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Metal-induced Layer Exchange for Multilayer Graphene on Insulator: Effects of Metal Species

Y. Nakajima, H. Murata, T. Suemasu, and K. Toko

Institute of Applied Physics, University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan
Phone: +81-29-853-5472, Fax: +81-29-853-5205, E-mail: y418nakajima@gmail.com

Abstract

We summarized the solid-phase interactions between transition metals and amorphous carbon thin films. Late transition metals induced layer exchange growth resulting in the direct low temperature synthesis of high-quality multilayer graphene on an insulator.

1. Introduction

Graphene and multilayer graphene (MLG) on arbitrary substrates will lead to various advanced electronic devices. High-quality graphene on insulators has been produced using mechanical transfer techniques; however, there are still concerns regarding imperfections in graphene such as wrinkles. These have motivated researchers to fabricate a transfer-free process for practical applications. Graphene has a unique two-dimensional structure, whose characteristics are anisotropic and deteriorated by grain boundaries. In line with this, the direct synthesis of large-grained, highly oriented few-layer graphene on insulators has been widely investigated.

The metal-induced layer exchange (MILE) has been actively studied in the field of group-IV semiconductors including Si, Ge, and SiGe [1–3]. In MILE, an amorphous semiconductor layer crystallizes through "layer exchange" between the amorphous layer and a catalyst metal layer. We previously reported the formation of large-grained, highly-oriented MLG on insulators at low temperature by MILE using Co or Ni as the metal catalyst (Fig. 1(b)) [4–6]. However, it was still not clear what type of metal induces the layer exchange growth of MLG. This study investigates the effect of the species of transition metal in the layer exchange growth of MLG.

2. Experimental Procedures

The schematic of the sample preparation procedure is shown in Fig. 1. 50-nm-thick metal (Fe, Co, Ni, Ru, Ir, Pt, Ti, Mo, Pd, Cu, Ag, Au) and 75-nm-thick amorphous carbon (a-C) thin films were prepared onto a quartz glass (SiO_2) substrate at room temperature using a radio-frequency magnetron sputtering (base pressure: 3.0×10^{-4} Pa) with Ar plasma. The samples were annealed at 600-1000 °C for 1 h in an N_2 ambient. After annealing, the samples were dipped in a wet etchant for removing each metal. The samples were evaluated using Raman spectroscopy (spot diameter: 5 μm,

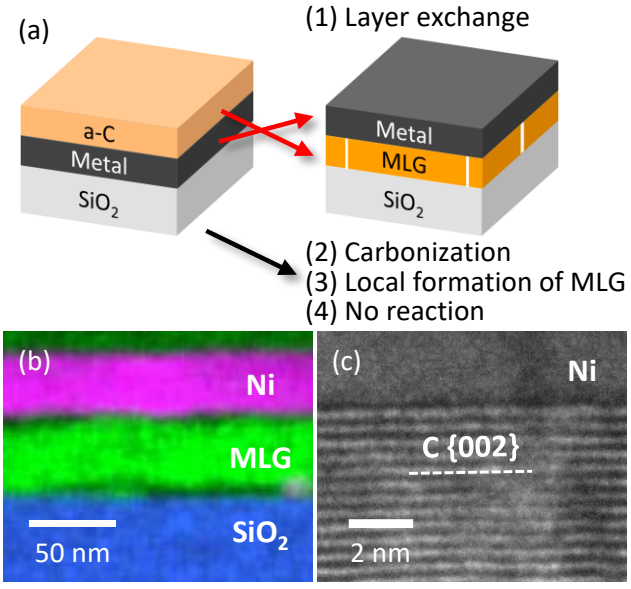

Fig. 1. (a) Schematic sample structure and interactions classified into 4 groups. (b) EDX image and (c) high-resolution lattice image of the MLG film grown by Ni-induced layer exchange.

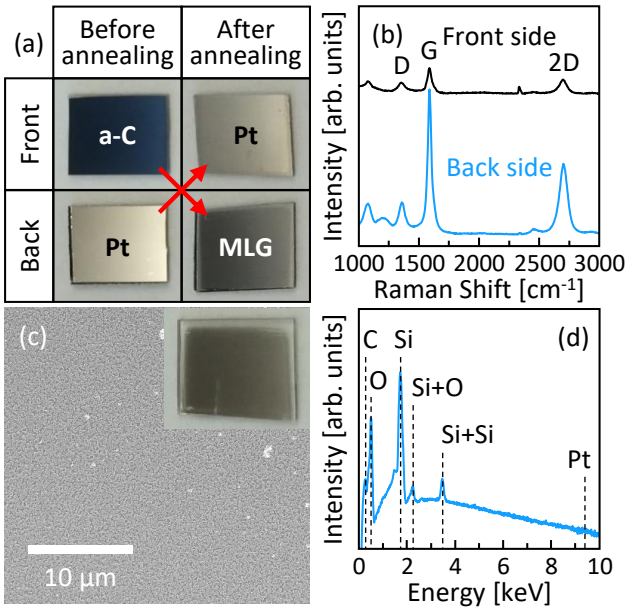

Fig. 2. Characteristics of the Pt sample annealed at 800 °C, representing group (1). (a) Photographs of the sample before and after annealing. (b) Raman spectra obtained from the front and back sides of the sample. (c) SEM image and photograph (size: 5×5 mm^2). (d) EDX spectrum after Pt removal.

wavelength: 532 nm), θ–2θ X-ray diffraction (XRD) measurement, scanning electron microscopy (SEM), energy dispersive X-ray (EDX) analysis, and transmission electron microscopy (TEM).

