EFFECT OF CURRENT STRESS ON FORMATION AND CRYSTALLINITY OF MULTILAYER GRAPHENE BY SOLID PHASE PRECIPITATION

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ABSTRACT: We fabricated multilayer graphene (MLG) on SiO_2 substrate by applying current stress during annealing of sputtered Co-C layer. The effect of current stress on formation and crystallinity of MLG was investigated by comparing the characterization of the MLG films produced at same temperature with current and without current by taking account the temperature rise due to Joule heating. The characterizations made by Raman spectroscopy, SEM and XRD measurement revealed that the crystallinity of MLG films produced by current stress during annealing was better than the MLG films produced without current at the same temperature. Beside Joule heating enhancement of Co grain size by agglomeration may be the reason behind improvement of crystallinity. With further optimization, current stress during annealing might be a potential method for MLG fabrication by solid phase precipitation at relatively lower temperature.

1. INTRODUCTION

Multilayer graphene (MLG) is considered to be the new candidate for narrow interconnects replacing Cu due to its potentially lower resistivity, [1,2] a higher thermal conductivity, [3,4] and higher current carrying capacity[5,6] than Cu. Nowadays, there have been tremendous achievements in fabrication and applications of MLG for narrow interconnects. MLGs with higher crystallinity is a prerequisite for application in narrow interconnects. Several methods have been proposed for fabrication of MLG films, such as exfoliation from highly oriented pyrolytic graphite (HOPG),[7] high temperature decomposition of SiC substrate,[8] thermal chemical vapor deposition (CVD) on metal catalysts such as Ni,[9] Co [10] and Cu[11-13], conversion from solid carbon sources,[14-16] and by annealing sputtered amorphous carbon by solid phase precipitation.[17-19]

CVD is a popular technique of low cost fabrication of MLG, but MLG cannot be fabricated directly onto the substrate[20] and a thick catalytic layer is required to stop aggolomeration.[21] MLG can be fabricated directly on dielectric substrate by solid phase precipitation without transfer process.[18] However, a high temperature annealing is required to obtain desired crystallinity.[18] Therefore, synthesis of MLG films with higher crystallinity at comparatively lower temperature with good uniformity over the substrate is a critical challenge for interconnect application.

Applying a current stress during thermal CVD can improve the crystallinity of MLG significantly and is already published by our group.[22] In this study, we have fabricated MLG films by solid phase precipitation by applying current stress during annealing. The effect of current stress on formation and crystallinity of MLG films were investigated by comparing the properties of MLG films fabricated with current stress and without current stress. We succeeded in fabricating of better quality of MLG films by applying current during annealing in comparism with MLG films produced at same temperature annealing without current.

2. EXPERIMENTAL

The experimental set up and the process flow of MLG fabrication is shown in Figs. 1 (a) and 1 (b) respectively. The carbon doped cobalt (Co-C) layer of thickness 100 nm on the SiO_2/Si substrate was deposited by magnetron sputtering. The percentage of C in Co was 20 at. %. The flow rate of Ar was 20 sccm and the pressure was 1 Pa with the base pressure of 7.00×10^{-4} Pa. The sputtering power for Co and C was 100 W and 400 W, respectively. The structure of the sputtered film was Co-C/SiO_2/Si. Effect of current stress was investigated by comparing the crystallinity of MLG films annealed at same temperature without current and with current. The annealing time was 30 minutes in vacuum of 8 × 10^{-3} Pa. The annealing temperatures were varied between 600 °C to 800 °C and the current stress between 2 to 10 A dc.

The structural properties of the MLG films were analyzed by Raman spectroscopy using an exciting LASER of wavelength 532 nm and X-ray diffractometer by Cu-Kα radiation. The surface of the films was observed by field emission SEM (JEOL JSM-7400F).

