

Precise control of layer number in graphene grown on Ni(111)

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1. Introduction

Graphene proved interesting for nanoelectronics and spintronics. There have been plenty of attempts to fabricate graphene devices. To realize the nanoelectronic and spintronic devices using graphene, particular concerns should be addressed to the following two issues: The first one is to form the well-defined interface between graphene and metal electrodes. The elucidation and control of the injection/detection processes of spin-polarized carriers through the graphene/metal interface are essential for designing device properties [1]. The second one is to synthesize the graphene film with large area and uniform layer number. The most conventional and commonly used fabrication method of graphene is the micromechanical cleavage of graphite. However, the process cannot satisfy the above requests due to the following reasons: limited sizes with large distribution in shape and layer number as well as the contamination and impurities introduced during the fabrication process. From this view-point, ultra high vacuum chemical vapor deposition (UHV-CVD) [2] can be promising alternative method, since a large area graphene monolayer is known to be formed on the surfaces of the catalytic metal single crystals. In UHV-CVD, it is considered that graphene grows due to the dissociation the precursor hydrocarbon molecules and the graphitization of carbons on the metal surfaces. This would allow us to control the crystallinity and layer number depending on the growth condition and the prevent samples from contaminations.

In the present study, the precise control of layer-number in graphene on the Ni(111) epitaxial thin film by UHV-CVD is investigated using *in-situ* reflection high energy electron diffraction (RHEED), Auger electron spectroscopy (AES) and atomic force microscopy (AFM).

2. Experimental

The graphene growth on Ni(111) was performed in an UHV chamber with a base pressure of 3×10^{-7} Pa. Before the graphene growth a Ni(111) thin film was epitaxially grown on an α -Al₂O₃(0001) substrate. The α -Al₂O₃(0001) substrate was annealed at 1173 K for 60 min in an open air to prepare an atomically flat surface. The Ni(111) thin film (30 nm thick) was deposited on the α -Al₂O₃(0001) substrate kept at 423 K using an electron-beam evaporator, and successively a Ni(111) single-crystalline surface was obtained by a short annealing at 823 K. The deposition rate

was monitored with a quartz crystal microbalance and was about 1.6 Å/min. The graphene film was grown by exposing the Ni(111) surface to benzene vapor in the range of less than 3×10^5 langmuirs (L, 1 L = 1.33×10^{-4} Pa·s) at the substrate temperature of 823 – 973 K. Benzene was purified by repeating the freeze-pump-thaw cycle several times. Values of benzene exposure shown in this manuscript are not corrected with the sensitivity factor (5.2) of the ionization gauge [3]. The surface crystallinity and crystallographic relationship were characterized *in-situ* by RHEED at 20 keV. Chemical composition of the film-surface was analyzed by AES with keeping UHV condition. The spectra were measured with a double pass cylindrical mirror analyzer in the pulse counting mode using a 3 keV electron beam normal to the sample surface. The derivative spectrum was obtained through numerical differentiation technique.

3. Results and discussion

The RHEED patterns *in-situ* measured before benzene exposure and after 100 L and 1.8×10^5 L exposure are shown in Fig.1. The direction of the incident electron beam was set parallel to the [110] (i, iii, v) and [112] (ii, iv, vi) azimuths of the Ni(111) thin film. The result of RHEED patterns indicates that the Ni film grows epitaxially on α -Al₂O₃(0001). The epitaxial relationship is the [110] and [112] directions of the Ni(111) film are parallel to the

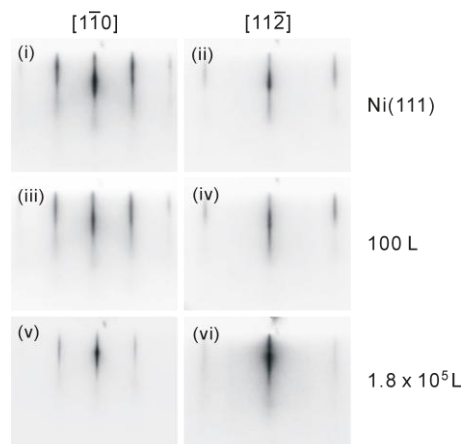


Fig.1 RHEED patterns (i, ii) before exposure and after (iii, iv) 100 L and (v, vi) 1.8×10^5 L exposure at 823 K, respectively.

