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Comprehensive Study of Metal-Induced Layer-Exchange for High-Quality Multilayer Graphene

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Abstract

Metal-induced layer exchange of multilayer graphene (MLG) is comprehensively studied using various metal catalysts. Ni allows us to form high-quality MLG on glass at low temperatures with a wide range of thickness.

1. Introduction

MLG has excellent characteristics, such as high electrical and thermal conductivities and current-carrying capacity. Therefore, application of MLG on arbitrary substrates is expected in various applications. As the required MLG thickness depends on the application, a technique for controlling the thickness of high-quality MLG is essential.

Metal-induced layer exchange (MILE) has been actively studied in the field of group-IV semiconductors, including Si, Ge, and SiGe. In MILE, an amorphous semiconductor layer crystallizes through "layer exchange" between the amorphous layer and a catalyst metal layer. We found that the MILE can be applied to C, resulting in MLG [1-6]. This study comprehensively shows the effect of metals and an interlayer (IL) on layer exchange of MLG with various thicknesses.

2. Experimental Procedures

The concept of this study is shown in Fig. 1. First, we investigate the effect of metals on layer exchange growth of MLG. The metals and amorphous carbon (a-C) layers (each 50 nm thick) were prepared on a SiO_2 glass substrate. The samples were annealed at 500-1000 °C for 1 h. Then, we investigate the effect of IL and initial metal thickness on layer exchange. Ni films (5-200 nm thickness) were prepared on SiO_2 glass substrates. The thickness of the initial Ni layer determines the resulting MLG thickness, *t*, after layer exchange. Subsequently, SiO_2 and AlO_x were employed as the IL. The thickness of SiO_2 (t_{SiO2}) and AlO_x (t_{AlOx}) was 0.5-5 nm in four different samples. Subsequently, a-C thin films were prepared, wherein the thickness ratio of C:Ni = 3:2. For comparison, we prepared the samples without the IL. The samples were annealed at 800 °C for 1 h.

3. Results and Discussion

From the experimental results, the interactions between the metals and a-C were classified into four groups: (1) layer exchange (pink), (2) carbonization (green), (3) local MLG formation (yellow), and (4) no graphitization (blue) (Fig. 2(a)). The Raman spectra for the group (1) samples have D, G, and 2D peaks corresponding to MLG (Fig. 2(b)). Fig. 2(b) shows that the G/D intensity ratio indicating the crystal quality of MLG strongly depends on both the growth temperature and the metal species. Thus, Ni produced MLG with relatively low crystallinity at low temperature. Fig. 2(c) shows that layer exchange between Ni and C layers occurred and the MLG layer ripples between the Ni layer and the substrate. Fig. 2(d) shows that the MLG layer in contact with the Ni layer is completely {002} oriented.

To improve the crystal quality of the MLG, we prepare AlO_x or SiO_2 ILs between a-C and Ni layers, which controls the diffusion of C atoms into the Ni layer. Fig. 3(a) shows that the morphology differs depending on both the IL material and its thickness. Fig. 3(b) shows that layer exchange between the C and Ni layers occurred and MLG was formed on the SiO_2 substrate in all samples. For t_{SiO2} = 2 nm and t_{AlOx} = 1 and 2 nm, a dendrite structured MLG called "island" is formed on the front sides. For t_{AlOx} = 1 and 2 nm, the MLG was formed uniformly on the back side of the samples. Fig. 3(c) shows that the G/D ratio strongly depends on the IL thickness. When

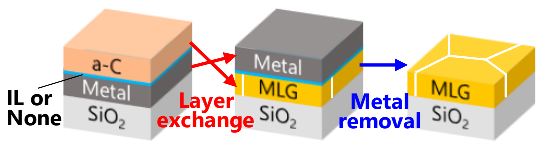

Fig. 1. Concept of this study.

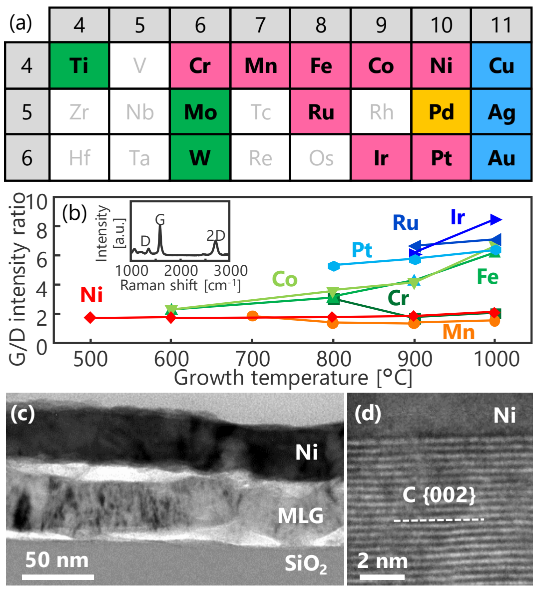

Fig. 2. (a) Periodic Table colored by the classification of interactions between metals and carbon. (b) G/D intensity ratio as a function of growth temperature in group (1). (c) Cross-sectional TEM image and (d) high-resolution lattice image of the Ni sample at 600 °C.

