventional EG process.

The graphene was characterized with the Raman scattering spectroscopy, which presents several important peaks. The G band, appearing at around 1580 cm⁻¹,
FIG. 1: Raman spectra from GOS (top) and mechanically exfoliated graphene (middle) and graphite (bottom).

arises from a pair of LO and TO phonons degenerated at the Γ point. The D (1350 cm$^{-1}$) and the 2D (2700 cm$^{-1}$) bands arise from a double resonant Raman scattering in the vicinity of the K point with the latter being the overtone of the former [12]. The D band, however, is in principle Raman inactive in graphene, and its presence suggests presence of defects within the layer. From their origins, the D and 2D bands should be excitation-energy dependent while the G band should be independent. As the excitation energy increases, the resonant energy of the π-band electrons in the vicinity of the K point increases, which shifts the energy of the relevant phonons involved in the scattering. The peak position of the 2D band, therefore, should be sensitive to minute modifications in the electronic band structure at the K point. In other words, the line-shape analysis of the 2D band can be a good tool to characterize the number of layers in the graphene layer. In this study, we have evaluated the graphene layer in our GOS structure by using a Raman scattering spectroscopy.

II. EXPERIMENTAL

Boron-doped, p-type Si(110) wafers were used in the experiment, which were cut to 7 × 35 mm$^2$ in size. After a wet clean, samples were introduced into the vacuum chamber, where flash annealings were conducted for several times at 1200°C to yield a clean surface. Sample heating was conducted by passing a DC current through the sample. 3C-SiC film has been grown with a gas-source molecular beam epitaxy (GSMBE) using monomethylsilane (MMS, 99.999%) at 3.0 × 10$^{-2}$ Pa as a single source [13]. The growth consists of a pair of stages: the buffer layer formation at 600°C [14] and the SiC growth at 1050°C. After the growth, MMS was evacuated from the chamber, and a 1200°C annealing was conducted for 90 min to form graphene on top of the 3C-SiC film. The graphene layer was evaluated with a micro-Raman spectroscopy (Renishaw) with the laser-spot diameter of 1 μm and the excitation photon wavelength of 514 nm. For measurements of the excitation-energy dependence, another Raman setup [15] was used.

FIG. 2: The excitation-energy dependence of the D and 2D bands.

III. RESULTS AND DISCUSSIONS

The middle (bottom) Raman spectrum in Fig. 1 is from a free-standing graphene (graphite), which has been transferred from a HOPG crystal onto a SiO$_2$ film by a mechanical exfoliation method. The one in the top is from the UHV-annealed 3C-SiC film in our GOS structure. We can see distinct G and 2D bands in the spectrum, which
The presence of the D band, however, suggests presence of graphitic layers including graphene. The presence of the D band, however, suggests presence of defects as well. The spike at 2300 cm⁻¹, as well as the inclination of the baseline from 1200 to 1700 cm⁻¹, is related to amorphous carbon [16] although there are portions where no spikes are observed.

The excitation-energy dependence of the peak positions of the D, G, and 2D bands also supports the presence of graphene (Fig. 2). As we increase the photon energy from 2.41 to 2.54 or to 2.71 eV, the D and 2D bands show a shift towards high wavenumbers with gradients of 62 and 2.41 to 2.54 or to 2.71 eV, the D and 2D bands show a shift towards high wavenumbers with gradients of 62 and 2.41 to 2.54 or to 2.71 eV, respectively (Fig. 3). The G band stays unchanged. These results are consistent with the band structure of graphene and with previous results [16, 17] as well, suggesting that our GOS film is highly crystallized.

The peak position of the G band suggests presence of a compressive strain in the graphene layer in the present GOS structure. As we notice in Fig. 1, the peak position of the G band is blue-shifted from those from the free-standing graphene (graphite). This kind of blue shifts have also been observed in epitaxial graphene layers formed on hexagonal SiC substrates, which has been related to compressive strains due either to the lattice mismatch at the film/substrate interface [18] or to the difference in the thermal expansion coefficients [19]. Since our SiC film is highly relaxed after a high-temperature annealing [20], the latter possibility still holds in our GOS structure. As the number of graphene layers increases, the blue shifts in EG tend to disappear [18]. From these considerations, it is highly likely that the present GOS film consists of few layer graphene with compressive strain. The 2D band was best fitted with four components (Fig. 4), which implies that the current GOS film consists mainly of two-layer graphene [21].

IV. CONCLUSION

Graphene layer on Si substrate, or GOS, has been fabricated by GSMBE of 3C-SiC(111) on Si(110) substrate followed by a vacuum annealing. Raman-scattering spectroscopy indicates that the film contains compressively strained two-layer graphene.

Acknowledgments

This work has been supported by JST-CREST as well as by the Specially Promoted Research in Center for Interdisciplinary Research, Tohoku University. This work was partly supported by Grant-in-Aid for Young Scientists (B) (20760485).


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