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Formation of Carbon Nanostructures with Ge and SiC Nanoparticles Prepared by Direct Current and Radio Frequency Hybrid Arc Discharge

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Carbon nanocage structures with Ge and SiC nanoparticles were synthesized by direct current and radio frequency (dc-rf) hybrid arc discharge of C, Ge, and Si elements. High-resolution images showed the formation of Ge and SiC nanoparticles and nanowires encapsulated in carbon nanocapsules and nanotubes. The growth direction of the Ge nanowires was found to be $\langle 111 \rangle$ of Ge, and a structure model for Ge/C interface was proposed. The present work indicates that the various carbon nanostructures with semiconductor nanoparticles and nanowires can be synthesized by the dc-rf hybrid arc-discharge method.

Various carbon nanocapsules filled with Au, LaC_2, Co, Fe, Ni, Cu, CrC_x, MoC_x, MoO_3, WC_x, WO_3, TiC, and other elements have been synthesized by an ordinary arc-discharge method,[1–5] which are expected to be used for both scientific research and future device applications such as cluster protection, nano-ball bearings, nano-optical–magnetic devices, catalysis, and biotechnology. Although these metal nanoparticles had been successfully enveloped inside the spherical graphene sheets, few works have been reported for encapsulation of semiconductors such as Si, SiC,[6,7] and Ge.[7,8] Although semiconductor nanoparticles are expected to show luminescence by the quantum size effect, they are easily oxidized by exposure to air. Encapsulation of these semiconductor nanoparticles by the graphene layers is expected to provide a stable surface structure and new properties.

Recently we have succeeded in the formation of carbon nanocapsules by thermal decomposition of poly(vinyl alcohol) with SiC nanoparticles at 500 °C in an Ar gas atmosphere.[6,7] We have also produced Pd-intercalated onions by electron-beam irradiation.[9,10] These materials are expected to be used as solid-state lubricants and magnetic materials, respectively. However, the starting materials of SiC nanoparticles and Pd clusters should be prepared by other methods before producing the carbon nanocapsules, and a new method for the formation of nanocapsules filled with semiconductor nanoparticles is needed.

The purpose of the present work is twofold. The first is to synthesize carbon nanocapsules with semiconductor nanoclusters by direct current and radio frequency (dc-rf) hybrid arc discharge. In the present work, Ge and SiC with the band structures of indirect transition were selected. Ge and SiC semiconductors are extensively used and studied in the electronic industrial field. It has been reported that the band structure of Si with indirect transition could be changed into that of direct transition by the downsizing of the nanoparticles.[11] The second purpose is to understand the nanostructures of the carbon nanocapsules with Ge and SiC. The atomic structural analysis was carried out by high-resolution electron

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microscopy (HREM).[12–15] These studies will give us guidelines for the formation of carbon nanocapsules with the semiconductor nanoparticles with various band gap energies.

Samples were prepared by a modified arc discharge using pair anodes in order to enhance the Ge and Si evaporation. A graphite hollow cylinder (0.6 cm in diameter, 30 cm in length) is used for the main dc arc discharge. The gap distance between the main discharge electrodes is approximately 0.4 cm. A subanode of a carbon cylinder (1.5 cm in diameter, 10 cm in length) with the semiconductor (Si or Ge) powder is used, and a main anode of a carbon rod is partially mixed with the semiconductor powder. The dc arc discharge is initiated between a cathode electrode and the pair anodes. A rf antenna of water-cooled spiral copper pipe is installed 3 cm above the arc point to generate auxiliary plasma produced by an rf discharge around the dc arc plasma. When rf power is applied to an antenna through a matching circuit, the antenna dc current is also generated. The experimental parameters are as follows: dc arc current = 100 A; subanode current 80 A; rf power = 600 W (13.56 MHz); helium gas pressure = 100 torr. A detailed illustration of the apparatus was provided in the previous work.[16,17] The plasma produced by this dc-rf hybrid discharge is much more voluminous than that by the ordinary dc arc discharge.

