

## Analysis of the Electronic and Crystal Structures of Graphene Multi-layers by Hard X-Ray Photoelectron Spectroscopy and Grazing Incidence X-Ray Diffraction

Graphene has been considered to be one of materials for future electronic devices since it was discovered in 2004 [1] in which it was shown to have an extremely high electron mobility and thermal conductivity [2]. On the other hand, low-temperature synthesis, which is essential for various electronic applications, has not been achieved yet [3]. Recently, we have succeeded in synthesizing graphene multi-layers at low temperatures of 510 and 620°C. In this paper, two approaches to low-temperature graphene synthesis will be introduced.

A novel carbon composite structure consisting of graphene multi-layers and aligned multi-walled carbon nanotubes (MWNTs) has been obtained at a temperature of 510°C [4]. The composite structure, which was synthesized by chemical vapor deposition (CVD), has graphene multi-layers combined with the upper ends of vertically aligned MWNTs on a substrate. Figure 1(a) shows a cross-sectional image of the composite on a silicon substrate by scanning electron microscopy (SEM). A flat structure on vertically aligned MWNT bundles is clearly observed. Analyzing this flat structure by transmission electron microscopy (TEM) in Fig. 1(b), we have found that the flat structure is composed of multiple graphite domains next to each other, whose thickness was estimated to be approximately 18 nm. This thickness can be controlled by the growth condition and catalyst composition [4]. Furthermore, from the growth-time dependence, it is found that graphene multi-layers were firstly synthesized, which implies the possibility of low-temperature synthesis of graphene.

The CVD process was performed at 510°C. As a catalyst, a 2.6-nm cobalt (Co) film on a 5-nm titanium

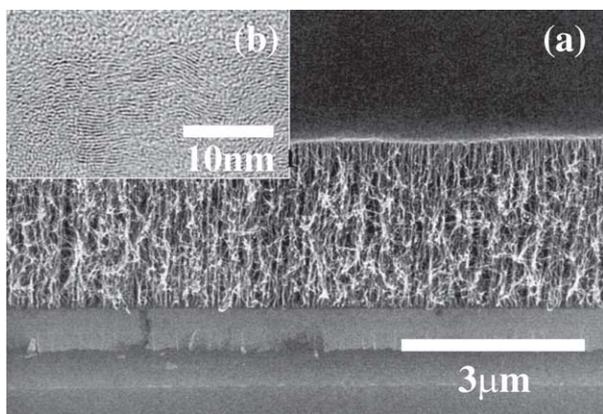


Fig. 1. (a) SEM image of the new carbon structure composed of graphene multi-layers and MWNTs; (b) TEM image of the graphene multi-layers.

nitride (TiN) film was used. While the obtained structure is clearly different from usual MWNTs, its origin has not been completely understood yet. To elucidate roles of catalyst films in synthesizing the composite, we have investigated the electronic structures of the composite by hard X-ray photoelectron spectroscopy (PES). The PES measurements were performed at beamline BL47XU, using SES-R4000 analyzer.

Figure 2 shows Co 2*p* core level spectra of (a) the usual MWNTs grown from a 1-nm Co film and (b) the composite structure measured by PES. The PES spectrum indicates that the catalyst after synthesizing the composite mainly consists of pure cobalt. On the other hand, the catalyst for the MWNTs was mainly oxidized. Taking into account the fact that the Co film was mostly oxidized before synthesis, these results mean that the Co film of the composite was much more reduced during the growth, implying that high catalyst activity of the Co film is one of the origins of the composite structure.

At a higher temperature of 620°C, graphene multi-layers can be synthesized [5]. The quality of graphene is better and their domain size is bigger than the former case. Figure 3(a) shows SEM images of the samples observed after CVD growth. A film-like structure with multiple domains was observed on the substrate. Analyzing the cross-sectional structures of this flat structure by TEM in Fig. 3(b), we have found that the flat structure is composed of graphene

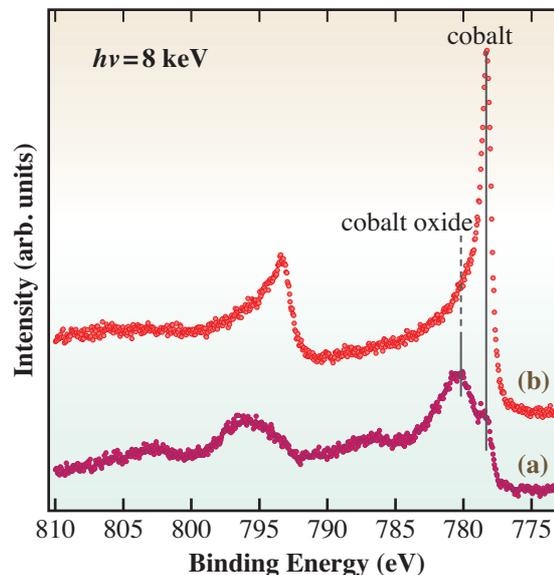


Fig. 2. Co 2*p* core level spectra of (a) usual MWNTs and (b) the composite structure.

multi-layers, whose thickness was estimated to be approximately 13 nm. The thickness of graphene multi-layers can be controlled by the growth condition and catalyst composition as in the former case.