3. Results and Discussion

As summarized in Fig. 1(a), interactions between transition metals and a-C were classified into 4 groups: (1) Layer exchange (Fe, Co, Ni, Ru, Ir, Pt), (2) Carbonization (Ti, Mo), (3) Local formation of MLG (Pd), and (4) No reaction (Cu, Ag, Au). Figs. 1(b) and 1(c) show the cross-section of a representative sample formed by layer exchange [5].

Fig. 2 shows the characteristics of a Pt sample, representing group (1) Layer exchange. The color of front and back sides of the sample changed by annealing, as shown in Fig. 2(a). Raman spectra obtained from the front and back sides of the samples (Fig. 2(b)) have D, G, and 2D peaks corresponding to MLG. The relatively small peaks from the front side is derived from the islands: a typical feature in the crystallized layers via MILE [6]. After Pt removal, a uniform MLG layer covers the entire substrate (Fig. 2(c)). We note that the Pt concentration in the MLG layer is below the detection limit of EDX (~1 %) (Fig. 2(d)).

Fig. 3(a) and 3(b) show the results of the Mo sample annealed at 1000 °C, representing group (2) Carbonization. A broad Raman peaks corresponding to a-C are observed (Fig. 3(a)), while the XRD peaks corresponding to carbide (Mo_2C) are observed (Fig. 3(b)). Fig. 3(c) shows the results of the Pd sample annealed at 1000 °C, representing group (3) Local formation of MLG. Although Raman peaks corresponding to MLG are observed, broad peaks corresponding to a-C are also observed. This is because the Pd layer agglomerated during the annealing, producing MLG only around the dotted Pd (~2 μm diameter). Fig. 3(d) shows the results of the Cu sample annealed at 1000 °C, representing group (4) No reaction. No Raman peaks corresponding to MLG are observed, while broad peaks corresponding to a-C are observed from the front and back sides of the sample due to Cu agglomeration.

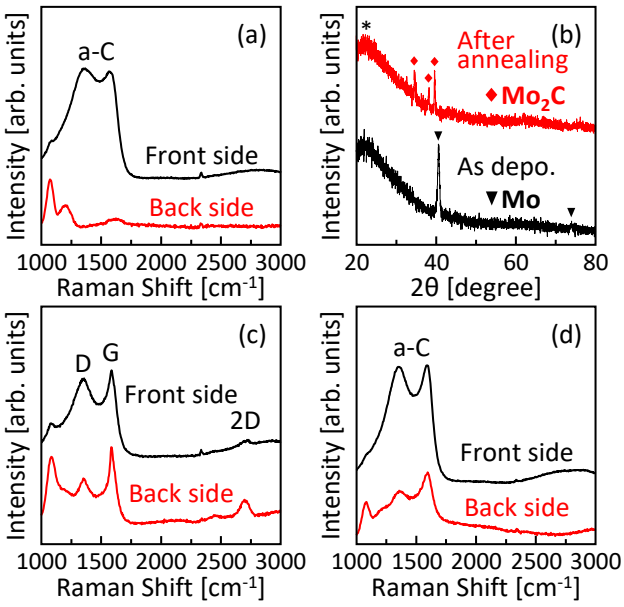

Fig. 3. Characteristics of the samples in groups (2)-(4). (a) Raman spectra and (b) XRD patterns of the Mo sample representing group (2). (c),(d) Raman spectra of the Pd and Cu samples representing groups (3) and (4), respectively.

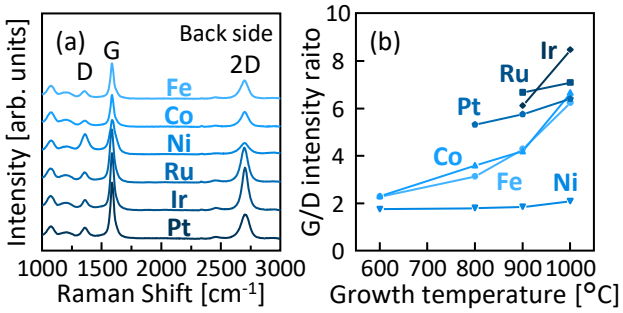

Fig. 4. (a) Raman spectra obtained from the back side of the samples annealed at 1000 °C. (b) G/D intensity ratio as a function of growth temperature in group (1).

Interactions between transition metals and a-C are deeply related to the arrangement of each element in the periodic table. While early transition metals form stable carbides, late transition metals form solid solution of carbon. In late transition metals, group 11 have low carbon solubility and weak carbon-metal interaction. Others have high carbon solubility and therefore induced the layer exchange. Pd has an intermediate characteristic because it is located in the middle in the early and late transition metals.

Fig. 4(a) shows Raman spectra obtained from the back sides of the Gr. 1 samples annealed at 1000 °C. From these spectra, we evaluated the intensity ratio of the G peak to the D peak in the group 1 samples. The G/D ratio indicates the crystal quality of MLG. Fig. 4(b) shows that metals are roughly divided into 2 types: (i) Fe, Co, and Ni samples produce MLG at low temperature while the MLG has low crystallinity; (ii) Ru, Ir, and Pt samples produce high crystallinity MLG while they need high temperature.

4. Conclusion

Interactions between transition metals and a-C were classified into 4 groups. The layer exchange was achieved for late transition metals, such as, Fe, Co, Ni, Ru, Ir, and Pt. These metals were divided into 2 types: low temperature growth or high crystallinity growth of MLG. Thus, we constructed the guidelines for selection of catalyst metal species in the layer exchange growth of MLG.

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