Samples for HREM observations were prepared by dispersing materials, which consist of soot collected in the upper region of the arc-discharge chamber, on holey carbon grids by using ethanol. HREM observations were performed with 1250 and 300 kV electron microscopes (ARM-1250 and JEM-3000F) (JEOL, Ltd., Tokyo, Japan) equipped with top and side entry goniometers having point-to-point resolutions of 0.12 and 0.17 nm, respectively. To avoid sample damage by electron irradiation, the electron beam for HREM observations was minimized by using the smaller spot size. To compare observed images with calculated ones, HREM images were produced by the multislice method[18] using the MacTempas software (Total Resolution, Berkeley, CA). The parameters used in the calculations are as follows: accelerating voltage = 300 kV; radius of the objective aperture = 5.9 nm^{-1}; spherical aberration C_S = 0.6 mm; spread of focus Δ = 8 nm; semiangle of divergence α = 0.55 mrad; defocus values Δf = −41 nm; crystal thickness t = 1.6 nm.

A HREM image of carbon nanocapsules with SiC nanoparticles is shown in Fig. 1(a). SiC nanoparticles with sizes of 6–10 nm are observed. The material encapsulated in graphene sheets only consists of the SiC nanoparticles, and the number of the graphene sheets was in the range of 3–10 layers. A HREM image of a carbon nanocapsule and nanocage is shown in Fig. 1(b). The 5–6 graphene layers are observed around the nanoparticle,
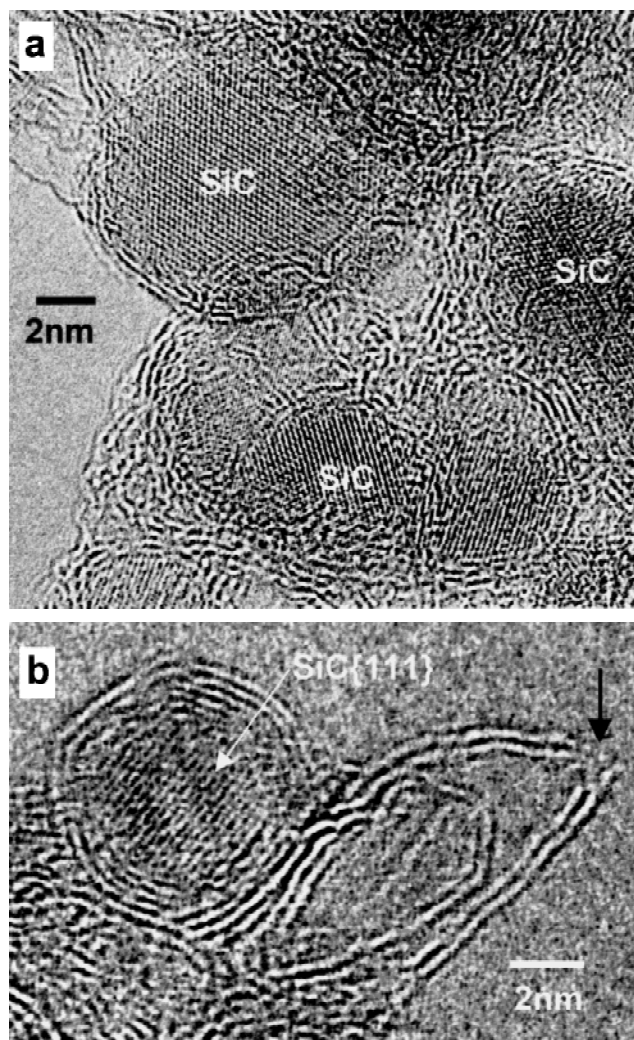

FIG. 1. HREM images of (a) carbon nanocapsules with SiC nanoparticles and (b) a carbon nanocapsule and nanocage.

and the size of the carbon nanocapsule is 4 nm. Lattice fringes with a distance of 0.25 nm which corresponds to the distance of {111} planes of β-SiC are observed in the cluster. A carbon nanocage with three graphene sheets is also observed. The tip of the cage is smeared as indicated by arrows. Reproducibility of the carbon nanocapsules was confirmed.

