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Ni-induced layer exchange crystallization of sputtered amorphous carbon for multi-layer graphene on insulator

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Abstract

Multi-layer graphene are directly synthesized on an insulating substrate at 600 °C using metal-induced crystallization through layer exchange between sputtered Ni and amorphous C layers.

1. Introduction

Multi-layer graphene (MLG) has been widely investigated because of its high electrical and thermal conductivities. The direct synthesis of MLG on insulators at low temperatures has attracted increasing attention in recent years for fabricating graphene-based thin film devices at low cost [1]. Because graphene has a unique two-dimensional structure, its characteristics are anisotropic and deteriorated at grain boundaries. Therefore, large-grained, highly-oriented MLG on insulators are strongly desired. In line with this, the solid-phase crystallization of amorphous carbon (a-C) using catalyst metals (e.g., Cu, Ni, Fe, and Co) has allowed for the direct synthesis of MLG on insulators at relatively low temperatures (700-1000 °C) [2-8]. However, there are still more investigations necessary to achieve large-grained, highly-oriented MLG on insulators.

In the field of group-IV semiconductors including Si and Ge, metal-induced layer exchange (MILE) has accomplished large-grained (> 30 μm), highly-oriented thin films on insulators [9,10]. In MILE, an amorphous semiconductor layer crystallizes through "layer exchange" between the amorphous layer and a catalyst metal layer. From binary phase diagrams, we found that Ni would work as a catalyst metal for the layer exchange crystallization of a-C. In this study, we applied the MILE to a-C for fabricating a high-quality MLG on an insulator at low temperatures.

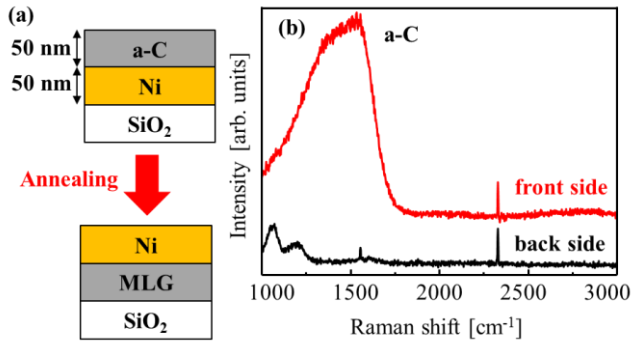

Fig. 1. (a) Concept of this study. (b) Raman spectra obtained from the front and back sides of the sample before annealing.

2. Experimental Procedures

The concept of this study is shown in Fig. 1(a): we aimed at layer exchange between a-C and Ni layers. Ni and a-C thin films (50-nm thickness each) were sequentially prepared onto a quartz glass (SiO_2) substrate at 200 °C and room temperature, respectively, using a radio-frequency magnetron sputtering (base pressure: 3.0×10^{-4} Pa) with Ar plasma. The sample was annealed at 600, 800, and 1000 °C for 10 min in an Ar ambient. After annealing, the samples were dipped in a $FeCl_3$ solution for removing Ni. The samples were evaluated using scanning electron microscopy (SEM), energy dispersive X-ray (EDX) analysis, and Raman spectroscopy (spot diameter: 5 μm, wavelength: 532 nm).

3. Results and Discussion

Fig. 1(b) shows Raman spectra obtained from the front and back sides of the sample before annealing. From the front side of the sample, a broad peak corresponding to a-C is observed at around 1500 cm^{-1}. In contrast, from the back side of the sample, there is no peak related to a-C. These results

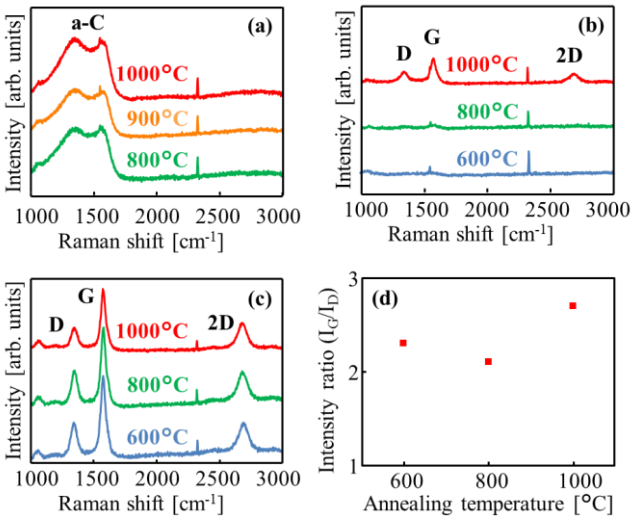

Fig. 2. Raman spectra obtained from (a) the samples without a Ni layer and (b) the front and (c) back sides of the Ni-inserted samples after annealing. (d) I_G/I_D intensity ratio derived from (c).

ensure that the a-C layer is stacked on the Ni layer without a mixed structure before annealing.

