Epitaxial Growth and Electronic Properties of Large Hexagonal Graphene Domains on Cu(111) Thin Film

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1. Introduction

Graphene has been attracting a great interest as a new type of two-dimensional atomic sheet owing to its high carrier mobility, optical transparency, mechanical flexibility, and thermal conductivity, which promise applications in many electronic devices [1]. Recent progress of chemical vapor deposition (CVD) growth using Ni, Co, and Cu substrates offers a promising route to produce large-area graphene with low cost, which is essential for future applications of graphene. In particular, Cu foil is widely used because of the selective growth of single-layer graphene on the Cu surface due to the low carbon solubility, explained by self-limiting mechanism [2,3]. However, the as-grown single-layer graphene on Cu foil is generally polycrystalline with a number of graphene domains separated by domain boundaries. Transmission electron microscope (TEM) analysis indicated that the domain size of graphene is relatively small (~1 µm), and these domains have different orientations [4]. Such small graphene domains with random orientations are originated in both polycrystallinity of the Cu foil and un-matured growth condition. The presence of domain boundaries limits the physical properties of graphene, reducing carrier mobility and mechanical strength. Therefore, synthesizing single-crystalline graphene free from domain boundaries is required for the future applications of graphene.

Several groups have reported the increasing domain size of single-layer graphene on Cu foil. Yu et al. precisely controlled the supply of the CH₄ feedstock to develop graphene domains on Cu foil, and they observed hexagonal graphene domains whose size is about 5-10 µm [5]. The CVD at 1090 °C that is higher than Cu melting temperature (1083 °C) were demonstrated to give a number of large hexagonal domains with approximately 10-100 µm size [6]. However, such high reaction temperatures induce thermal agglomeration of Cu, resulting in Cu spheres, which makes difficult to transfer graphene to other substrates. From the electron diffraction analysis using TEM, these hexagonal graphene domains were found to be single-crystal. More recently, the large domains with 2 mm size is reported on Cu foil by low vacuum CVD, but the orientation of the domains is not controlled due to polycrystalline nature of the Cu foil [7]. Also, the low pressure CVD limits the scalability and, at the same time, contaminates a CVD chamber with evaporated Cu metal.

Here, we present the growth of large hexagonal graphene domains on a heteroepitaxial Cu films by ambient pressure CVD. These hexagonal domains are large,



Square in (a) shows the mapping area (10 μ m × 10 μ m).

Fig. 1 (a) Optical microscope image of a large graphene domain. Raman mapping images of G-band (b), D-band (c), and 2D-band (d).

50-100 μ m, and have the identical orientation on Cu(111) plane. We report the studies of angle-resolved photoelectron spectroscopy (ARPES) and carrier transport for the orientation-controlled hexagonal domains.

2. Experimental

A 500 nm-thick Cu(111) film was deposited on sapphire c-plane (α -Al₂O₃(0001)) at high temperature by radio frequency sputtering. Graphene was grown by ambient pressure CVD (APCVD) with CH₄/H₂/Ar mixed gas at 1050-1083 °C. ARPES was measured at BESSY II for the as-grown sample. Raman and transport measurements were performed for the graphene transferred on SiO₂/Si wafer by a polymer-mediated transfer technique.

3. Results and discussion

Previously, we reported the epitaxial growth of uniform single-layer graphene on crystalline metal films of Co and Cu by APCVD [3,8-11]. The orientation of graphene hexagons is consistent with the underlying Co(0001) and Cu(111) lattice. In this work, we develop our epitaxial CVD method to obtain large domain graphene by optimizing the growth condition.

Figure 1a shows the optical micrograph of CVD grown graphene transferred on a SiO₂/Si substrate. To visualize the graphene domains, the graphene growth was terminated before the single-layer graphene fully covers the Cu(111) On Cu(111), we obtained the large domains surface. with 50-100 µm size, while the conventional Cu foil gave 10 µm domains under the same growth condition. Moreover, we observed clear hexagonal domains, signifying the single crystalline nature for these domains. From the relationship with the underlying Cu(111)/sapphire, we determined that the hexagonal graphene domains have near zigzag edges. Shown in Fig. 1b-d is Raman mapping images. The hexagonal domain showed negligible D-band except for wrinkles and domain edges. This fact proves that the growth of high quality single-layer graphene on the heteroepitaxial Cu films.

The ARPES measurement of the domains clearly showed the band dispersion and the clear Dirac cone. Previous ARPES data measured for graphene grown on single-crystalline Cu substrates showed a blur spectrum with several Dirac cones originated in rotated graphene domains [12]. Thus, our band structure is much clearer than the previous data due to high crystallinity and the controlled orientation of the graphene domains which are realized by our optimized growth condition [13].

The transport property in the graphene domains was al-

so measured by attaching multiple electrodes on one single domain. High carrier mobilities exceeding 4,000 cm²/Vs were obtained on the SiO₂/Si substrate, indicating the high quality of the CVD domain.

4. Conclusions

We have studied the APCVD growth of large hexagonal graphene domains on the heteroepitaxial Cu(111) film and obtained the large domains up to 100 μ m. This is the first time of the growth of such large graphene domains by APCVD on a Cu thin film. The orientation of domains as well as the orientation of carbon hexagons is well controlled on the Cu(111) due to the epitaxial graphene growth. The high crystallinity of these graphene domains are proved by ARPES and transport measurements. Our new approach to control the orientation of graphene domains can be developed to various electronic devices as well as high quality uniform graphene films.

Acknowledgements

This work was supported by JSPS Funding Program for Next Generation World-Leading Researchers (NEXT Program) and FIRST Program. We thank H. Honjo for the discussion and HZB for the allocation of synchrotron radiation beamtime, and W. Mahler and B. Zada for the support during the beamtime.

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