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Direct formation of graphene layers on top of SiC during the carburization of Si substrate

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ABSTRACT

We grow graphene film on silicon substrates having various orientations by simple heating in the presence of carbon source gas. We observed that a 3C-SiC (111) film would form upon carburizing silicon with carbon deposited from a carbon source because it is well lattice-matched with Si (110) (less than 2%). Graphene grew on the buffer layer of 3C-SiC (111). The surface consists of hexagonal arrays that can act as a template for graphene growth. This simple and inexpensive method of forming graphene on silicon wafer in situ is compatible with silicon technology.

1. Introduction

Graphene is a single atomic layer consisting of hexagonal array of sp^2 bonded carbon atoms. Since its discovery [1], research interest for graphene has drastically increased due to its outstanding electrical [1–3], optical [4], thermal [5], and mechanical [6] properties. Graphene can be formed by top-down approaches such as liquid exfoliation [7], or by bottom-up approaches such as chemical vapor deposition (CVD) [8,9] on metal substrate, and epitaxial growth on silicon carbide (SiC) substrate [10]. In the epitaxy on silicon carbide substrate, SiC becomes a template for graphene growth with Si atoms selectively sublimating, thereby making high quality graphene growth possible. Direct fabrication of graphene devices can be realized with a SiC substrate [11] due to the wide energy gap of SiC (3.05 eV for 6H-SiC), contrary to the graphene formed on a metal substrate in the CVD process.

Many polytypes of SiC (6H- [12], 4H- [13], 3C-SiC[14]) have been used for graphene growth. However, high cost of SiC substrate is a major hindrance to practical application of graphene on SiC. To overcome this problem, a well-established method of growing SiC on Si substrate has been utilized [14–16], in which SiC is grown by chemical vapor deposition (CVD) on silicon with carbon and silicon gas sources and then the resulting structure is subjected to vacuum sublimation, thereby leading to the formation of graphene (graphene/3C-SiC/Si). Whatever technique is used, however, vacuum sublimation is involved. The sublimation temperature is quite high (~1400 °C), which in turn causes defects in silicon substrate.

Here, we report direct graphene formation on Si substrate by simply heating the substrate in the presence of a carbon source gas. The carbon in the gas carburizes the surface of silicon substrate, which results in the formation of a SiC structure (3C-SiC). The growth of the SiC layer is self-regulated due to the limitation of Si out-diffusion and carbon in-diffusion at a given temperature [18], and therefore, graphene starts forming on the grown SiC (3C-SiC/Si) with the carbon supplied from the gas phase. Graphene deposition on hexagonal SiC surface has already been demonstrated [17], which does not require as high a temperature as in the traditional SiC growth because it does not involve sublimation of Si atoms. The key concept in this work is that graphene can be grown directly on SiC substrate, which is made possible by forming a 3C-SiC film on Si substrate by carburizing [18] Si substrate *in situ* prior to growing graphene.

The lattice match between 3C-SiC and the orientation of the underlying Si surface would have a significant effect on the growth of graphene. Therefore, various Si surface orientations ((100), (110), (111)) were used in this study to optimize 3C-SiC/Si interface and to subsequently investigate graphene/3C-SiC interface. The thickness

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of 3C-SiC is self-regulated due to diffusion limitation of silicon and carbon atoms at a given temperature [18]. The 3C-SiC formed on Si substrate here is not used as a platform that is self-converted to graphene but rather as a host structure for graphene to grow on it. The attractive feature of the proposed method is its conciseness and simplicity.

2. Experiments

The formation of graphene via carburization process is illustrated in Fig. 1. Si wafers were loaded in a quartz type rapid thermal annealing chamber after dipping into diluted hydrofluoric (HF) acid (diluted 10:1 in water) solution for 5 min without rinsing to avoid native oxide formation. The chamber was evacuated to ~1 mTorr, and only C_2H_4 gas was introduced. Process pressure was 5 Torr and temperature was raised to 1100 °C by halogen lamp heating (heating rate was 80 °C/s such that the temperature was reached in 15 s). After just 1 min of annealing, a few-layer graphene was formed on top of 3C-SiC (111)/Si (110). As discussed earlier, 3C-SiC forms on Si substrate first, followed by graphene growth on the 3C-SiC. Formation of SiC structure was confirmed by Fourier transform Infrared spectroscopy (FT-Ir, Nicolet 6700, Thermo Scientific), and graphene layers were observed by Raman (Horiba Jobin Yvon, LabRam) spectroscopy. Microstructure (inter-plane relationship) of the samples was investigated by high-resolution transmission electron microscopy (TEM; JEOL 3000F) and X-ray photoelectron spectroscopy (XPS; AXIS-His, KRATOS) was used for the carbon phase analysis.

