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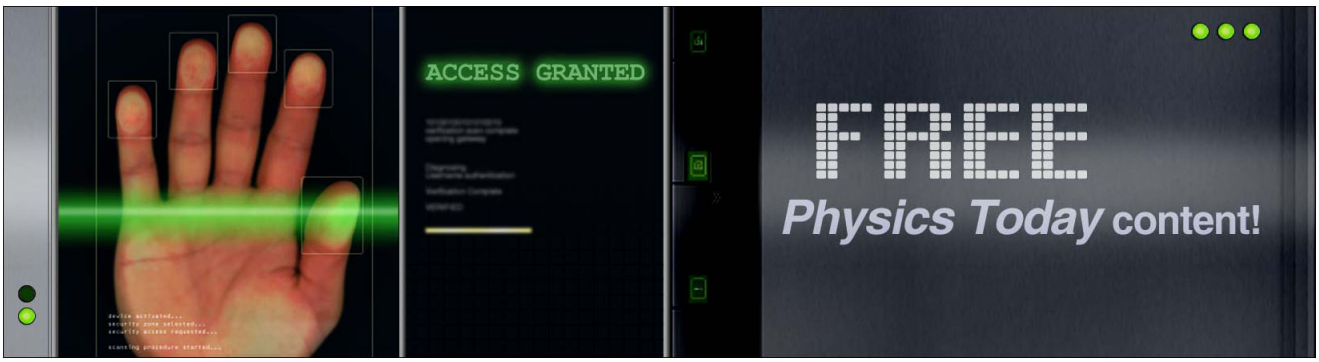

Transfer-free graphene synthesis on insulating substrates via agglomeration phenomena of catalytic nickel films

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Graphene layers were synthesized by annealing amorphous carbon (a-C) thin films on Ni/SiO_2/Si(111) substrates grown using pulse arc plasma deposition. Although the graphene layers were formed by catalytic reaction between a-C films and Ni metals, they were observed to be directly on the insulating SiO_2/Si substrates with island-shaped metallic particles. These particles presumably resulted from agglomeration phenomena of thin Ni films at a high temperature. We speculated that the agglomeration phenomena allowed the graphene formation on SiO_2/Si substrates. It was also confirmed that the particle size and graphene layer thickness depend on the starting Ni thickness. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4818342]

Graphene has attracted much attention due to its novel characteristics such as extremely high carrier mobility and ballistic transport properties.[1,2] Potential application of this material has been revealed with the fabrication of graphene transistors operated in gigahertz range.[3,4] For the past several years, various techniques for graphene synthesis have been suggested, such as the sublimation of silicon from SiC surfaces,[5–7] chemical vapor deposition,[8–10] and plasma-assisted vapor deposition.[11–14] Also, kinds of metals have been known to act as catalysts to segregate graphene. Therefore, catalytic metals such as Ni or Co have often been used for the synthesis of graphene on their surfaces.[9–12,14–17] While this method can be a promising candidate for graphene synthesis, there seems to be a disadvantage that the device design and operation will be limited to a certain extent since graphene layers must be stacked on conductive metal materials.

Recently, we have reported that graphene layers can be synthesized on a catalytic Ni film by the combination of amorphous carbon (a-C) film growth on a Ni/SiO_2/Si (111) substrate by the pulse arc plasma deposition (PAPD) and subsequent annealing processes.[14] The PAPD technique has an advantage of enabling to form ultra-thin films by controlling the number of discharge pulses. We have therefore attempted to grow graphene layers using the PAPD technique. In this study, we report that graphene layers can be formed directly on insulating SiO_2/Si substrates, without any substrate-transfer technique, by only using thin Ni films as catalytic metals. This presumably resulted from the agglomeration effects of the thin Ni films at a high temperature.

Ni/SiO_2/Si stacking structures with different Ni film thicknesses of 10, 20, and 35 nm were used as starting materials for graphene layer synthesis. The thin Ni films were deposited on 100-nm-thick SiO_2 films on Si(111) substrates by electron-beam (EB) evaporation. The a-C thin films were grown on the Ni/SiO_2/Si substrates in an ultrahigh-vacuum PAPD chamber. The detailed information on PAPD processes is described elsewhere.[14] In this study, the discharge pulse number was maintained at 50 pulses, which corresponds to the a-C thickness of approximately 5 nm. After the deposition of a-C films, samples were annealed under a condition of 900 °C for 5 min in nitrogen (N_2) gas flow ambient. For the sample characterization, various techniques were employed as follows. In order to confirm the existence of graphene layers on sample surfaces, Raman spectroscopy was carried out, in which a 532-nm-wavelength solid-state laser with the output power of 10 mW was used as an excitation light source. Surface morphology was observed by scanning electron microscope (SEM). Cross-sectional transmission electron microscope (TEM) images were taken to observe the nanostructure of graphene layers. In the TEM study, energy dispersive X-ray spectroscopy (EDS) was also carried out for elemental analysis. The specimens for TEM were prepared by the focus ion beam (FIB) technique.

