Initial Growth Observation of Multilayer Graphene on SiO₂/Si substrates Using Raman Spectroscopy and XPS

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1. Introduction
Graphitic materials such as carbon nanotubes, and graphene have attracted much attention as the candidates of materials for interconnects in LSI. Growth process of these graphitic materials for interconnects requires a low temperature growth on whole large sized wafers without any catalysts. For this purpose, we have proposed photoemission-assisted plasma enhanced chemical vapor deposition (PA-PECVD) [1]. By using PA-PECVD, we can obtain the networked nanographite (NNG) on SiO₂/Si substrates. Furthermore, a horizontally oriented few layer graphene (multilayer graphene: MLG) is formed at the interface between SiO₂ and NNG without any amorphous transition layers [2]. If MLG can be grown to ~20 nm of thickness with keeping the horizontal orientation, the application for interconnects can be expected. However, the mechanism of MLG growth at the interface between SiO₂ and NNG. In this study, the thickness dependence of crystallographic quality of multilayer graphene is evaluated using Raman spectroscopy and hard X-ray photoelectron spectroscopy (PES) to form the high-quality MLG growth using PA-PECVD on the SiO₂/Si substrates.

2. Experimental methods
Growth experiments were perfumed using a photoemission-assisted plasma enhanced CVD apparatus placed at Tohoku University. The NNG and MLG were grown on the SiO₂/Si substrates whose thickness of SiO₂ was 350 and 90 nm. The growth temperature was ~650°C. The Ar/CH₄ mixture gas (CH₄ concentration: 16%) was introduced into process chamber to NNG and MLG growth. The UV light (λ= 172 nm) from a Xe excimer lamp was irradiated to the substrates as shown in Fig. 1(a). When the UV light turned off, the plasma disappeared. The bias voltage between substrates and electrode was ~290 V on SiO₂(350 nm)/Si substrates and ~250 V on SiO₂(90 nm)/Si substrates, respectively. The discharge currents on the SiO₂(350 nm)/Si substrates and consumption powers were under ~5μA and 3 mW, respectively but NNG can be grown as shown in Fig. 1(b).The growth periods were changed from 10 s to 30 min. The hard X-ray PES measurements were performed at BL47XU, SPring-8. The energy of X-ray was 7940 eV.

3. Results and discussion
Growth period dependence of Raman spectra of MLG grown on the SiO₂(90 nm)/Si substrates are summarized in
Fig. 2. The G and D bands derived from a graphite structure and its overtone bands are observed. It has been reported that the graphene grown on SiO₂(90 nm)/Si substrates has a higher Raman enhancement factor than that on SiO₂(350 nm)/Si substrates [3], so that D and G bands of the sample grown for even 2 min. can be clearly observed.

The growth period dependence of the film thickness measured by XPS is shown in Fig. 3 (a). From this result, the growth rate is obtained as approximately 0.56 nm/min. The G band width and its positions are shown in Fig. 3(b), and (c). The G band position shifts toward a low wave-number with increasing the growth period while the G band width increases. The grain size obtained G and D bands intensity ratio[4] is summarized in Fig. 3 (d). The grain size slightly increases from ~11.30 nm up to ~11.45 nm with increasing the film thickness. The cross-sectional TEM image of interface between NNG and the SiO₂ substrate shows in Fig. 4. The horizontally oriented MLG can be observed at the interface, and its thickness is approximately ~0.3 nm.

Here, we discuss the results of Raman spectra. The G band position corresponds to the grain size of graphite [4] or the curvature of graphene sheets [5]. In our case, the grain size is almost constant at 11.3-11.4 nm, so that it is thought that the shift of G band position shown in Fig. 3(b) is due to the bending of graphene sheets. At the initial stage of MLG growth, the highly oriented graphene sheets (small curvature) form on the SiO₂ surface. By proceeding the formation of MLG, the curvature of graphene sheets increases. When the growth time reaches 5 min., the curvature of graphene sheets also become maximum, leading to NNG growth. This model is consistent with the TEM image in Fig. 4. The thickness of MLG is about 3 nm, this thickness agrees with the transition of the Raman spectra (broken line in Fig. 3). In the conference, the electric resistivity of MLG will be reported.

4. Conclusions

The NNG crystallographic quality dependence on the thickness grown on the SiO₂/Si substrates was investigated using Raman Spectroscopy and hard X-ray PES. The growth of MLG can be clearly observed using Raman spectra by using SiO₂(90 nm)/Si substrates. The G band width, G band position, and grain size of NNG changes at approximately 3 nm of the thickness. This corresponds to the change of growth direction from horizontal growth (MLG) to randomly oriented growth (NNG).

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