HREM images of Ge nanoparticles encapsulated in graphene sheets and amorphous carbon are shown in Figs. 2(a) and 2(b), respectively. In Fig. 2(a), the Ge nanoparticle is surrounded by 1–3 graphene sheets. In Fig. 2(b), Ge nanoparticle has a nanocrystalline structure and is surrounded by amorphous carbon with thickness of ca. 3 nm.

Figure 3(a) is a HREM image of Ge nanowire encapsulated in a carbon nanotube with 1–2 graphene sheets. The diameter is 10 nm, and the length is 70 nm. The Ge nanowire has a microtwin structure in region A as indicated by arrows. The Ge has a single-crystal structure in
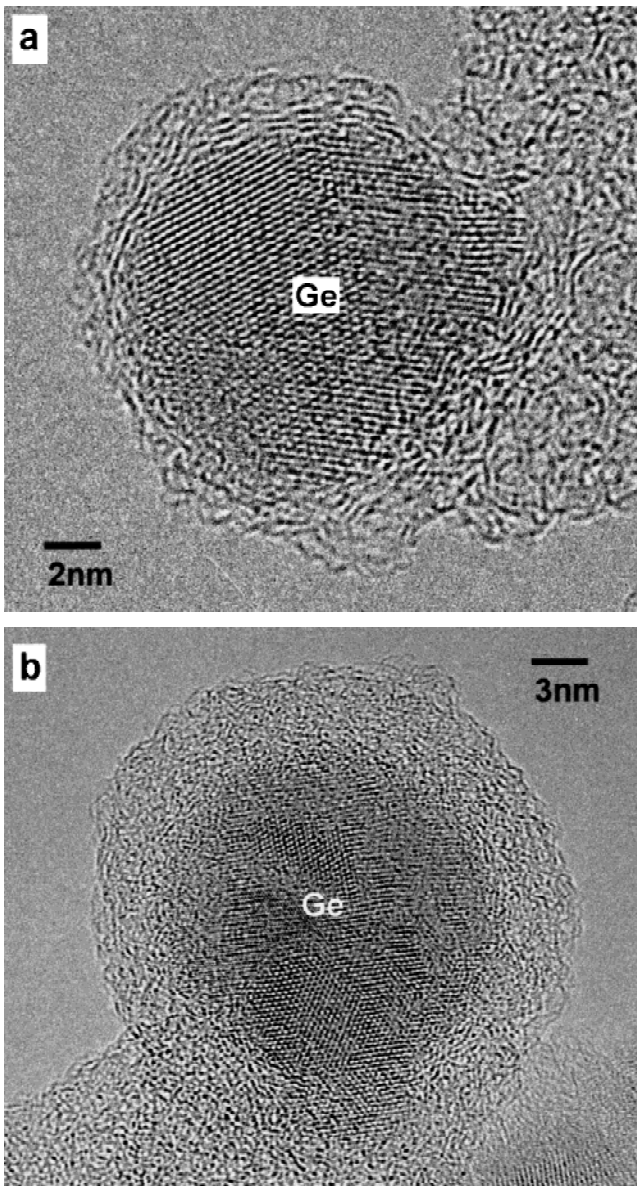
J. Mater. Res., Vol. 15, No. 10, Oct 2000

2183

FIG. 2. HREM images of Ge nanoparticles encapsulated in (a) graphene sheets and (b) amorphous carbon layers.

