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Effect of Current Stress during Thermal CVD of Multilayer Graphene on Cobalt Catalytic Layer

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Abstract

The crystallinity of multilayer graphene (MLG) films was improved by applying current during thermal CVD as reported in our previous report [1]. To make the mechanism of the improvement clear, the current effects on the temperature-rise, C precipitation, MLG grain size, and Co catalysts were investigated with changing the current. It was found that the current has a direct effect on enhancing the MLG grain size besides the Joule heating effect, but it has not so much effects on the C precipitation and the Co catalysts.

1. Introduction

Nanocarbon materials such as multilayer-graphene (MLG) is one of the candidates for advanced interconnect materials, because it has longer mean free path and higher electromigration (EM) endurance than Cu [2]. One of the issues for low resistance the MLG interconnects is the deposition method for MLG films with high crystallinity. Chemical vapor deposition (CVD) using catalytic metals such as cobalt (Co) and nickel (Ni) is a candidate due to the capability of large area deposition at relatively low temperatures. We have reported that MLG quality was remarkably by applying current during thermal CVD, and named current enhanced CVD (CECVD) [1]. However, the mechanism for the current effects in the CECVD have not been sufficiently clear. In this study, we have investigated the effects of current stress on the MLG growth reactions and the Co catalysts.

2. Experiment

A 100 nm-thick Co was deposited by a magnetron sputtering as the catalytic layer for CVD on 1.5 cm×2 cm Si substrates with 100 nm-thick SiO_2. Fig.1 illustrates the schematic diagram of the used CECVD system. The electrodes for supplying current to the sample are connected as an extra feature in conventional thermal CVD apparatus. After connecting the electrodes, the substrate was installed into the furnace. MLG was grown by thermal CVD with current (CECVD) or without current at the set up temperatures summarized in Table1. The temperatures without current were set to be the same temperature of the samples with current including the Joule heating. In the case of CECVD, DC current between 2 and 10 A was applied. The MLG crystallinity was analyzed by Raman spectroscopy. The surface morphology was observed by scanning electron microscopy (SEM). The grain size of the Co films was derived from the full width at the half maximum (FWHM) of the X-ray diffraction (XRD) peaks.

3. Results and Discussion

Current effects on MLG crystallinity at the same temperature including Joule heating

The Raman spectra of CVD-MLG with and without current stress are shown in Fig. 2. The G peak at 1580 cm^{-1} and the D peak at 1350 cm^{-1} correspond to the graphitic and defective structures of sp^2 nanocarbons, respectively. The peak intensity ratios (G/D ratios) can be used as the index of graphene crystallinity, and they increased gradually with the increase of temperature or current as shown in Fig. 2. It indicates that the MLG crystallinity was improved by heating. Comparing the G/D ratios at the same temperatures, those with current were much higher than those without current as shown in Fig. 3. From the result, it is considered that current has more effects besides the Joule heating effect.

Current effects besides Joule heating effect

To determine the current effects besides the Joule heating, the current effects on the amounts of carbon (C) precipitates was investigated by measuring the area intensities of the G and D peaks. In addition, the current effects on the grain sizes of MLG crystallite and Co catalysts were investigated.

Fig. 4 shows the comparison of the C precipitates for the samples with and without current. Since there were no clear differences in the amount of C precipitates, it is considered that the current has almost no effects on the C precipitation.

Fig. 5 shows the MLG grain sizes derived from the Raman spectra [3]. It is noted that the grain sizes of the MLG with the current stress increased more abruptly than those without current, especially above 6 A (660 ^{o}C). There was a change in the surface morphology between 4 A and 6 A as shown in Fig. 6. The cause of that change may be due to change of Co crystal structure from hexagonal closed pack (hcp) to face centered cubic (fcc).

On the other hand, there were almost no difference in the Co grain sizes between with and without the current stress as shown in Fig. 7, indicating that the current had almost no effects on the Co catalysts besides temperature.

From the results, current stress should have a direct effect on the grain growth of MLG, which indicates that the current stress applied in our experiment acts as driving force for MLG formation, leading to the improvement of crystallinity at low temperature.

4. Conclusions

We have investigated the effects of current stress on the improvement of MLG crystallinity in CECVD. It was found that current can be a driving force of the MLG grain growth besides temperatures. On the other hand, current has almost no effects on the C precipitation and Co grain sizes. Current stress can be a promising method for improving the MLG quality at low temperatures to fabricate low-resistance MLG interconnects.