To clarify the role of the catalyst metal on growth temperature, an a-C layer (50-nm thickness) directly formed on a SiO_2 substrate was annealed at 800, 900, and 1000 °C. As shown in Fig. 2(a), broad peaks corresponding to a-C are observed for all samples. These results indicate that the a-C layer does not crystallize without a metal catalyst even after annealing at a high temperature of 1000 °C. We note that sharp peaks at around 2300 cm^{-1} originate from the Raman equipment used in this study.

Fig. 2(b) and 2(c) show, respectively, the Raman spectra of the front and back sides of the Ni-inserted sample after annealing at 600, 800, and 1000 °C. Fig. 2(b) indicates that the sample annealed at 1000 °C has D, G, and 2D peaks corresponding to MLG, while the samples annealed at 600 and 800 °C have no peaks corresponding to C. It is worth noting that a-C peaks, observed before annealing as shown in Fig. 1(b), have disappeared for all samples. On the other hand, Fig. 2(c) indicates that all samples have sharp D, G, and 2D peaks corresponding to MLG on the back side of the sample. These results suggest the following phenomena. When the growth temperatures are lower than 800 °C, the layer exchange between C and Ni layers occurs and then MLG forms on the substrate. Note that the Ni catalyst has lowered the crystallization temperature of a-C by more than 400 °C considering the results shown in Fig. 2(a). On the other hand, when the growth temperature is as high as 1000 °C, the agglomeration of the Ni layer begins and results in non-uniform layer exchange.

We evaluated the intensity ratio of the G peak to the D peak (I_G/I_D) because the ratio indicates the crystal quality including domain size and defects of MLG. Fig. 2(d) shows the intensity ratio for each annealed sample derived from Fig. 2(c). For all samples, the intensity ratios are more than 2.0, indicating relatively high crystal quality among the MLG directly formed on insulators [2-8]. The control of the layer exchange behavior will further enhance the crystal quality of the MLG formed by MILE [9,10].

Fig. 3 shows the characterization of the annealed samples after Ni removal. As representatively shown in Fig. 3(a), semi-transparent films uniformly covered the substrates for all samples. EDX and Raman measurements, shown in Fig. 3(b) and 3(c) respectively, ensured that the films were MLG. In addition, the Ni concentration in the MLG layers were below the detection limit of the EDX (~1%). From the SEM images shown in Fig. 3(d)-(f), we found that the lower annealing temperature provides the more uniform MLG layer. In particular, the uniformity of the 600 °C grown MLG is the highest level among the MLG directly formed on insulators. This behavior is likely attributed to the suppression of Ni agglomeration at a low temperature of 600 °C.

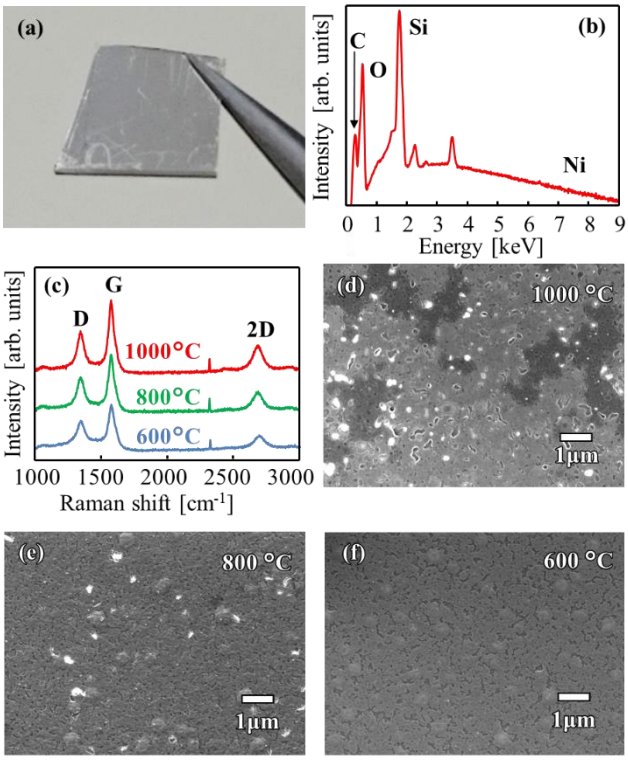

Fig. 3. Characterization of the annealed sample after removing Ni. (a) Photograph, and (b) EDX spectrum for the sample annealed at 600 °C. (c) Raman spectra obtained from the front side of the samples. SEM images for the samples annealed at (d)1000 °C, (e) 800 °C, and (f) 600 °C.

4. Conclusion

We achieved the direct synthesis of multi-layer graphene (MLG) on an insulating substrate using metal-induced layer exchange (MILE) between sputtered a-C and Ni layers. Lowering the annealing temperate improved the uniformity of the MLG layer: 600 °C annealing provided the most uniform MLG with a good crystal quality. Now we are investigating the detailed crystal quality and the electrical properties of the resulting MLG layers.

Acknowledgments

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