

# Raman Spectroscopy, TEM and Bulk-sensitive XPS Study of Multi-layer Graphene Grown on SiO<sub>2</sub>(350 nm)/Si

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## 1. Introduction

The graphene is one of the potential materials applicable for interconnections of LSI, because of high electrical and thermal conductivity, high elasticity, and intrinsically higher electromigration tolerance compared with those of Cu. For growing a multi-layer graphene film on SiO<sub>2</sub> layers without any catalysts, we have developed a photoelectron-assisted plasma chemical vapor deposition process [1]. In this study, we report the crystallographic quality evaluation of multi-layer graphene grown on SiO<sub>2</sub>(350 nm)/Si substrate by means of microscopic Raman spectroscopy, transmission electron microscopy (TEM) and bulk sensitive X-ray photoelectron spectroscopy.

## 2. Experimental

Multi-layer graphene was grown on SiO<sub>2</sub>(350 nm)/Si and Si substrates with native oxide of 1-2 nm using a photoelectron-assisted plasma CVD apparatus at Tohoku University. The sample size was of 11×6 mm<sup>2</sup>. Neither wet nor dry cleaning of the substrates were performed before CVD growth. The samples were mounted on a Si heater with a Mo foil clamp. The temperature of the sample was measured by an infrared pyrometer, which was calibrated by a K thermocouple. The sample was irradiated through a fused quartz window by a UV light ( $\lambda = 172$  nm) from Xe excimer lamp, and the resultant photoelectrons were utilized to control a DC glow discharge. The details of the photoemission mechanism from the thick SiO<sub>2</sub> surface will be discussed in another paper [2]. A Ar-diluted CH<sub>4</sub> gas was introduced into the process chamber. The pressure of the mixture gas and plasma power were 1.6 kPa and 30W, respectively. The growth period was changed from 1 min. to 10 min, while the growth temperature was fixed at ~630°C.

In the microscopic Raman spectroscopy measurement, Ar ion laser ( $\lambda = 488$  nm) was employed as an excitation light source with output power of 0.3 W. The magnification of object lens was 50 times. Bulk-sensitive XPS was conducted at BL47XL, SPring-8, Japan.

## 3. Results and Discussion

Figure 1 shows the Raman spectrum and cross-sectional TEM images of multi-layer graphene grown on Si substrate. In the curve-fitting analysis of the Raman spectrum, three

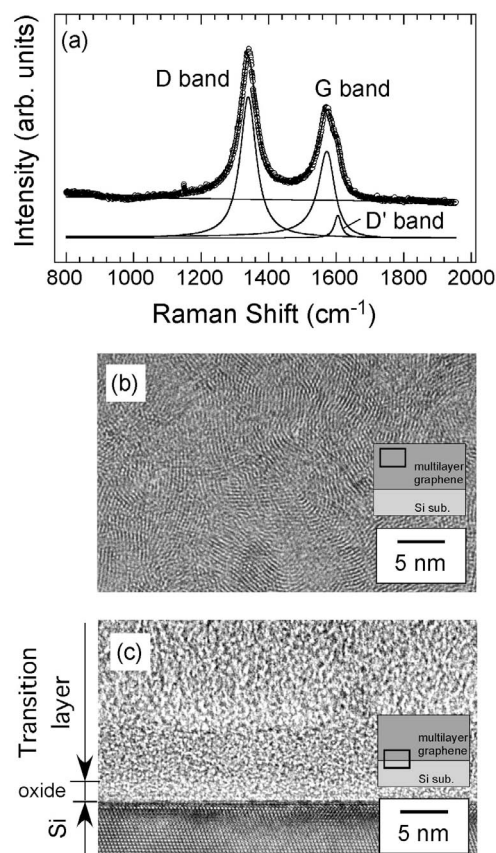


Fig. 1 (a) Raman spectrum of a multi-layer graphene grown at 688°C on Si substrate, and cross-sectional TEM images of (b) a portion below 2  $\mu$ m from the surface, and (c) an interface region for the sample in (a). The growth time and film thickness were 20 min. and ~40  $\mu$ m, respectively.

peaks G, D and D' appear. Here G and D bands correspond to the graphite and disordered component, respectively. In addition, D' band indicates defects such as the edge of graphene sheets. Both G and D' bands suggest the existence of well-ordered graphene sheets. As shown TEM image of Fig. 1 (b), it is apparently observed that the deposited film of ~40  $\mu$ m in thickness is mainly composed of small grains of multi-layer graphene connected closely to each other by graphene sheets. The average grain size is of