3. Results and discussion

Spectroscopic studies were carried out to investigate the formation of SiC on Si surface and that of graphene on the SiC. FT-IR absorbance is shown in Fig. 2(a). It is quite surprising that we observed chemisorbed hydrocarbon molecules at 1000 °C, Si–CH_2 bond forms with the breaking of carbon to carbon bonding as indicated by the peak at ~1080 cm^{-1} [19]. At higher temperatures, Si–C bond is seen to form as confirmed by the peak at ~790 cm^{-1} [20]. IR absorption gradually increases with increasing annealing temperature, indicating a thicker SiC formation. We couldn't observe SiC formation at a certain condition such as high partial pressure of hydrocarbon source, which is from amorphous carbon (a-C) deposition. We believe that this is due to overfeeding of carbon source gas, in which carbon atoms cannot form SiC structure because carbon monomer flux is too high compared to surface reaction rate for SiC formation. We found out the formation of relatively thick a-C (depending on pressure and temperature) by HR-TEM analysis, so adequate partial pressure of carbon source is critical in this process.

Shown in Fig. 2(b) are Raman spectra of the graphene grown on 3C-SiC formed on Si. Prominent in the spectra are D (~1350 cm^{-1}) and G (~1580 cm^{-1}) peaks [21]. However, 2D (~2650 cm^{-1}) peak was rarely detected, indicating the formation of low quality graphene due to pit formation in the Si substrate as shown in the low magnification TEM images in Fig. 2(c). The peak at around 990 cm^{-1} is the 2nd order peak of Si substrate. Comparison between Raman spectra of bare Si substrate and those of graphene grown on 3C-SiC in Fig. 2(b) clearly indicate that graphene was formed on Si substrate. Graphene growth is possible since 3C-SiC formation is limited due to diffusion limitation of silicon and carbon through the SiC. The 3C-SiC layer was only several nanometers thick. Once this thin self-limited film of 3C-SiC forms, the subsequent carbon from the source gas appears to deposit on the hexagonal arrays of 3C-SiC that acts as a template for graphene growth.

High-resolution TEM study in Fig. 3(a) revealed that a few-layer graphene (<10 layers) was grown on top of 3C-SiC (111) layer. We confirmed that the spacing between graphene layers is ~0.34 nm. Fig. 3(a) also shows that a 3–4 nm-thick 3C-SiC layer was grown

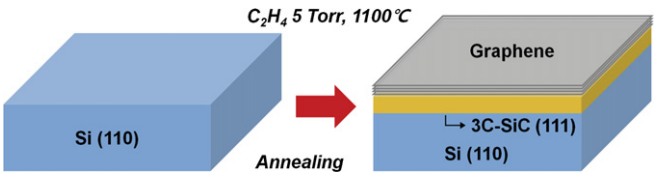

Fig. 1. Schematics showing graphene formation on SiC/Si substrate by direct carbon feeding.

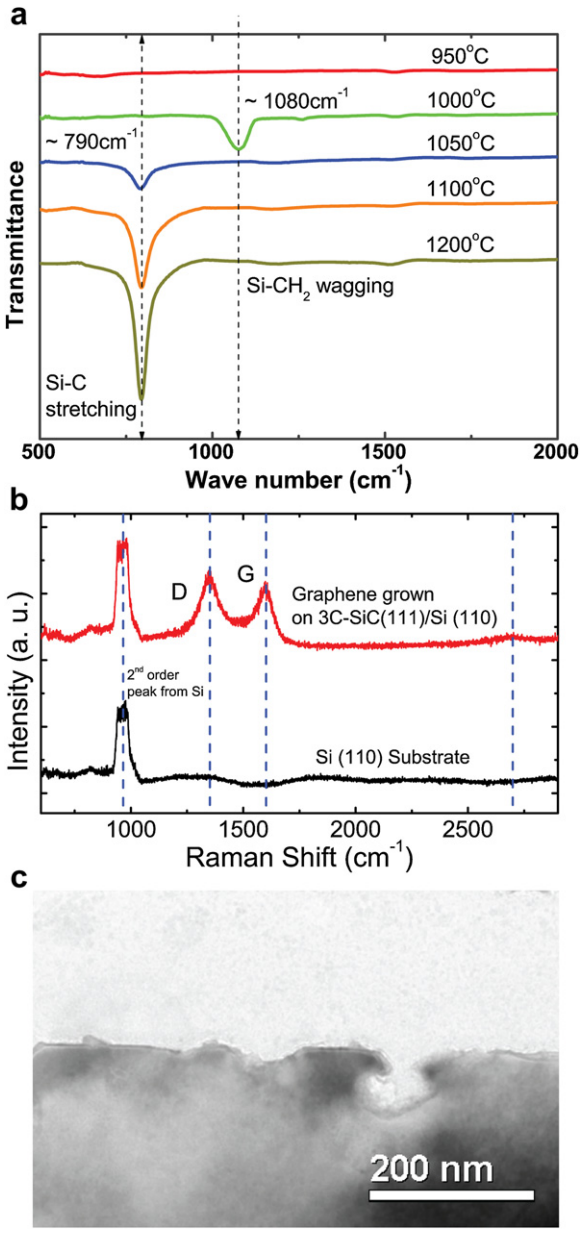

Fig. 2. (a) FT-IR spectra of the carburized (110) Si substrate as a function of annealing temperature, and (b) Raman spectra of the as-prepared Si substrate and graphene/3C-SiC(111)/Si(110) after 1100 °C annealing for 1 min. Incident wavelength of laser was 532 nm. Spectral resolution was 1.47 cm^{-1} and (c) low magnification cross-sectional TEM image of graphene/3C-SiC (111)/Si (110) structure.