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Effect of Carrier Gas (Ar and He) on the Crystallographic Quality of Multi-layer Graphene Grown on Si by Photoemission-assisted Plasma CVD

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1. Introduction

Multi-layer graphene is expected as a new interconnection material for LSI devices because of high electrical conductivity and intrinsically higher electromigration tolerance compared with those of Cu. For this application, multi-layer graphene has to be formed at temperatures as low as ~400℃ without any metal catalysts over a Si wafer as large as 12-inch in diameter. To achieve such goals, we have proposed a photoemission-assisted plasma CVD process[1]. In this study, the effect of carrier gas (Ar and He) on the crystallographic quality of the multi-layer graphene layers grown on a native oxide of Si(001) substrate by photoemission-assisted plasma CVD was investigated by microscopic Raman spectroscopy and grazing incidence X-ray diffraction (GIXRD) at BL47XL, Sring-8. It was found that He has a significant effect to improve the crystallographic quality in the temperature region lower than ~500℃, even at room temperature in comparison to Ar.

2. Experimental

The CVD growth experiments were performed by using a photoemission-assisted plasma CVD apparatus equipped with Xe excimer lamp (Ushio, UER20H-172A: λ = 172 nm). The substrate was a Si wafer with native oxides of 1-2 nm in thickness. The sample with a size of 3×10 mm^2 was mounted on a Si heater with Mo clamp. The temperature was measured by an infrared pyrometer calibrated by K thermocouple. The growth temperature was ranged from room temperature (RT) to 700°C. Ar or He of 99.9999% purity was employed as a carrier gas after being mixed with CH_4 of 99.999%. A mechanism of photoemission-assisted plasma CVD is described elsewhere [1]. Here it is emphasized that photoabsorption of Ar, He and CH_4 at 172 nm is negligibly small and therefore photodissociation of all gases has no concern with this process. When the growth period was 10 min, the thickness of samples was 10-40 μm. Therefore the growth rate of 1-4 μm/min was accomplished, although electric power consumption was as low as 0.03 - 0.06 W for plasma generation.

Microscopic Raman spectroscopy was conducted with an excitation light of 488 nm from an Ar^+ ion laser at output power of 0.3 W. The probing area size by Raman spectroscopy was 2 μm in diameter when an object lens with 50 times magnification was mounted. The X-ray incident angle and energy for GIXRD were 0.2° and 10 keV, respectively.

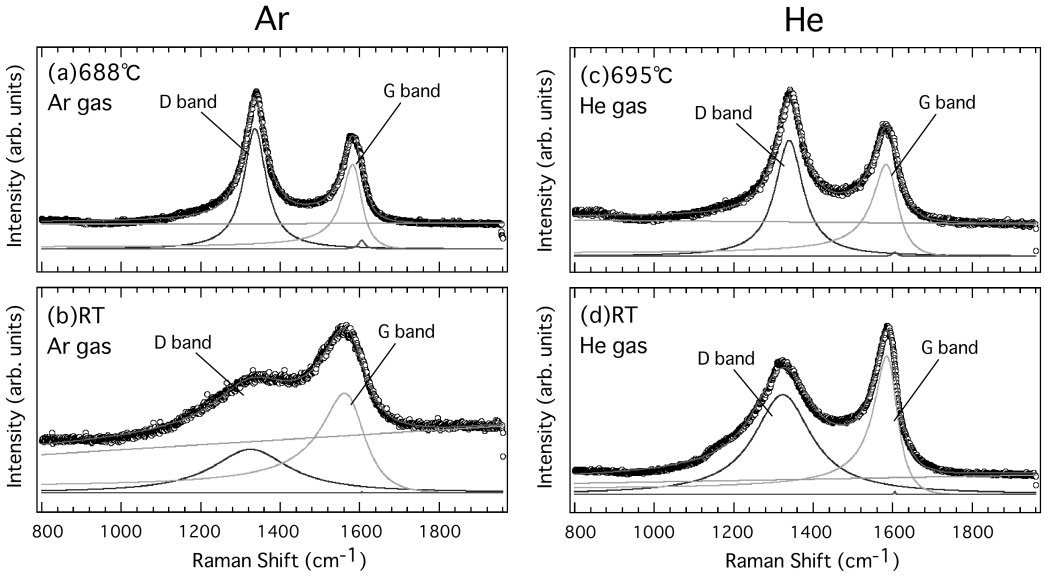

Fig. 1 Raman spectra of multi-layer graphene grown at ~700℃ (a and c), and room temperature (b and d) with Ar-diluted and He-diluted CH_4, respectively.