Figure 1 shows Raman spectra for an as-grown sample and after-annealing ones. For the as-grown sample, 2D peak is not observed, which indicates no formation of graphene. On the contrary, for the after-annealing samples, sharp G peak (1589 cm^{-1}) and 2D peak (2699 cm^{-1}) are clearly observed, which shows the existence of graphene layers. Also, the evolution of D band (1349 cm^{-1}) indicates the structural disorder or defects. The results shown in Fig. 1 indicate that the annealing process caused dissolution of carbon into Ni films and resulted in the formation of graphene. These results are completely consistent with our previous study.[14]

Figure 2 shows SEM images of surfaces for after-annealing samples. From these images, many island-shaped particles are observed on surfaces for all samples, and the particle size clearly depends on the Ni film thicknesses. In the case of our previous study, however, for a sample with the starting Ni thickness of 100 nm, such particles were never observed.[14] We have only confirmed that a nano-ordered step structure is formed on the Ni surface.[14] In comparison with our previous results,[14] there was no distinctive morphology

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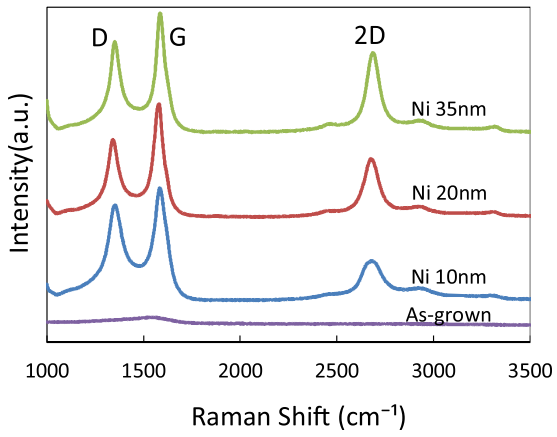

FIG. 1. Raman spectra for (a) an as-grown sample and after-annealing samples with different starting Ni thicknesses of (b) 10 nm, (c) 20 nm, and (d) 35 nm, respectively.

observed on the surface for the present samples, except for the presence of particles. Therefore, it is clear that the generation of these particles was caused by only using the thin Ni films. Recently, Kim *et al.* reported results similar to our study.[10] They state that agglomeration phenomena of Ni metals at a high temperature caused their surface roughness, and that the roughness strongly depended on the Ni film thicknesses.[10] It has also been reported that kinds of thin metal films can easily agglomerate and transform into metallic particles at a high temperature due to the dewetting phenomena on surfaces.[18] From these, it seems only natural to consider that the particles as observed in Fig. 2 were formed via the surface migration and agglomeration of Ni films as a continuation of the nano-step structure formation. In order to obtain more detailed information, TEM and EDS studies were carried out.

Figure 3(a) shows a cross-sectional TEM image for a sample with the starting Ni thickness of 20 nm. Figs. 3(b)–3(d) show magnified cross-sectional TEM images for samples with the different starting Ni thicknesses. These images clearly show the formation of graphene layers for all samples. Most noteworthy is that they seem to be formed only on SiO_2 films. The dark rounded area shown in Figs. 3(a) and 3(c) corresponds to the island-shaped particle as observed in Fig. 2. From these, the particles seem like penetrating onto the SiO_2 surface. Figs. 3(e) and 3(f) show cross-sectional TEM images for a sample treated in hydrochloric acid solution. Fig. 3(e) shows that the particle can be etched by the acid treatment, with a caved hollow remaining on the surface as vestiges of the particles. This indicates that the

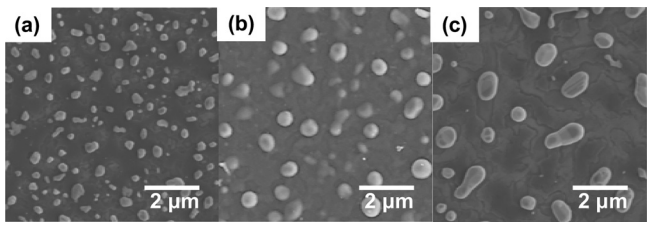

FIG. 2. SEM images of surfaces for after-annealing samples with different starting Ni thicknesses of (a) 10 nm, (b) 20 nm, and (c) 35 nm, respectively.

particles were formed via some reaction with SiO_2. On the other hand, Figs. 3(a) and 3(e) also show that SiO_2 surface seems to be widely covered with the graphene layers regardless of the acid etching.