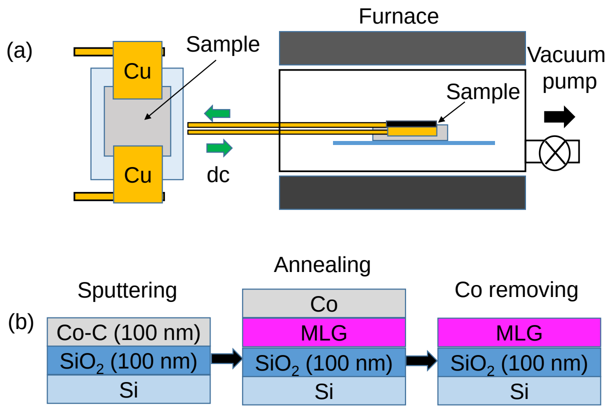

Fig. 1. Fabrication of MLG directly on SiO_2 substrate: (a) Experimental set-up for annealing with current stress and (b) Process flow of fabrication of MLG.

3. RESULTS AND DISCUSSION

Figures 2 (a) and 2 (b) show the comparison of Raman spectra between MLG films annealed at the same temperature without current and those with current. For example, we can see in Fig. 2 (b) for Raman spectrum of 600 °C plus 3 A current, the sample temperature was measured as 680 °C due to Joule heating. Similar position in Fig. 2 (a) corresponds to Raman spectrum for 680 °C without current. So in both cases, the sample temperature was 680 °C but (a) without current and (b) with current. By comparing the two Raman spectra, we can investigate the effect of 3 A current at 680 °C. From Raman spectra of Fig. 2, we can see that each spectrum is characterized by G, D and 2D peaks. The G band is derived from graphitic structure and the D band appears from

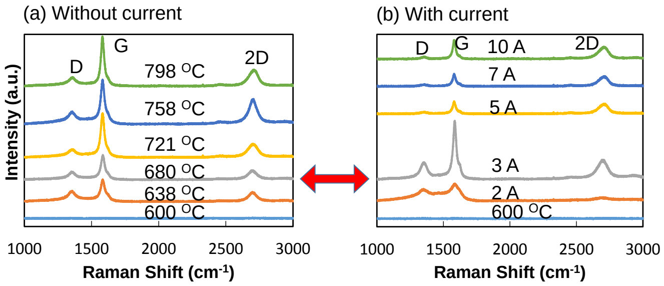

Fig. 2. Comparism of Raman spectra of MLG films annealed at different temperatures, (a) without current and (b) with current.

disordered structures such as edges and grain boundaries.[23)] The MLG crystallinity is determined by G/D ratio. Higher G/D ratio leads to higher crystallinity. The G/D ratio at 680 °C by 3 A current was larger than the G/D ratio at the same temperature without current.

The comparison of G/D ratios between MLG films annealed at same temperature with current and without current is shown in Fig. 3. It is seen from Fig. 3 that the G/D ratio is increasing with the increase of current in case of with current. The G/D ratios without current is increased with temperature and again decreasing. Above the temperature of 758 °C the G/D ratio of those with current stress was higher than those without current. Since the annealing is made at the same temperature, the increase of G/D ratio with current stress indicates that the effect of current stress was not only Joule heating but there was another effect which is enhancing the G/D ratio as well as the crystallinity of MLG films.

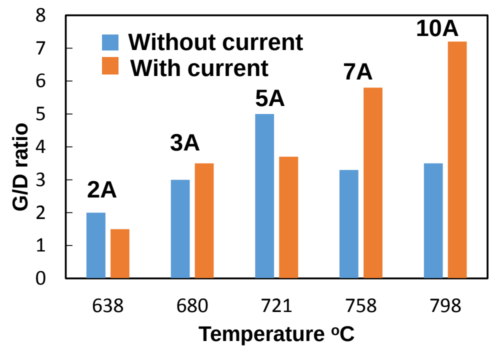

Fig. 3. Comparism of G/D ratios of MLG films annealed at same temperature without current and with current.

