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Efficient $MoCl_5$ Intercalation Doping of Multilayer Graphene for Low-Resistance and Low-Damage

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Abstract

Damage-less doping process with $MoCl_5$ intercalation for multilayer graphene (MLG) has been developed by optimizing the chemical concentration and temperature using an exfoliated highly oriented pyrolytic graphite to mimic a high crystallinity MLG. We found that the thick MLG films are more susceptible to the intercalation damage than few-layer graphene (FLG) reported previously. The damage was found to be reduced by lowering the chemical concentration. An efficient doping with 73% reduction of sheet resistance without serious damage was obtained with the further optimization of temperature.

1. Introduction

Multilayer graphene (MLG) intercalated with metal-chlorides has been expected as low-resistance materials for electronic devices applications such as interconnects [1-2]. Among the metal-chlorides, $MoCl_5$ has an advantage of its environmental stability in narrow width [3]. In our previous study, we have optimized the $MoCl_5$ intercalation condition for few-layer graphene (FLG) such as tri-layer graphene (TLG), and it was found that higher temperature is required for more numbers of graphene layers [2]. For the device applications such as interconnects, MLG with more layers than FLG are need to be intercalated. However, a serious damage in such MLG was observed with using the previous condition for FLG in our preliminary experiment. It is speculated that the stress induced by the intercalation may cause the damage since the spacing between the graphene layers is expanded by the $MoCl_5$ intercalation and the total stress may become larger as the layer number increases. Here, we have optimized the intercalation condition with changing the chemical concentration and temperature in terms of the doping efficiency, damage and reduction of sheet resistance for a thick MLG.

2. Experimental Methods

Fig. 1 shows the schematic diagram of experimental setup for $MoCl_5$ intercalation process. Two sizes ($7\times7mm^2$ and $3\times7mm^2$) of films exfoliated from a highly oriented pyrolytic graphite (HOPG) were transferred to a SiO_2/Si substrate to mimic a high crystallinity MLG film. The thickness is relatively thick as about 10μm. The samples were inserted to a glass capsule with the different amount of chemicals. The standard (STD) chemical amount was 1706 g-$MoCl_5$ and 0.0333 g-MoO_3, and it was varied as STD/2, STD/4, and STD/5. After enclosing the glass capsule, it was inserted into the glass tube. Before reaction, the glass tube was pre-annealed at 110ºC for 120 min in an Ar-atmosphere. The reaction temperature was varied between 200ºC and 250ºC for the fixed reaction time of 30 min. The doping efficiency and morphology were analyzed using Raman spectroscopy and scanning electron microscope (SEM), respectively. The sheet resistance was characterized by 4-point probe method.

3. Results and Discussion

Chemical amount dependence of doping and damage

Fig. 2 shows the G-band spectra of MLG after intercalation using 200ºC for 30 min at different chemical amount. According to the position of G-band, we can determine the intercalation stage. The G-band position around 1582 cm^{-1} (G_0) corresponds to the pristine graphite. After $MoCl_5$ intercalation, G-band position shifts to higher wave number (G_1 around 1605 cm^{-1} and G_2 around 1625 cm^{-1}) [3,4]. The G_2 and G_1 correspond to the stage-1 and stage-2 structure, respectively. In the case of higher stage structures, the peak position depends on the ratio between the intensity of G_1 and G_0 bands (I_{G0}/I_{G1}). With the STD chemicals, stage-1 intercalation was obtained. With reducing the chemicals, the G-band position shifted to the lower wave number, indicating stage-2 intercalation for the STD/2 and STD/4 chemicals. Further reduction of chemicals to STD/5 resulted in non-doping state.

Fig. 3 shows the surface SEM images after intercalation with different chemical amount at 200ºC for 30 min. The damage of samples was reduced with reducing the chemicals. The surface for STD/5 shows a smooth surface as same as the pristine surface. The results indicate that both the doping efficiency and the damage were reduced by reducing the chemicals, and the trade-off need to be solved.

Reaction temperature dependence of doping and damage

To enhance the doping efficiency of the damage-less STD/5 condition, the effect of temperature was explored. Fig. 4 shows the G-band spectra after intercalation using the STD/5 chemicals at different temperature for 30 min. At 225ºC, the G-band shows a mixture of G_0 and G_1 peaks and the I_{G0}/I_{G1} was 0.22 which is lower than 0.5 (stage-3) [3,4], indicating that stage-3 and -2 were mixed. After rising the temperature to 250ºC, the G-band shows only G_1 peak (stage-2) and the position is higher than 225ºC. The results indicate that the doping efficiency was enhanced by increasing the temperature. Fig. 5 shows the surface SEM images after intercalation process at different temperature. The damage was also enhanced with increasing the temperature. However, the damage at 225℃ was less than that of STD/4 at 200℃.