For elemental analysis around the particles, EDS measurement was carried out. Figs. 4(a)–4(c) show EDS spectra taken by focusing with the electron-beam spot size of less than 1 nm on the particle, the graphene layer, and the graphene/SiO_2 boundary, respectively. The results revealed that the particles contain a large amount of Ni, and that Ni and the other elements, except for C, O, and Si, do not exist around the graphene layers. Thus, we concluded that the particles consist mainly of metallic Ni, and that the graphene layers are definitely formed not on Ni films but directly on SiO_2 surfaces. In Fig. 4(a), a small amount of Pd is observed inside the metallic particle. This is probably a result of a contamination incorporated from our EB evaporation furnace.

On the basis of the above, we state a hypothesis on the graphene synthesis process as drawn in Figure 5. First, a high-temperature annealing causes the carbon dissolution in Ni films. Then, during the cooling-time, graphene layers are formed selectively on the hollow lower face in the Ni microstructure,[14] which structure has been reconstructed during high temperature annealing. Such phenomena has already been observed not only in our previous TEM study[14] but also

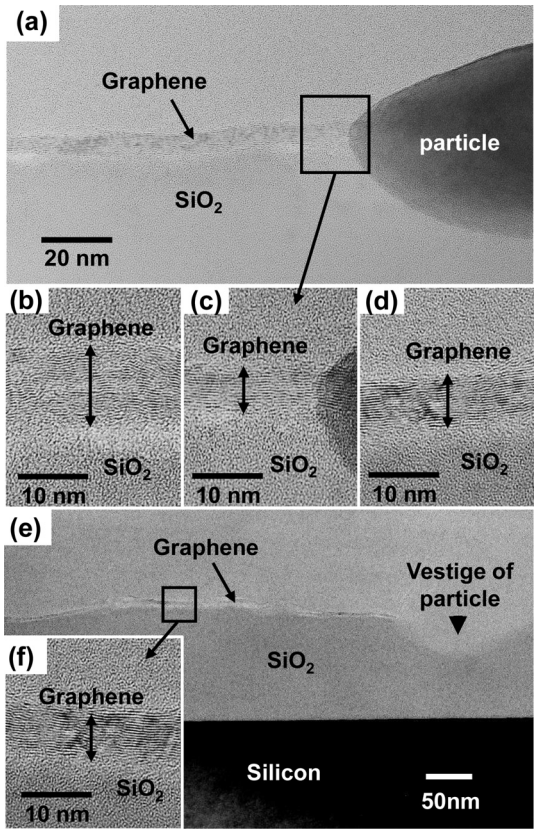

FIG. 3. (a) Cross-sectional TEM images for the sample with a starting Ni thickness of 20 nm, in which the dark rounded area corresponds to the island-shaped particles as observed in Fig. 2. Magnified TEM images for samples with starting Ni thicknesses of (b) 10 nm, (c) 20 nm, and (d) 35 nm, respectively. (e) Cross-sectional TEM image and (f) magnified TEM image for a sample with starting Ni thicknesses of 35 nm, which was treated in hydrochloric acid solution.

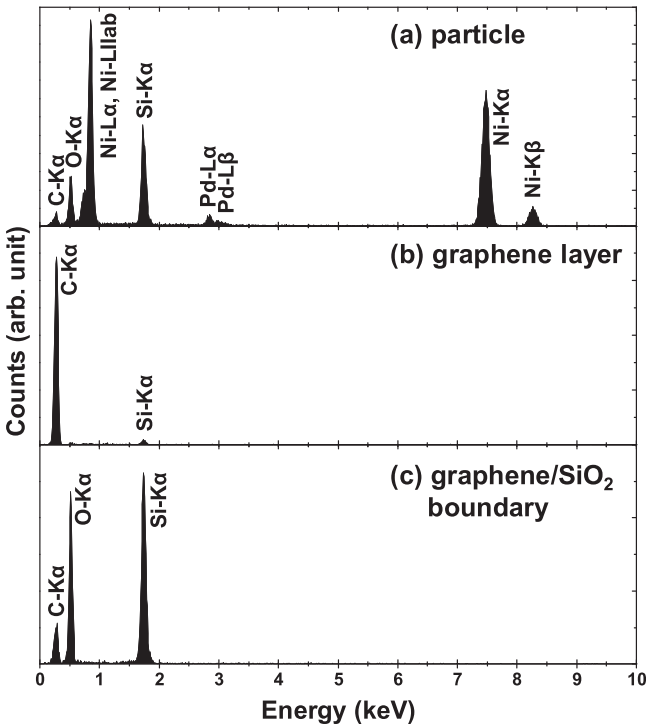

FIG. 4. EDS spectra taken by focusing on the observed cross sections of (a) the particle, (b) the graphene layer, and (c) the graphene/SiO_2 boundary, respectively. A small amount of Pd observed inside the particles is presumably the contamination incorporated from our EB evaporation furnace.

