Extended Abstracts of the 2013 International Conference on Solid State Devices and Materials, Fukuoka, 2013, pp432-433

Epitaxial CVD graphene growth on Cu/mica for gate-stack research

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Abstract

The graphene substrate is highly demanded for the gate-stack research. In this study, the epitaxial graphene growth on the Cu(111)/mica substrate at the atmospheric pressure is investigated to reduce the Cu evaporation. This sample can be used as the graphene substrate.

1. Introduction

For practical application of graphene electronic devices, the establishment of the electrically reliable gate stack using the high-*k* insulator is highly demanded without introducing any damage to the graphene channel. However, the "graphene substrate" for the gate stack research is not available at present because the small grain size in HOPG as well as the limited area of graphene by the mechanical exfoliation prevents the electrical characterization of the gate stack on graphene.

Here, catalytic chemical vapor deposition (CVD) of graphene has succeeded because of the wide window for the sufficiently high-quality graphene growth. Recently, the epitaxial graphene growth on the Cu(111)/mica substrate is reported at a gas pressure of 30 Torr [1]. This can be used as the graphene substrate because the atomically flat surface of mica provides a good opportunity to electrically characterize the high-*k* insulator with a few nm thickness.

The key to further improve the quality of graphene is the reduction of the agglomeration and evaporation of Cu during the growth, because the stable decomposition of CH_4 on Cu surface is inhibited. In this study, the effect of total pressure on the quality of graphene was investigated using the Cu(111)/mica substrate to use as the graphene substrate.

2. Growth & Characterization

Single crystal mica(001) with the area of 10×10 mm^2 and the thickness of 0.5 mm was used as a substrate. The newly cleaved surface of mica with RMS of ~0.05 nm is available, which is a big advantage because high temperature surface treatment around 1500 °C is not required. The Cu film with the thickness of ~800 nm deposited on mica was single crystal oriented to (111), which was confirmed by the X-ray diffraction. **Figure 1** shows the atomic force microscope (AFM) images for (a) the as-deposited Cu surface and (b) the Cu surface annealed at 1000 °C in Ar/H_2 gas flow (100/50 sccm). The surface roughness (RMS) was reduced from 13.6 nm to 0.5 nm after annealing. Since RMS of mica is ~0.05, this can be improved further. The CVD graphene growth was carried out under the $CH_4/H_2/Ar$ gas flow in the three-zone tube furnace with the uniform temperature range of ~ 5cm at 1000 °C (±1°C). After transferring graphene from Cu/mica substrate to SiO_2/n^+-Si substrate, the electrical properties of monolayer graphene was measured in a vacuum.

3. Results & Discussion

For the epitaxial catalytic CVD growth of graphene on Cu(111), gas flow rates of CH_4 and H_2 during the growth determines the final quality of graphene because the CH_4 adsorption on the Cu surface, the decomposition rate of CH_4, and the nucleation and growth rates of graphene are controlled by these flow rates. First, the gas flow rates of Ar/CH_4 are fixed as 100/20 sccm and, then, the effect of the gas flow rate of H_2 on the crystalinity is studied. The total pressure is adjusted as around ~1kPa since this is typical condition for graphene CVD. **Figure 2(a)** shows the single layer graphene (SLG) coverage and I_D/I_G ratio as a function of H_2 gas flow rate. SLG coverage is defined as

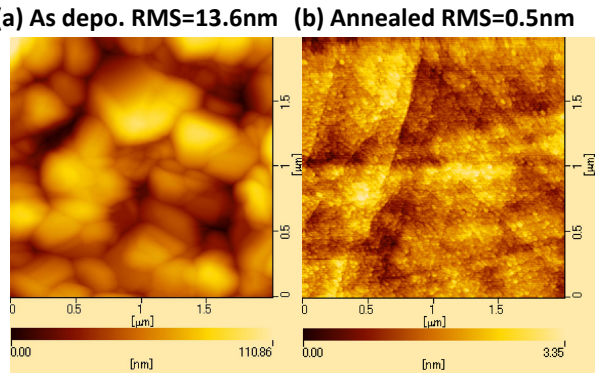

Fig. 1 AFM images for (a) the as-deposited Cu surface and (b) the Cu surface annealed at 1000 °C in Ar/H_2 gas flow (100/50 sccm).

$A_{SLG}/(A_{SLG}+A_{MLG})$, where A and MLG are the area and multilayer graphene, respectively. The growth temperature and growth time are fixed at 1000 °C and 15 min, respectively. With increasing H_2 flow rate, the SLG coverage increased monotonically, while the I_D/I_G ratio shows the minimum value at H_2 = 200 sccm. When the H_2/CH_4 ratio exceeds unity, the nucleation rate of graphene is reduced because the coverage ratio of H_2/CH_4 on the Cu surface might be reversed. Moreover, at high H_2 flow rate around 200 sccm, H_2 might prevent the decomposition of CH_4. In this condition, the growth rate of graphene is kept slow and the crystalinity is increased, as indicated by the I_D/I_G ratio. However, when the H_2 flow rate exceeds 200 sccm, the increase in I_D/I_G ratio suggests that the defects such as C-H bonding are introduced in graphene. These results indicate that there are optimal H_2 gas flow rate for the fixed CH_4 flow rate and the fixed total pressure. Moreover, the SLG coverage can be increased up to ~97% by reducing the growth time from 15 to 7.5 min, while the I_D/I_G ratio is not significantly improved.