Acknowledgements

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References

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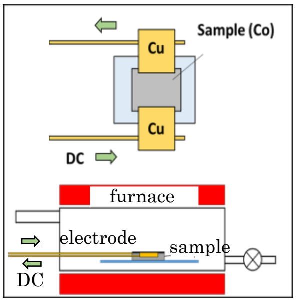

Fig. 1 Experimental set up of CECVD system.

Table 1 Set up temperature

with Current	without Current
500 °C+ 0 A	500 °C
500 °C+ 2 A	560 °C
500 °C+ 4 A	620 °C
500 °C+ 6 A	660 °C
500 °C+ 8 A	680 °C

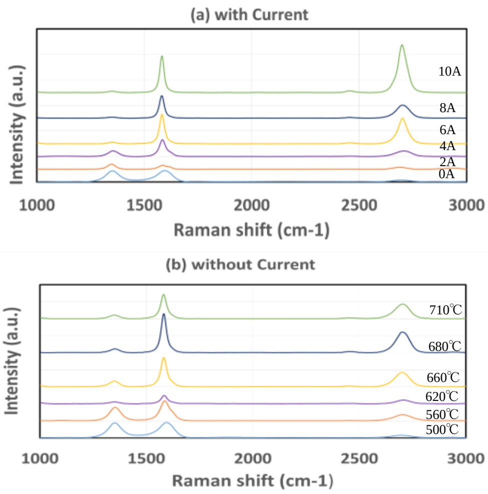

Fig. 2 Raman spectra of MLG film (a) with and (b) without current.

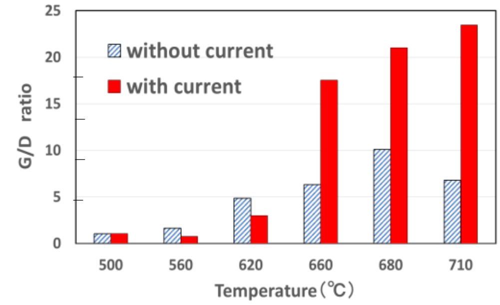

Fig. 3 Comparison of G/D ratios between with and without current.

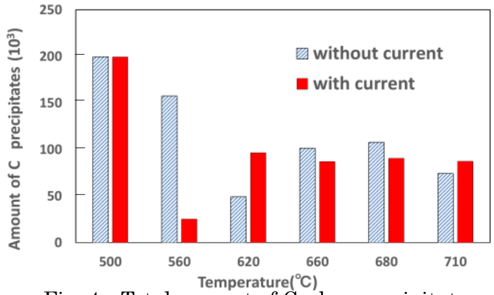

Fig. 4 Total amount of Carbon precipitates as a function of temp with and without current.

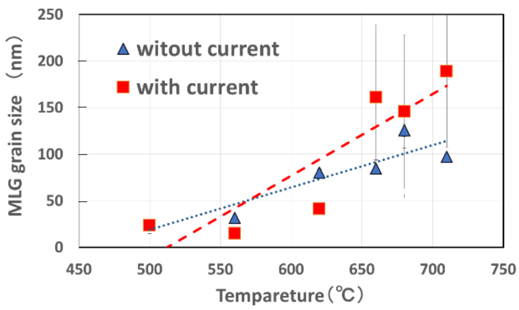

Fig. 5 Grain size of MLG with and without current.

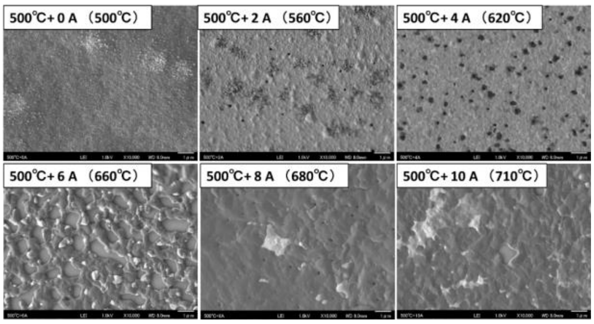

Fig. 6 Surface morphology by SEM with current stress between 2A to 10A.

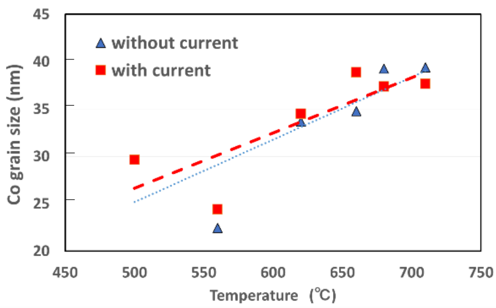

Fig. 7 Grain size of Co with and without current.