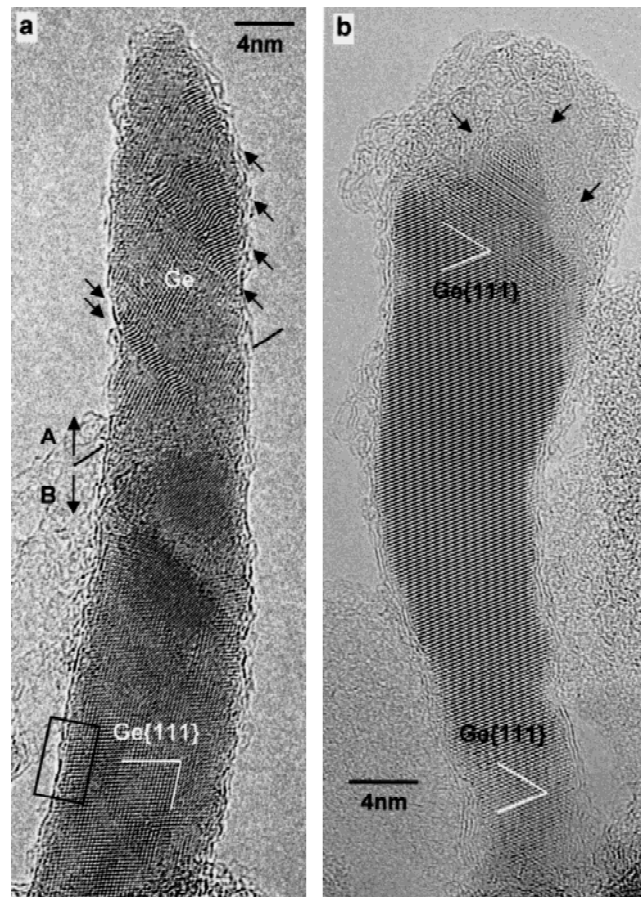
FIG. 3. HREM images of Ge nanowires encapsulated in carbon nanotubes: (a) crystalline Ge and graphene sheets and (b) amorphous carbon and Ge tip.

region B. The growth direction of the nanowire is ⟨111⟩ of Ge. Another type of Ge nanowire encapsulated in a carbon nanotube with 2–3 graphene sheets is shown in Fig. 3(b). The diameter is 10 nm, and the length is 60 nm. Although the Ge nanowire has a single-crystal structure, disordered–amorphous Ge and amorphous carbon are observed at the Ge nanowire tip as indicated by arrows. The growth directions of both the nanowires are ⟨111⟩ of the Ge crystal.

Epitaxial growth of carbon {002} on the Ge{111} planes was often observed at the nanocapsule/nanowire interface in the present work, as shown in Fig. 4(a). A similar epitaxial relationship was observed at the carbon/ β–SiC in the previous works.[7] The information on atomic arrangement at the carbon/Ge interface was ob-

tained from the HREM images in the present work, and a structural model of the carbon/Ge interface was constructed, as shown in Fig. 4(b). In Fig. 4(b), Ge atoms directly connect with carbon atoms of the graphite. From the present high-resolution observation, carbon {002} is parallel to Ge{111}, and carbon [110] is nearly parallel to Ge [011]. (If the incidence is parallel to carbon [010], two-dimensional lattice fringes should be observed.) The Ge{111} is the most stable and flat dense plane in the atomic level for Ge crystal, and the graphene sheet would be easy to grow on that atomically flat plane. Although there is lattice mismatch at the Ge/C interface, it is considered that the Ge{111} layer is connected with a graphene sheet by the van der Waals force as well as the *c* plane of graphite. The distance between the Ge crystal and graphene layer was assumed to be 0.33 nm, which is almost the same as that of graphite {002} planes. On the basis of this model, a HREM image is calculated as shown in Fig. 4(c). In the observed images of Fig. 4(a), the distance between the dark contrast of the first carbon layer and top of the Ge crystal is almost the same as that of carbon {002}, which indicates that carbon atoms of
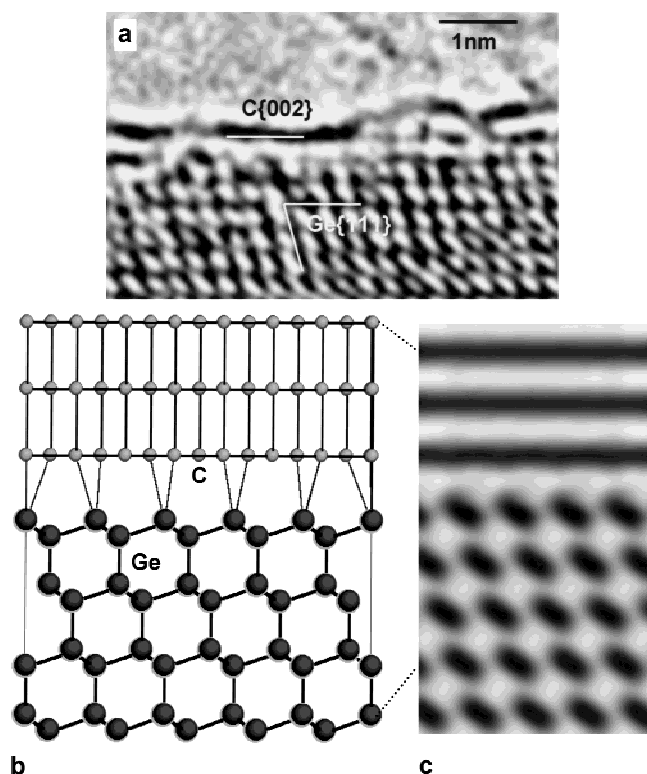
FIG. 4. (a) Enlarged HREM image of a rectangle of Fig. 3(a), (b) structural model of Ge/C interface, and (c) simulated image of the Ge/C interface.

