

Surface morphology changes of CVD-graphene/Cu{120} induced by post-annealing processes

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1. INTRODUCTION

A chemical vapor deposition (CVD) growth of graphene over Cu surfaces, especially on commercial Cu foils, is a promising scalable method for obtaining graphene with high quality. An interesting effect of Cu crystal orientation on charge doping and mechanical strain of CVD graphene has been discussed based on low Miller index planes which are Cu{111}, {001}, and {101} [1-3]. Here, we report an investigation of CVD-graphene/Cu{120}: surface morphology changes and related doping and strain effects due to a post-annealing in an ultra-high vacuum (UHV) environment.

2. EXPERIMENT

Cu foil (Alfa Aesar, 99.8%) was pre-annealed with Ar containing more than 5% H₂ at over 1000°C and 3.5 x 10³ Pa for two hours to obtain re-crystallized-single-crystal-like grains. Subsequently, the graphene was synthesized on the surface of the Cu foil using the CVD method with 60-ppm CH₄ as carbon source diluted by Ar-H₂ gas. Next, the graphene/Cu{120} was post-annealed in the UHV (7.5 x 10⁻⁷~8.5 x 10⁻⁹ Pa) at 200 to 700°C in 10-min 100°C steps to examine how the surface morphology changed depending on the post-annealing temperature. Electron back scattering diffraction (EBSD) mapping, X-ray diffraction (XRD), and low energy electron diffraction (LEED) were used to evaluate the Cu foil's crystal orientations. The number of layers, quality, and effects of mechanical strain and charge doping in the graphene were characterized by Raman spectroscopy. The laser excitation wavelength (energy) was 532 nm (2.33 eV). The surface morphologies of Cu covered by the CVD graphene as well as the alignment of graphene to the Cu surface were observed by atomic force microscopy (AFM), scanning tunneling microscopy (STM), and low energy electron microscopy (LEEM).

3. RESULTS AND DISCUSSION

Commercial Cu foils generally have a micrometer-order multi-domain structure. We performed a pre-annealing process at high temperature to enhance recrystallization, i.e. individual Cu grains within the Cu foils reaching a centimeter scale. EBSD, XRD, and LEED results revealed that the pre-annealed Cu foil mainly had {100} and {120} planes. Here, we have focused on a graphene/Cu{120} area, whose surface morphology showed a unique pattern different from that on low Miller index planes. Fig. 1 (a) and (b) depicts Cu {111}, {100}, {110}, and {120} planes in the unit cell of the face center cubic (fcc) structure and a surface atomic arrangement of Cu{120}, respectively.

We observed two features of the surface morphology of CVD-graphene/Cu{120} at each post-annealing temperature (200 to 700°C): step-terrace structures, which are bunching parallel to Cu [121] direction with 500- to 600-nm wide terraces, and triangular facet patterns in the Cu [121] and [123] directions on the

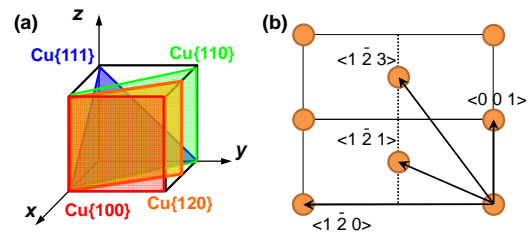


Fig. 1. (a) Schematic of crystal planes of Cu in the unit cell. (b) Atomic arrangement of Cu{120}. Arrows indicate step directions in surface morphology observed by AFM.

terrace area. Fig. 2 shows AFM height images of typical patterns of the (a) as-grown graphene/Cu{120} and (b) after post-annealing at 500°C. These directions are marked by white arrows in Fig. 2 (a). The step-terrace structure remained unchanged during the post-annealing, while the triangular facet patterns on the terrace area were changed into the small size [Fig.1 (b)]. Notes that CVD graphene is important for maintaining the step-terrace structure of Cu{120} because bare Cu areas do not show such a structure. However, the orientation relationship between graphene and Cu{120} does not affect the surface morphology changes considering that the LEED and LEEM results indicate no specific alignment of CVD graphene against the Cu {120} surface.