Figure 4 shows the SEM photograph of the surface of the MLG films annealed at 680 °C (a) without current and (b) with 3 A current. SEM photograph shows the non-uniform growth of MLG over the substrate. From SEM photograph, one can observe the increase of MLG grain size by applying 3 A current in comparism with that of same temperature without current. The reason behind improvement of MLG grain size might be the enhancement of the crystallization of Co catalyst by agglomeration. As a result of grain size increase of Co by current stress, the number of MLG grains may be decreased and MLG grain size may be increased. We reported that current stress during thermal CVD can improve the MLG crystallinity significantly.[22)] The results shown here are in accordance with our previous result. Therefore current stress is considered as a potential method to improve the crystallinity of MLG both in solid phase precipitation and thermal CVD.

Figure 5 shows the XRD spectra of MLG films annealed at 680 °C and set temperature plus 3A equal to 680 °C. From Fig. 5, it is seen that the intensity of graphite peak as well as the Co peaks were increased with applying current stress at the same temperature annealing. The existence of graphite peak confirms the formation of MLG. The increase of Co grain size after applying current stress may be another reason for improvement of MLG crystallinity.

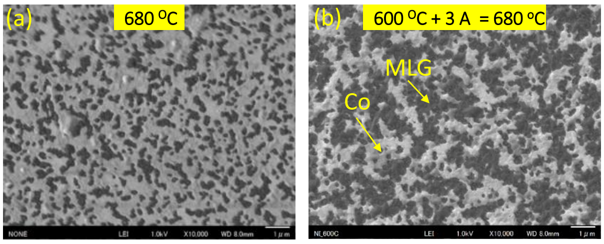

Fig. 4. SEM image of the surface of the annealed films annealed at 680 °C, (a) without current and (b) with 3 A dc.

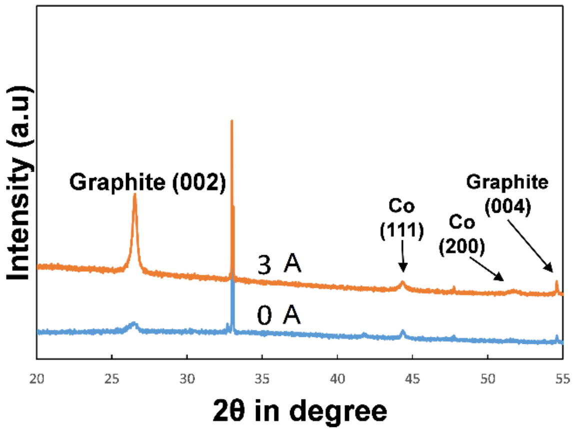

Fig. 5. XRD spectra of MLG films annealed at 680 °C and set temperature plus 3 A ~ 680 °C.

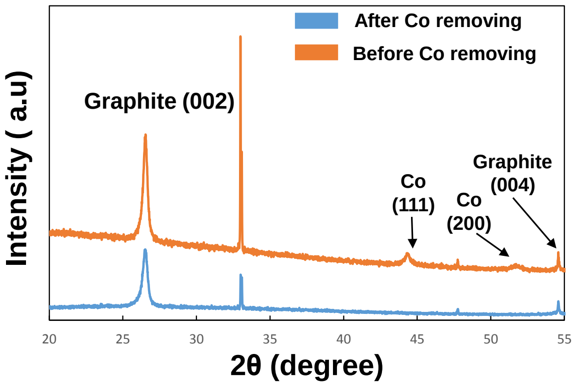

Fig. 6. XRD spectra of MLG films annealed at 600 °C + 3A before and after Co removing.

Figure 6 shows the XRD spectra of MLG films annealed at 600 °C plus 3A dc before and after Co removing. It is seen that, both the Co peaks exist before Co removing but after Co removing Co peaks disappears but both graphite peaks exist. Therefore MLG remain on substrate even after Co removing that confirms the direct deposition of MLG on dielectric substrate. Further development is required to improve the MLG uniformity for device application.

4. CONCLUSION

We fabricated MLG films directly on SiO_2 substrate by solid phase precipitation by applying current during annealing of sputtered Co-C layer. The crystallinity of MLG films prepared by annealing with current stress was better than that of without current at the same temperature. With further optimization of processes, our proposed technique might be potential for fabricating MLG films with improved crystallinity without transfer process.

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