Graphene multi-layers were obtained by hot-filament CVD at 620°C. As a catalyst, an iron (Fe) film with a thickness of 100 nm on a silicon substrate was used. To elucidate roles of catalyst films in synthesizing graphene, we have investigated the crystal and electronic structures of graphene by grazing incident X-ray diffraction (GIXRD). The GIXRD measurement was performed at beamline BL46XU, using ATX-GSOR.

Figure 4 shows the XRD patterns of (a) before and (b) after CVD process measured by GIXRD. After CVD, several new structures were found, which were assigned to be originated from graphene multi-layers and iron carbide ( $\text{Fe}_3\text{C}$ ). In the case of MWNT synthesis, this kind of metal carbide has also been observed [6]. Taking into account that there was no crystallized structure originated from Fe before CVD, these observations indicate that formation of graphene multi-layers and  $\text{Fe}_3\text{C}$  occurs successively or at the same time. Although the direct contribution of  $\text{Fe}_3\text{C}$  to

the synthesis of graphene is not clear, it implies that the role of  $\text{Fe}_3\text{C}$  may be important in the synthesis process of graphene.

In summary, we show two approaches to graphene synthesis at a temperature lower than those reported previously. The low-temperature synthesis methods reported here have brought the application of graphene to electronic devices one step closer to practical use. We will also continue to investigate the mechanisms by which the graphene multi-layers form, in order to develop future electronic devices, such as graphene-based transistors.

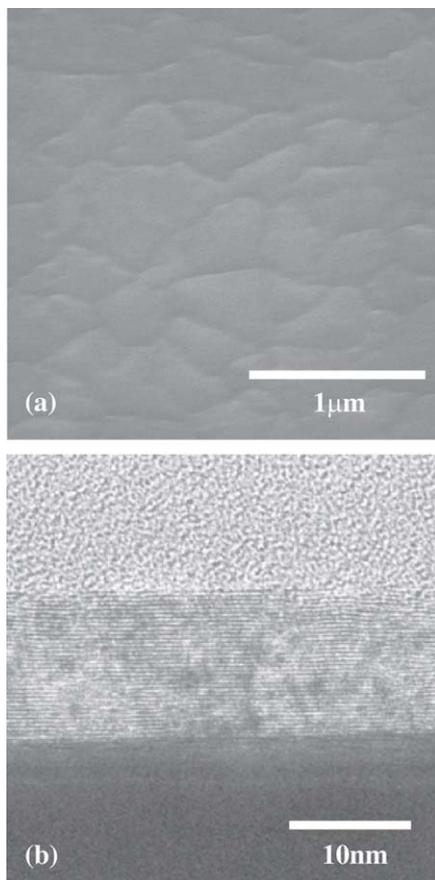


Fig. 3. (a) SEM image of the graphene multi-layers. (b) TEM image of the graphene multi-layers.

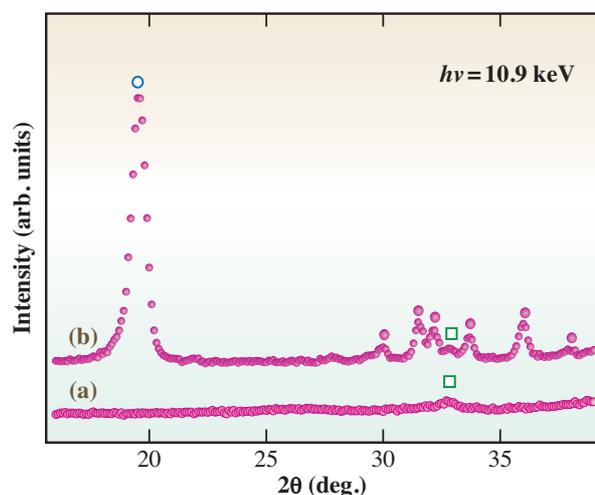


Fig. 4. XRD patterns of (a) before the CVD growth and (b) after the CVD growth of graphene multi-layers. Open circles: graphene multi-layers, open square: Fe, solid circles:  $\text{Fe}_3\text{C}$ .

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## References

- [1] K.S. Novoselov *et al.*: Science **306** (2004) 666.
- [2] A.A. Balandin *et al.*: Nano Lett. **8** (2008) 902.
- [3] M. Yudasaka *et al.*: J. Vac. Sci. Technol. A **13** (1995) 2142.
- [4] D. Kondo, S. Sato and Y. Awano: Appl. Phys. Express **1** (2008) 074003.
- [5] D. Kondo *et al.*: Abst. 36th Fullerene Nanotubes General Symposium 2-15, 2009.
- [6] K. Nishimura *et al.*: Jpn. J. Appl. Phys. **43** (2004) L471.