The crystal orientation relation and macroscopic surface roughness in hetero-epitaxial graphene grown on Cu/mica

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Abstract
Clean, flat and orientation-identified graphene on a substrate is in high demand for graphene electronics. In this study, the hetero-epitaxial graphene growth on Cu(111)/mica(001) by chemical vapor deposition is investigated to check the applicability for top-gate insulator research on graphene, as well as graphene channel research, by transferring graphene on to SiO\(_2\)/Si substrates. After adjusting the graphene growth conditions, the surface roughness of the graphene/Cu/mica substrate and the average smoothed areas are \(\sim 0.34\) nm and \(\sim 100\) \(\mu\)m\(^2\), respectively. The orientation of graphene in the graphene/Cu/mica substrate can be identified by the hexagonal void morphology of Cu. Moreover, we demonstrate a relatively high mobility of \(\sim 4500\) cm\(^2\) V\(^{-1}\) s\(^{-1}\) in graphene transferred on the SiO\(_2\)/Si substrate. These results suggest that the present graphene/Cu/mica substrate can be used for top-gate insulator research on graphene.

Keywords: graphene, CVD, transistor

(Some figures may appear in colour only in the online journal)

1. Introduction

Practical applications of graphene electronic devices require the establishment of an electrically reliable top-gate insulator on graphene [1–4]. However, the progress in the insulator research on graphene is slow in spite of its importance, because clean, flat and orientation-identified graphene on substrates is not widely available, compared with conventional Si substrates. For example, the small grain size in highly-oriented pyrolytic graphite and the limited area of graphene made available by mechanical exfoliation prevent the systematic and reliable study for physical, chemical and electrical characterizations of a top-gate insulator on graphene.

The conditions required for top-gate insulator research on graphene are as follows: (i) large area single-crystalline graphene, (ii) low surface roughness on a relatively large area (RMS < \(\sim 0.5\) nm for \(\sim 100\) \(\mu\)m), (iii) negligible defects, (iv) a resist-residue-free and wrinkle-free surface and (v), a well-identified crystal orientation. Namely, for the insulator research on graphene it is not necessary to remove the catalytic metal under it. Thus, we define this system as the graphene substrate.

So far, using chemical vapor deposition (CVD), single-crystalline graphene is successfully grown on Cu(111) grown hetero-epitaxially on sapphire substrates [5–7], mica substrates [8] or on bulk single crystal Ni(111) [9] substrates. Mica seems most likely to be the best of the aforementioned
substrate choices because the flat Cu(111) surface is attainable on the atomically smooth surface of mica. Moreover, mica can be reused by peeling off the Cu-deposited mica surface and does not require high-temperature surface treatment at 1500 °C to obtain atomically flat surfaces, compared with sapphire. Although it can be expected to use the graphene/Cu/mica sample as the graphene substrate, detailed information on crystal orientation relations in graphene/Cu(111)/mica(001) and macroscopic surface roughness have not been reported.

Concerning the crystalline quality of graphene grown by CVD, the heavy evaporation of Cu at low-pressure conditions has been shown to affect the nucleation and subsequent growth of graphene and its electrical properties [10–13]. Therefore, the key to further improvement of the quality of graphene is to reduce both agglomeration and evaporation of Cu during the CVD growth.

In this paper, the hetero-epitaxial graphene growth on Cu (111)/mica(001) by chemical vapor deposition is investigated to assess the applicability as the graphene substrate from the viewpoint of surface roughness and crystal orientation relations in graphene/Cu(111)/mica(001). Furthermore, we show crystalline quality improvement of graphene by CVD growth at ambient pressure.

2. Experimental procedure

The atomically flat surface of single-crystal mica (001) (KMg₃(AlSi₃O₁₀)F₂) substrate (10 × 10 × 0.5 mm³) was simply obtained by cleaving with the tape. Cu films with a thickness of ~800 nm were hetero-epitaxially deposited on the mica substrate heated to 500 °C. Film thicker than ~600 nm was required to avoid the agglomeration and void formation during the CVD growth at 1000 °C.

Before graphene growth, the Cu/mica substrate was annealed in an H₂/Ar gas flow (100/50 sccm) at 1000 °C for 30 min, in a three-zone tube furnace with the uniform temperature range (±1 °C) of ~10 cm. Subsequently, graphene was grown on the Cu/mica substrate by introducing CH₄ in the chamber at the same temperature. The total pressure in the chamber was kept roughly at 1000 Pa or at ambient pressure. The crystallographic characterization was performed using x-ray diffraction (XRD) and electron backscattering patterning (EBSP). The surface roughness (RMS) was analyzed by atomic force microscopy (AFM).