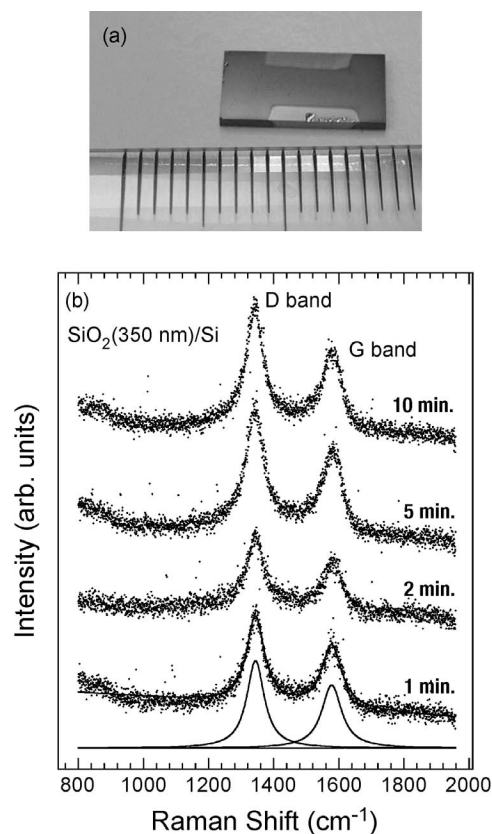


Fig. 2 (a) Picture of a multi-layer graphene grown on  $\text{SiO}_2(350 \text{ nm})/\text{Si}$  substrate at  $\sim 630^\circ\text{C}$ . (b) Growth period dependence of Raman spectra of multi-layer graphene layers grown on  $\text{SiO}_2(350 \text{ nm})/\text{Si}$  substrate at  $\sim 630^\circ\text{C}$ . The solid lines indicate the peak components G and D.

5-10 nm. However, there are not high-quality grains of multi-layer graphene but a transition layer, maybe composed of amorphous carbon in addition to native oxide as shown in Fig. 1 (c). Thus it is implied that the high-quality grains of multi-layer graphene can grow following the deposition of amorphous carbon as a buffer layer for thin  $\text{SiO}_2$  layers below 1-2 nm in thickness.

On the other hand, a carbon layer was also uniformly deposited on thick  $\text{SiO}_2$  layers up to 350 nm as shown in Fig. 2 (a). The small areas at both the long edge sides are due to the mask effect of the Mo clamp. In order to investigate the thickness dependence of the crystallographic quality of multi-layer grown on  $\text{SiO}_2(350 \text{ nm})/\text{Si}$ , Raman spectra is shown as a function of growth period in Fig. 2 (b). Even at 1 min, the D and G bands are well separated as in Fig. 1(a) for the case of Si substrate, indicating that the high-quality grains of multi-layer graphene can grow at the beginning of CVD growth. The height and width of G and D bands are almost unchanged independent of growth period. This tendency suggests that there is a very thin or no transition layer of amorphous carbon at the interface. To confirm this suggestion, the cross sectional TEM images are demonstrated in Fig. 3. As observed in Fig. 3(a), the deposited layer itself is dominantly composed of the small grains of multi-layer graphene, whose size is of 5-10 nm

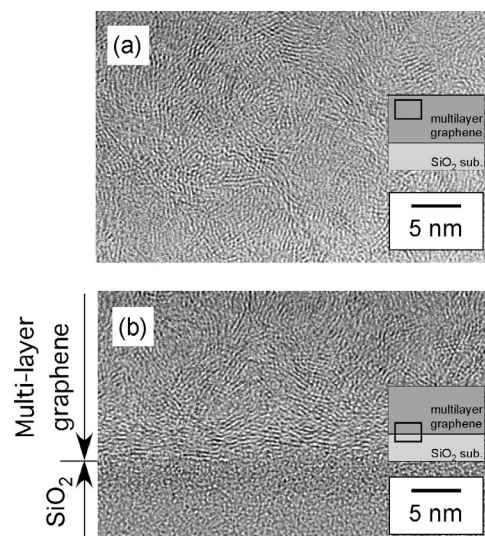


Fig. 3 Cross-sectional TEM images of (a) a portion near the surface, and (b) an interface region for the multi-layer graphene grown  $\text{SiO}_2(350 \text{ nm})/\text{Si}$  substrate at  $\sim 630^\circ\text{C}$ .

similar to those in Fig. 1(b). It is noteworthy that the small grains of multi-layer graphene can be clearly observed at the interface as seen in Fig. 3(b), and it is difficult to specify the transition layer of amorphous carbon. Therefore, it can be mentioned that the small grains of multi-layer graphene can be directly nucleated and grown on thick  $\text{SiO}_2(350 \text{ nm})$  substrate. This finding has a great meaning in the application of the photoemission-assisted plasma CVD process to grow multi-layer graphene on interlayer insulators of low- $k$  materials for the LSI interconnections.

#### 4. Conclusions

The small domains of multi-layer graphene closely connected to each other was grown on  $\text{SiO}_2(350 \text{ nm})/\text{Si}$  substrate as well as Si substrate with native oxide using the photoelectron-assisted plasma CVD process. Meanwhile the interface layer of amorphous carbon does not necessarily exist for the deposition on thick  $\text{SiO}_2(350 \text{ nm})$ , whereas it was observed at the interface for the CVD growth on Si substrate. Therefore, it is suggested that the small grains of multi-layer graphene can be grown in the order of nanometers in thickness on  $\text{SiO}_2$  layers.

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