Mechanical strain and charge-doping effects were compared between an as-grown and a 500°C post-annealed CVD-graphene/Cu{120} surface. Raman spectroscopy is a powerful tool for this purpose [4,5], because the Raman frequency of the G mode (ω_G) is sensitive for the charge doping, and that of the 2D mode (ω_{2D}) strongly reflects the strain. The D mode originating from defects and dangling bonds in the honeycomb lattice was scarcely detected from the graphene in this study, which is evidence of the graphene's high quality with a low number of defects. Fig. 3 shows a correlation map of ω_G and ω_{2D} for the as-grown and the post-annealed at 500°C graphene/Cu{120}. Both the red and green circles can be fitted by the linear correlation $\partial\omega_{2D}/\partial\omega_G \sim 2.2$. The post-annealing uniformly induced the hole charge doping to the CVD graphene with $4.7 \times 10^{12} \text{ cm}^{-2}$ carrier density. The variation of points in the correlation map indicates strain distributions of CVD graphene (-0.3 to 0 %), and the distribution widened after post-annealing. The post-annealing reduced the size of the triangular facet patterns and thereby increased the variation of Cu crystal planes on the terrace, which caused change in the strain and doping levels of CVD graphene.

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REFERENCES:

- [1] L. Zhao *et al.*, *Solid State Commun.* 151 (2011) 509.
- [2] O. Frank *et al.*, *Carbon* 68 (2014) 440.
- [3] A. L. Walter *et al.*, *Phys. Rev. B* 84 (2011) 195443.
- [4] J.-E. Lee *et al.*, *Nat. Commun.* 3 (2012) 1024.
- [5] S. D. Costa *et al.*, *Solid State Commun.*, 152 (2012) 1317.

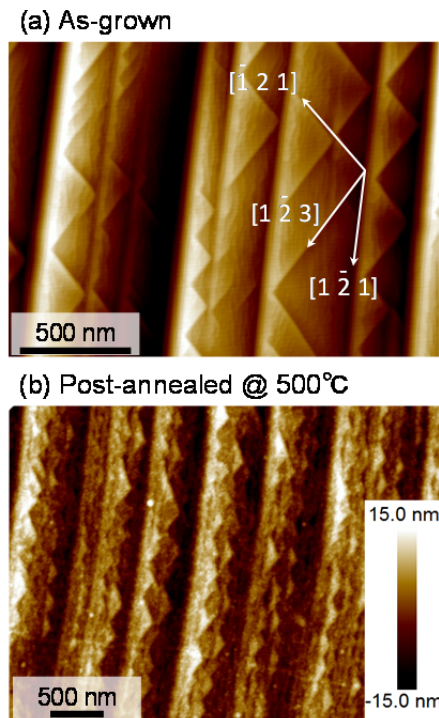


Fig. 2. AFM images of the (a) as-grown graphene/Cu{120} and (b) after post-annealing at 500°C. Arrows in (a) indicate crystallographic orientations on Cu{120}.

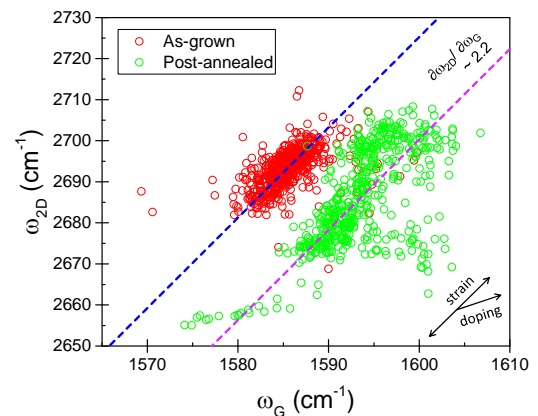


Fig. 3. Correlation map between the Raman frequencies of the G and 2D modes (ω_G and ω_{2D}) in the as-grown and the post-annealed graphene on the Cu{120} plane. Dash lines indicate fitting results.