The Cu film on mica was dissolved in HCl aqueous solution, and graphene was then transferred onto SiO₂ (90 nm)/Si substrate using the polymethyl methacrylate (PMMA)-assisted transfer method [14]. The transferred graphene was analyzed by the Raman microscope with an Ar laser unit of 488 nm excitation. Moreover, field effect transistors of single-layer graphene (SLG) were fabricated using conventional electron beam (EB) lithography techniques, and their electrical properties were characterized in vacuum at room temperature [15].
3. Results and discussion

3.1. Characterization of graphene/Cu/mica substrate

Figure 1 shows the AFM images for (a) the as-deposited Cu surface and (b) the Cu surface after annealing in Ar/H$_2$ gas flow at 1000 °C for 30 min. XRD analysis indicated that the Cu film was single crystal oriented to (111). Heating the mica substrate up to 500 °C during Cu deposition is critical for hetero-epitaxial growth. The triangular shape, which is characteristic of the (111) close-packed plane for fcc metals [16], can clearly be observed after the annealing of Cu/mica substrate. RMS was reduced from 13.6 nm to 0.5 nm after annealing, as shown in figure 1(c).

Subsequently, SLG was grown on Cu/mica. The detailed growth conditions are described in section 3.2. Figure 2 shows (a) the AFM image for graphene on the Cu/mica substrate with a relatively large area (150 $\mu$m$^2$) and (b) the height profile along the dotted line in (a). The inset in (a) indicates that the local area surface of the graphene/Cu/mica substrate is smoother than that of the Cu/mica substrate in figure 1(b) because the Cu surface covered by graphene is not

Figure 3. (a) Optical micrographs at the edge and center of the Cu/mica substrate (red circles in the inset). (b) EBSP map for the hexagonal void and the triangle shape. The EBSP map is colored for the transverse direction, not for the normal direction, because the triangular shape is distinct in green but not in red. The relationship between the hexagonal void and triangular shape is illustrated at the bottom.

Figure 4. Schematic of orientation relationship among mica(001), Cu(111) and graphene.
oxidized [17]. The triangular shape is also clearly evident in the inset of figure 2(a). On the other hand, the grooves, as indicated by black arrows, can be observed in the macroscopic image of (a) because of the twin formation as a result of relaxing the lattice mismatch. The average smooth area is ~100 μm², which is not large enough but is acceptable for the conventional electrode size in capacitance–voltage measurement when the graphene/Cu/mica substrate is used as the graphene substrate.

To identify the orientation of graphene on Cu/mica, the voids with a hexagonal shape in the Cu film were focused on. Figure 3(a) shows the optical micrographs at the edge and center of the Cu/mica substrate (red circles in the inset). This sample was annealed at 1000 °C intentionally for longer than 1 h to promote void formation in the Cu film. The voids appear preferentially along the step edge of mica. The orientation of the hexagonal shape for voids is consistent throughout the Cu/mica substrate, as indicated by the red dotted lines, suggesting that the Cu film is macroscopically single crystal. Figure 3(b) shows the EBSP map of the Cu film around the hexagonal void. The transverse direction is colored in this EBSP map using the inverse pole figure triangle (shown at the bottom right corner). Although the Cu film is macroscopically single crystal, the twins are often observed in the EBSP map, as indicated by a white arrow. The twin formed by 60° rotation on the <111> axis is not distinctly perceived in an observation from the <111> direction. Therefore, the twin can be identified from the EBSP map by tilting the sample slightly from the <111> direction. The important information in figure 3(b) is the triangular shape. To help to detect the triangle, a schematic illustration is also shown. This triangle is consistent with that observed in the AFM image in figure 1(b) and has the specific orientation relation with the hexagonal shape of the void. The orientations of hexagonal and triangular shapes are revealed based on the orientation of Cu, as shown by the cube on the right side of the figure.

Figure 4 is a schematic of orientation relationships among mica(001), Cu(111) and graphene. The surface structure of mica is referenced from the textbook [18], and the orientation relation between graphene and Cu(111) is based on previous reports [5, 6]. Two types of stable positions for graphene on Cu(111) are illustrated because its position has not been uniquely determined because of the small lattice mismatch. Regardless of these two types of stable positions, the macroscopic orientations of graphene, e.g., zigzag and armchair, can be recognized based on the hexagonal void shape of Cu (the dotted hexagonal shape in the figure). Although the voids in figure 3 were intentionally formed throughout the Cu/mica substrate for annealing times longer than one hour, they were also observed near the pin that is used to hold the substrate even for the present CVD growth condition. The position of the pin (no Cu film region) is shown by a white arrow in the inset of figure 3(a). This can be used as a mark to recognize the graphene orientation. Considering both the well-identified orientation of graphene and the reduced macroscopic surface roughness, graphene/Cu (111)/mica(001) can be used as the graphene substrate for top-gate insulator research on graphene.