the graphite-type structure directly connect with Ge atoms. Graphitization of amorphous carbon on Ge{111} planes would be easier compared to the other planes, and similar results were reported in the previous work for the SiC/C interface.[7] It is believed that the Ge{111} surface would have low activation energy for graphite growth, which results in the heterogeneous nucleation growth of graphite.

Structural difference of graphene sheets on SiC and Ge was observed in the present work. For SiC, excess carbon atoms in the SiC nanoparticles would precipitate and crystallize on the particle surface to form multicarbon layers during cooling. Because the carbon atoms are not soluble in Ge,[20] graphitization seems to be difficult compared to the precipitation on SiC. It is considered that carbon atoms would be supplied outside the Ge nanoparticles, and carbon layers form few graphene sheets or amorphous layers depending on the cooling rate and the surface structure.

Although many carbon nanocapsules with various elements and compounds have been prepared by an ordinary arc-discharge method, few nanocapsules filled with Ge and SiC have been reported. In the present work, the special dc-rf arc-discharge method was used, which results in the plasma-volume enlargement and the nanocapsule formation. The SiC nanoparticles would be formed by reaction of Si and C atoms in the dc arc plasma. The dc-rf arc-discharge plasma would be effective for the formation of semiconductor nanoparticles encapsulated in graphene sheets.

In the present work, the sizes of the semiconductor Ge and SiC nanoparticles were reduced to 10 nm, which indicates that widening of the band gap energy is expected by quantum size effects, and peculiar optoelectronic properties will be expected. Ge nanowires encapsulated in carbon nanotubes are also expected as one-dimensional devices, and crystallinity of Ge is important for the formation of graphene sheets as shown in Fig. 3. Hollow carbon clusters with diameters in the range of 0.7–1.0 nm are often observed at the surface of the carbon nanocapsules. They would be the higher fullerenes derived from the C_{60} series structures, which consists of 12 pentagons and arbitrary numbers of hexagons with approximately 60 carbon atoms. Recent HREM studies also showed the possibility of direct detection of C_{60} fullerene materials.[19] Si oxide and Ge oxide layers are not observed at the surface of the SiC and Ge nanoparticles, which indicates that the carbon nanocapsules are effective for cluster protection against oxidation in air.

In conclusion, carbon nanostructures with Ge and SiC nanoparticles and nanowires were synthesized by the dc-rf hybrid arc-discharge of C, Ge, and Si elements. High-resolution images showed the formation of carbon nanocapsules (2–8 carbon layers or amorphous carbon) with Ge and SiC nanoparticles with the sizes of 2–20 nm. Ge nanowires encapsulated in carbon nanotubes were also produced, and the growth direction of the Ge nanowires was ⟨111⟩. The structure model for Ge/C interface was proposed, which showed that carbon atoms of the graphite-type structure directly connect with Ge atoms. The present work indicates that the various carbon nanostructures with semiconductor nanoparticles and nanowires can be synthesized by the dc-rf hybrid arc-discharge method; the carbon nanocapsules are effective for stabilization of the semiconductor nanoparticles, and their new properties will be expected.

ACKNOWLEDGMENTS

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