[1100] and [2100] directions of the α - $\text{Al}_2\text{O}_3(0001)$ substrate, respectively. Streaks in RHEED patterns indicate appearance of a flat Ni(111) surface on the substrate. Even after benzene exposure, the RHEED streaks keep their sharpness almost unchanged. No obvious difference in the diffraction pattern is also seen before and after exposure. This is reasonable since it has been reported that the epitaxial graphene film with the commensurate 1×1 structure grows on the Ni(111) single crystal surface [4,5] and the increase of the amount of carbon after benzene exposure is confirmed by the AES measurements as discussed below.

Figure 2 (a) shows evolution of the AES spectra during benzene exposure. C_{KLL} (272 eV) and Ni_{LMM} (717, 783, and 850 eV) Auger signals are observed in the spectra. It is clear that the Ni_{LMM} Auger intensities decrease, while C_{KLL} increases with increasing benzene exposure. The atomic ratio of C to Ni is estimated by spectral analysis with consideration of Auger-electron emission probabilities and mean free path of the Auger electrons [6]. A change in the C/Ni atomic ratio during benzene exposure is represented in Fig.2 (b). The C/Ni ratio increases with increasing exposure, and two different stages can be seen depending on the amount of benzene exposure; the intensity ratio shows rapid increase at the initial stage of exposure up to about 100 L and subsequently shows a slow increase toward the saturation at the second stage up to approximately 1×10^5 L. The C/Ni ratios after 100 and 1×10^5 L exposure amount to $2.2 (\pm 0.2)$ and $3.8 (\pm 0.2)$, respectively. These C/Ni ratios are reasonably explained by the existence of single-layer graphene (SLG) and bi-layer graphene (BLG) on the Ni(111) surface because two carbon atoms belonging to two triangular sublattices of graphene sit on the nickel atom in the epitaxially grown SLG on Ni(111) and twice the number of carbon atoms exists in BLG compared to SLG. The growths of SLG and BLG are also confirmed with micro-Raman spectroscopy [7].

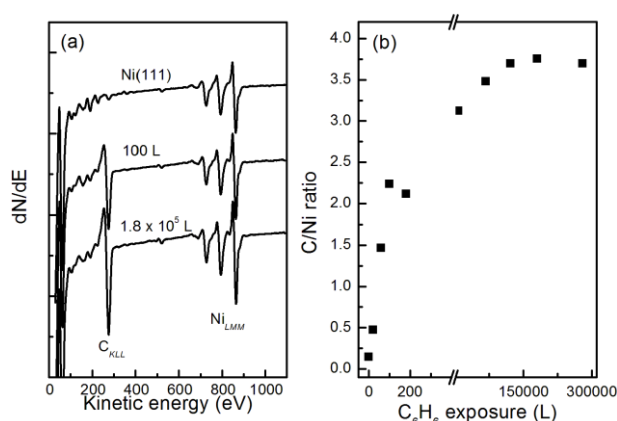


Fig.2 (a) AES spectrum of Ni(111) surface and spectra after 100 L and 1.8×10^5 L exposure at 823 K. (b) Plot of the C/Ni ratio estimated from the AES spectra.

In order to verify the validity of this estimation, the graphene films obtained after 100 L and 1×10^5 L exposure were characterized by using AFM (not shown). For the graphene films transferred onto SiO_2 surfaces, the heights

of the top surfaces of the graphene films from the SiO_2 surface are measured to be 0.8 ± 0.3 nm and 1.8 ± 0.3 nm for the samples after 100 L and 1.8×10^5 L exposure, respectively. These values are comparable with the previously reported values for SLG and BLG on SiO_2 [8]. These results demonstrate that the well-controlled exposure enables precise control of the layer number of graphene in the UHV-CVD process.

Since the exposure-dependent evolution of the Auger intensity ratio shown in Fig.2 can be attributed to the graphene growth based on the above discussion, the rapid and slow increases of the intensity ratios observed at the initial and second stage of exposure indicate a difference in the growth rate by three orders of magnitude in between the first and second graphene layer from the Ni(111) surface. Although the details on the growth processes of the individual graphene layers are not so clear, it can be speculated that the growth of the second graphene layer would be more difficult than that of the first layer possibly due to the decrease of the catalytic activity from the Ni(111) surface reflecting complete surface coverage by the first graphene layer. The growth of tri-layer graphene (TLG) is not seen in the exposure range of the preset study, implying, if it happens, the growth of the third graphene layer to be much lower than those of the first and second layer.

3. Conclusions

The UHV-CVD grown graphene films on the Ni(111) epitaxial thin film was examined by RHEED, AES and AFM. By choosing benzene exposure appropriately, the precise control of graphene layer number is successfully realized; 100 L for SLG growth and 1×10^5 L for BLG growth. The present results indicate the controlled growth of SLG and BLG growth by optimizing the dosage of precursors.

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