3.2. CVD growth of graphene and its electrical properties

During graphene growth on Cu/mica in CH₄/Ar/H₂ gas flow, H₂ gas plays multiple roles, such as the cleaning and chemical reduction of the Cu surface, edge reconstruction, the etching of graphene domain and the removal of surface-adsorbed C atoms [19–21]. Figure 5 shows the coverage ratio and $I_D/I_G$ ratio of SLG as a function of the H₂ gas flow rate. The gas flow rates of CH₄/Ar, the total pressure and the growth period were kept at 20/100 sccm, ~1000 Pa and 15 min, respectively. The SLG coverage ratio is defined as $A_{SLG} / (A_{SLG} + A_{MLG})$, where $A$ and MLG denote the area and multi-layer graphene, respectively. The SLG coverage ratio and $I_D/I_G$ ratio were measured for graphene transferred onto a SiO₂/Si wafer. The SLG coverage ratio increases monotonically with increasing H₂ gas flow rate, while the $I_D/I_G$ ratio shows the minimum value at a H₂ gas flow rate of 200 sccm. The nucleation rate of graphene is reduced when the H₂/CH₄ ratio exceeds unity because the coverage ratio of H₂/CH₄ on the Cu surface is reversed and the CH₄ decomposition is reduced by the high H₂ flow rate [19]. The growth rate of graphene is kept low in this condition, and the graphene quality is increased, as indicated by the $I_D/I_G$ ratio. However, when the H₂ flow rate exceeds 200 sccm (H₂/CH₄ flow ratio > 10), the increase in the $I_D/I_G$ ratio indicates the introduction of defects such as the C–H bonding in graphene [19, 20]. These results indicate that there is an optimal H₂ gas flow rate under the fixed CH₄ flow rate and fixed total pressure. Moreover, the SLG coverage can be increased by up to ~95% by reducing the growth time from 15 to 7.5 min (H₂/CH₄/Ar = 200/20/100 sccm).

To decrease the $I_D/I_G$ ratio, the total pressure was increased to the ambient pressure because the stable decomposition of CH₄ on the Cu surface was achieved by suppressing the evaporation and agglomeration of Cu [10–13].
The gas flow rates of H₂/CH₄/Ar and the substrate temperature were set at 20, 1 and 979 sccm and 1000 °C, respectively. Then, the growth time was decreased from 15 to 5 min. Figure 6(a) shows the optical micrographs of graphene transferred onto SiO₂/Si with different growth times, ranging from 15 min to 5 min. A typical Raman spectrum of graphene with the growth time of 5 min is shown in figure 6(b). It is evident that the film is the single-layer graphene and that the I_D/I_G ratio of graphene has significantly improved to 0.009 from 0.033 for the low-pressure case.

Figure 7 summarizes graphene growth on Cu(111) film and Cu polycrystalline foil for different total pressures. There are two dominant factors which result in the reduction of the nucleation rate and growth rate: the lattice mismatch between Cu and graphene and the evaporation of Cu. For graphene growth on Cu polycrystalline foil at a low total pressure, both the nucleation and growth rates are lowered by the lattice mismatch and the evaporation of Cu. On the other hand, for graphene growth on Cu(111) film at ambient pressure, both the nucleation and growth rates are the fastest among the three cases. Controlling these two factors is thus critical for growing high-quality graphene.

Finally, the electrical properties of graphene transferred onto SiO₂/Si were characterized using four-probe measurement. Figure 8 shows (a) the optical micrograph of the typical graphene field effect transistor, (b) the sheet resistivity as a function of carrier density and (c) the mobility extracted at a carrier density of 1 × 10¹² cm⁻² in the graphene obtained in figure 6(b). Compared with the data reported for the mechanical exfoliation of Kish graphite [15], there are still areas to be improved for CVD growth of graphene. For example, although graphene is hetero-epitaxially grown on Cu(111)/mica(001), small-angle grain boundaries caused by the growth from different nucleation sites may exist within the graphene channel ~10 µm in length. However, mobility as high as ~4500 cm² V⁻¹ s⁻¹ was achieved by reducing Cu evaporation during CVD growth. This result indicates that graphene grown under ambient pressure is highly recommend for the graphene substrate.

4. Summary

We have studied hetero-epitaxial graphene growth on Cu(111)/mica(001) by chemical vapor deposition to assess its applicability as the graphene substrate for top-gate insulator research on graphene. The AFM image indicates that the average smooth area is ~100 µm². The orientation of graphene in the graphene/Cu/mica substrate is identified from EBSP orientation mapping for the hexagonal void morphology of
Cu, based on previous reports on the orientation relation between graphene and Cu(111). Furthermore, the crystalline quality of graphene is improved by reducing the Cu evaporation in the ambient-pressure CVD growth. We demonstrate the high mobility of $\sim 4500 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in graphene transferred on the SiO$_2$/Si substrate. These results suggest that the present graphene/Cu/mica structure can be used as the graphene substrate for top-gate insulator research on graphene.

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