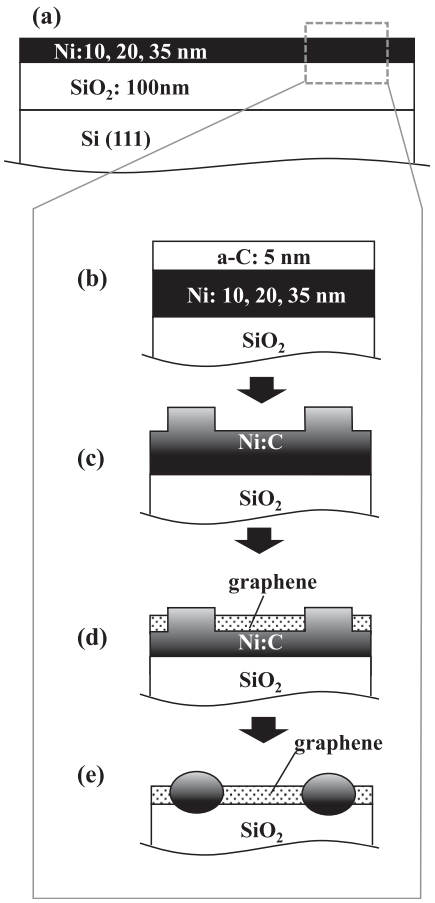

FIG. 5. Schematic drawings of the present graphene synthesis process. (a) Ni/SiO_2/Si(111) substrate. (b) Amorphous carbon (a-C) film was grown by PAPD. (c) At a high temperature, carbon dissolves in Ni films, and almost simultaneously a nano-step structure is formed on the Ni surface. (d) During gradual cooling, graphene layer segregated from the step sites of the Ni surface, and then (e) metallic particles and graphene layers are formed on SiO_2 film.

in other researcher's report.[9] This means that the graphene nucleation preferentially occurs around the step-sites or the hollow lower face adjacent to the step-sites. This is presumably due to the high surface energy around those areas. It seems possible to speculate that step-sites, which consist of grain boundaries of poly-crystalline Ni, and their contiguous areas have higher surface energy. Also, the present results indicate that the agglomeration of Ni films subsequently occurs as a continuation of the nano-step structure formation. As a result, the graphene layers are formed directly on SiO_2 films with the progress of the Ni agglomeration. Moreover, we have confirmed that the metallic particles can easily be removed by acid etching, with the graphene layer remaining on the surface. This means that Ni-free graphene layers can be realized on insulating substrates.

In addition to the above, the TEM results impart further information. For one thing, the graphene layer thickness increased only for a sample with the starting Ni thickness of 10 nm, as seen in Figs. 3(b)–3(d). This is probably because the carbon dissolution amount in the thin Ni film was limited due to the solid solubility limit. If the segregation of graphene occurs with subtle temperature lowering, the amount of segregation will increase with the decrease in carbon dissolution amount in the Ni film. For another thing, the metallic particles exist like penetrating onto SiO_2 surfaces, as seen in Fig. 3(a). This probably means that Ni reacted with SiO_2 during the progress of the agglomeration of Ni films. The EDS results also support this idea, which show that the metallic particle contains a certain amount of Si (see Fig. 4(a)). Also, in samples after acid etching, caved hollows were observed on the SiO_2 surface as vestiges of the particles. The uneven SiO_2 surface as observed in Fig. 3(a) or 3(e) is probably another evidence of the reaction. Further investigation is needed in order to control over the metal agglomeration processes, which must be important to grow an ideal graphene layer. Correspondingly, the size as well as the number of the hollows should be minimized to realize better graphene layers.

In summary, graphene layers were synthesized by annealing a-C films on Ni/SiO_2/Si (111) substrates deposited by PAPD. It was found that the graphene layers are formed directly on SiO_2/Si substrates with agglomerated metallic particles. The key parameter of the metallic particle formation was the thickness of starting Ni films. It was also confirmed that the graphene layer thickness as well as the particle size is dependent on the starting Ni thickness. We believe that the present results can expand the possibility of graphene synthesis by catalytic reaction, in terms of enabling to form graphene layers directly on insulating substrates without using any substrate-transfer technique.

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