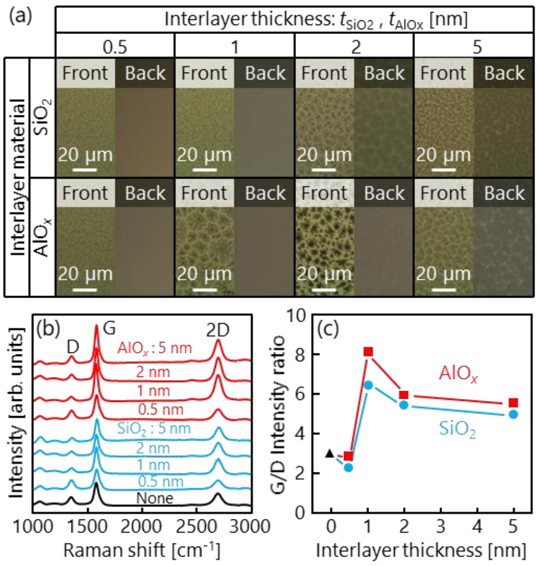

Fig. 3. Characterization of the sample for t = 50 nm and t_{AlOx} = t_{SiO2} = 0-5 nm. (a) Nomarski optical micrographs of the as-annealed samples. (b) Raman spectra obtained from the back side of the samples. (c) The G/D intensity ratio of the samples.

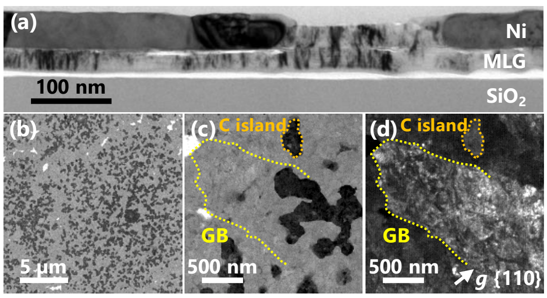

Fig. 4. Characterization of the sample for t = 50 nm and t_{AlOx} = 1 nm. (a) Bright-field cross-sectional TEM image of as-annealed sample. Plane TEM image of the sample after Ni removal. Bright-field at (b) low and (c) high magnifications and (d) dark-field, showing the same area as (c).

t_{SiO2} and t_{AlOx} are over 0.5 nm, the G/D ratios are dramatically improved and exhibit peaks for 1-nm thickness each. These results are consistent with the behavior shown in Fig. 3(a). The highest value of the G/D ratio is approximately 8.0 for t_{AlOx} = 1 nm. This value is the highest level among the MLG directly formed on insulators.

Fig. 4(a) indicates that the ripple of MLG was suppressed by inserting the IL. In some parts, C islands are stacked on the bottom MLG layer. Fig. 4(b) shows gray and black contrasts. These contrasts correspond to bottom and island MLG. This indicates that the bottom MLG covers almost the entire substrate and is consistent with Fig. 3(a). From Fig. 4(c) and (d), the grain size was found to be a few μm. This is one order of magnitude larger than the grain size of the sample without an IL.

We fixed t_{AlOx} = 1 nm and varied t from 5 nm to 200 nm to investigate the effects of t on the crystal and electrical properties of the MLG. For all samples, MLG layers were obtained on the substrate via layer exchange. As

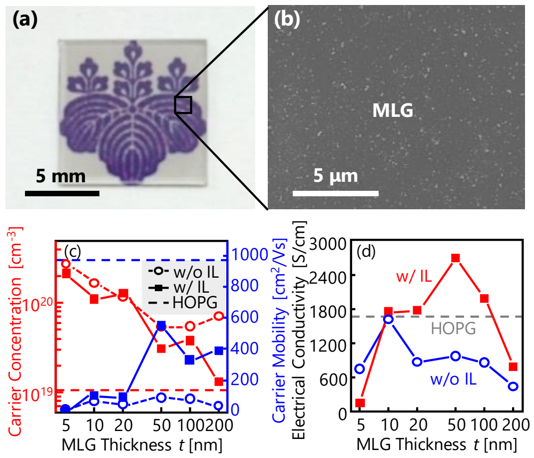

Fig. 5. (a) Photograph and (b) SEM image of the sample for t = 5 nm without IL after Ni removal. Electrical properties of the MLG layers after Ni removal as a function of t. (c) Carrier concentration and (d) Carrier mobility. (d) Electrical conductivity.

representatively shown in Fig. 5(a), thin MLG layers ($t \leq 10$ nm) exhibited transparency. The SEM image in Fig. 5(b) shows that although the MLG layer has submicron-size voids, it covers nearly the entire substrate. We note the Ni concentration in the MLG layer is below the detection limit of EDX (~1%).

Fig.5(c) and (d) show the electrical properties of the MLG strongly depend on t, and with or without the IL. Fig. 5(c) shows the carrier concentration of the MLG decreases with the increase of t and approaches and the carrier mobility dramatically increases for the $t \geq 50$ nm samples with the IL. Fig. 5(d) shows the behavior of the electrical conductivity reflects that of the carrier mobility. The electrical conductivity exhibits the maximum value of 2700 S/cm for the t = 50 nm sample with the IL, which exceeds that of the HOPG.

4. Conclusions

Layer exchange of C with appropriate metals and IL allows us to form high-quality MLG with a wide range of thickness at low temperature. This opens the door for a broad range of applications that combine advanced electronic devices with carbon materials.

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