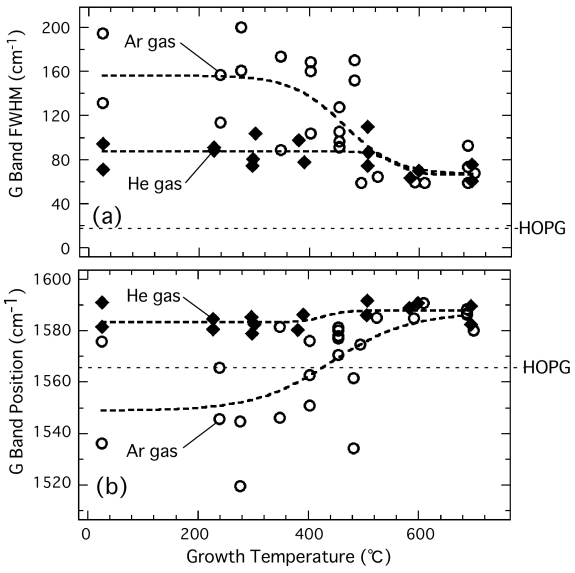

Fig. 2 Growth temperature dependence of (a) G band FWHM (b) G band position obtained from the Raman spectra in Fig. 1. The G band position and FWHM of HOPG are indicated with dot lines. The broken lines are guide for eyes.

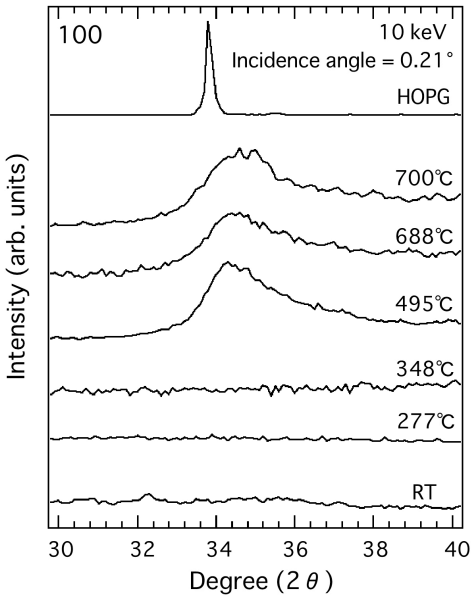

Fig. 3 Growth temperature dependence of X-ray diffraction patterns of 100 peak for graphite obtained from the samples grown using Ar-diluted CH_4 gas.

3. Results and discussion

Figure 1 shows the Raman spectra of samples grown at ~700℃ and RT with Ar- or He-diluted mixture gas. All spectra are mainly composed of two peaks assigned to D and G bands. It is noted that D band implies the existence of sp^3-bond configuration in diamond like carbon (DLC) and structural disorders such as amorphous. On the other hand, G band is due to the sp^2-bond configuration in graphene sheet. At ~700℃, D and G peaks are well separated for both Ar and He gases, indicating that the crystallographic quality is almost the same independent of carrier gas species. Regarding the full width at half maximum (FWHM) of G band, it is broader about two times than that of HOPG (highly oriented pyrolytic graphite) as shown in Fig. 2(a). This suggests that the grain size is rather small, while high-quality graphene sheets are contained. On the other hand, the spectral feature is considerably broad at RT for Ar gas, indicating the growth of DLC, the conductivity of which is too low to be utilized as an interconnection material. In fact, the sample grown at RT cannot be observed by XPS due to the charging-up effect. For the case of He, however, a well-separated doublet structure is still maintained at RT. Thus multi-layer graphene can be grown even at RT by changing a carrier gas from Ar to He.

In order to compare the growth temperature dependence for the Raman spectra between Ar and He , the FWHM and peak position of G band are summarized in Fig. 2. In case of Ar gas, the FWHM of G band increase with decreasing temperature, indicating that the grain size of graphite is reduced with decreasing temperature below ~500℃ [2]. This is also confirmed by GIXRD as demonstrated in Fig. 3. The 001 peak of graphite disappears below ~450℃. At temperatures above ~450℃, the grain size of multi-layer graphene is estimated as 5–10 nm. The disappearance of 100 peak implies that it is smaller than ~1 nm. Namely the deposited layer is thought to change from the grain structure of multi-layer graphene to DLC and/or amorphous carbon around ~450℃ for the Ar-diluted CH_4 gas in accordance with the results of Raman spectroscopy. Furthermore, this suggestion is agrees with the shift of G band position. As shown in Fig. 2(b), it lies around ~1585 cm^{-1} at ~700℃. With decreasing temperature, it shows a large shift toward the low wavenumber side below ~500℃ and eventually reach ~1540 cm^{-1} at RT.

On the other hand, both the FWHM and peak position of G band hardly change depending on temperature over an examined range of RT-700℃ for He-diluted CH_4 gas. There is no significant degradation of the crystallographic quality around ~500℃. Namely He carrier gas enables us to grow multi-layer graphene below ~400℃ that is a critical temperature for the interconnection application of multi-layer graphene as mentioned above. For the observed He effect, there are two plausible origins: (1) the He^+ ion impact effect and (2) the UV light irradiation due to recombination between He^+ and e^-, but not clear yet.

4. Summary

The effect of Ar and He carrier gas on the crystallographic quality of multi-layer graphene was investigated for photoemission-assisted plasma CVD. We found that multi-layer graphene can be grown even at RT by using He-diluted CH_4 gas, whereas DLC was deposited for Ar-diluted CH_4. Consequently it is of practical importance to further clarify the role of carrier gas for growing high quality multi-layer graphene at low temperature.

References

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