Fig. 6 shows the reduction ratio of sheet resistance between before and after intercalation for the different temperature. The sheet resistance was significantly reduced by 73% and 88% after increasing temperature to 225ºC and 250ºC, respectively. The reduction effect is comparable with that of Br_2 intercalation [5], and the resistivity is estimated as below 10μΩcm according to the relation between G-peak position and resistivity [3].

3. Conclusions

We have optimized the $MoCl_5$ intercalation process for relatively thick MLG films in terms of low-resistance and low damage. 73% reduction of sheet resistance with reduced damage were obtained with the condition of reduced chemicals to 1/5 of the FLG condition at 225ºC. Further damage reduction is expected for the thinner MLG. $MoCl_5$ intercalation will be promising for MLG applications due to the environmental stability and doping efficiency with the process optimization.

Acknowledgements

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References

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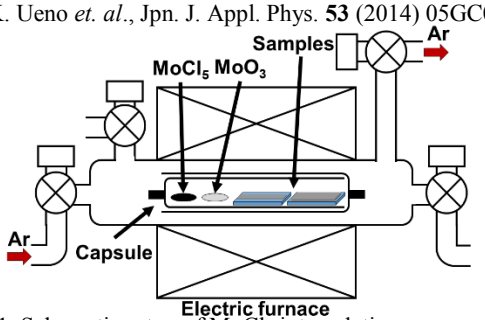

Fig. 1. Schematic setup of $MoCl_5$ intercalation process.

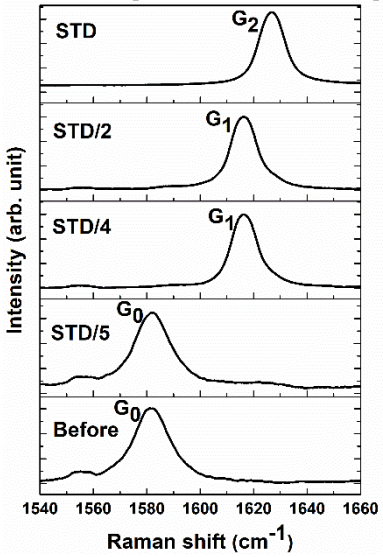

Fig. 2 G-band spectra of MLG after intercalation using 200ºC for 30 min at different chemical amount.

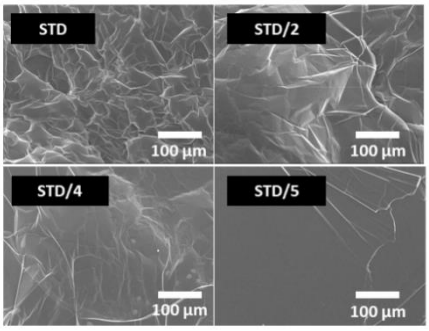

Fig. 3. Surface SEM images of MLG after intercalation using 200ºC for 30 min at different chemical amount.

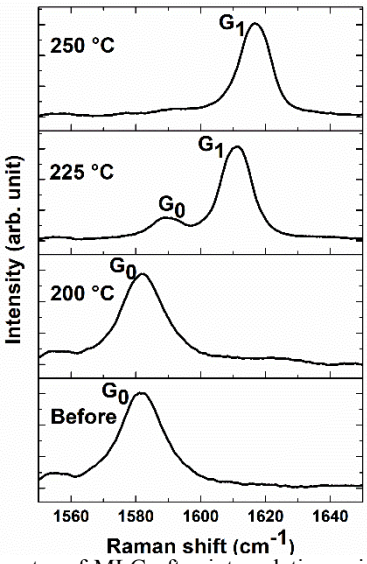

Fig. 4. G-band spectra of MLG after intercalation using STD/5 at different temperature for 30 min.

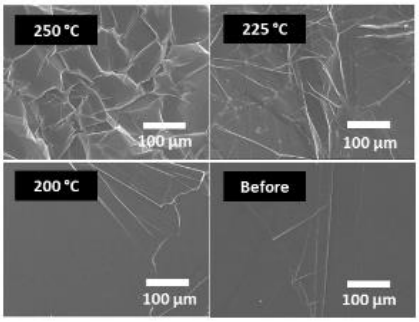

Fig. 5. Surface SEM images after intercalation using STD/5 at different temperature for 30 min.

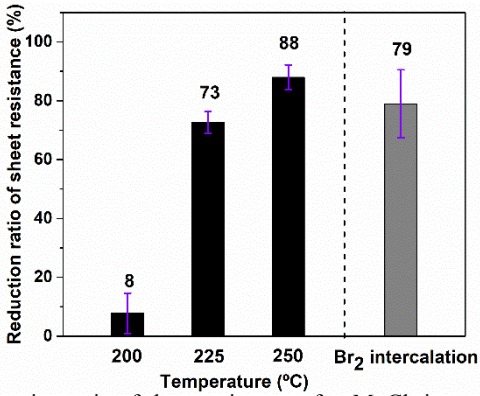

Fig. 6. Reduction ratio of sheet resistance after $MoCl_5$ intercalation using STD/5, comparing with Br_2 intercalation [5].