Next, in order to improve the I_D/I_G ratio, the total pressure was increased up to the atmospheric pressure because the stable decomposition of CH_4 on the Cu surface is inhibited due to the agglomeration and evaporation of Cu. **Figure 2** shows (b) the optical image of graphene transferred on SiO_2/Si and (c) Raman spectroscopy result for the CH_4/H_2 = 1/20 sccm for 5 min at 1000 °C. The I_D/I_G ratio is much improved with the SLG coverage of ~94 %. **Figure 3** summarizes the graphene growth from the view point of total pressure difference. There are two factors for the reduction of the nucleation and growth rate; the evaporation of Cu and lattice mismatch. These may cause the defect formation.

Finally, the electrical properties of monolayer graphene transferred on SiO_2/Si are analyzed by the four probe measurement. **Figure 4** shows (a) the sheet resistivity as a function of carrier density and (b) the mobility extracted at the carrier density of 1×10^{12} cm^{-2} for graphene obtained in **Fig. 2(b)**. Compared with the data obtained by the mechanical exfoliation from Kish graphite, there are lots of spaces to be improved for CVD graphene. However, the mobility as high as ~4500 cm^2/Vs is achieved by optimizing the growth condition, especially, the reduction of the Cu evaporation.

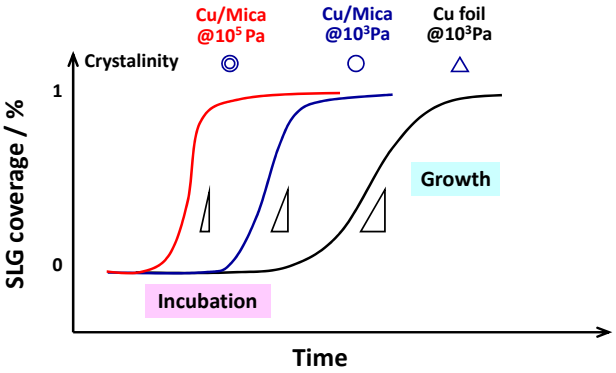

Fig. 3 Summary of the graphene growth from the view point of total pressure difference.

4. Conclusions

In this study, the large-area, high-quality graphene growth was achieved on Cu(111)/mica substrate. There are optimal H_2 gas flow rate for the fixed CH_4 flow rate and the fixed total pressure. The crystalline quality is improved by increasing the total pressure. The mobility as high as ~4500 cm^2/Vs is achieved. The gate stack research can be performed using this graphene substrate.

Acknowledgement

We would like to thank to Dr. Fujii for helpful discussion on graphene growth on Cu/mica. This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology.

References

[1] T. Fujii, et al., Graphene 2012 Int. Conf. abstract, 2012.

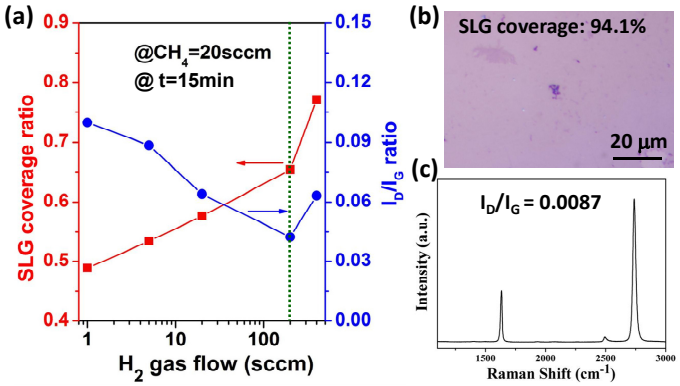

Fig. 2 (a) SLG coverage and I_D/I_G ratio as a function of H_2 gas flow rate. (b) Optical image of graphene on SiO_2/Si. (c) Raman spectroscopy result.

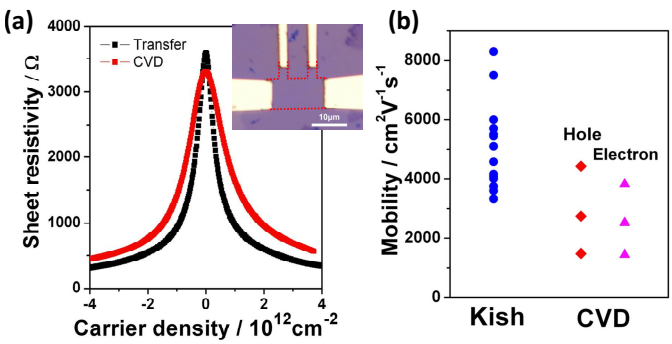

Fig. 4 (a) sheet resistivity as a function of carrier density and (b) extracted mobility at carrier density of 1×10^{12} cm^{-2} for graphene.