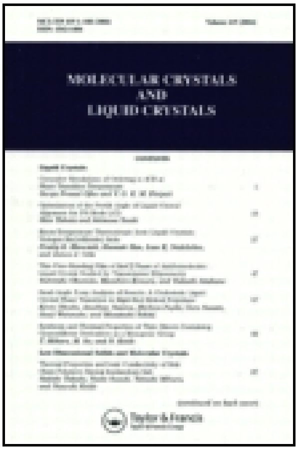

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Formation and Structure of Cluster-Included Carbon Nanocapsules Prepared by Polymer Pyrolysis

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Formation of carbon nanocapsules with various clusters (SiC, Au, Fe, Co, Ge, and GeO_2) by polymer pyrolysis was investigated, and nanocapsules with SiC and Au nanoparticles were produced by thermal decomposition of polyvinyl alcohol at ~500°C in Ar gas atmosphere. The formation mechanism of nanocapsules and a structural model for the nanocapsule/SiC interface were proposed. In addition, carbon clusters were formed at the surface of carbon nanocapsules, and carbon onions were produced by electron irradiation of amorphous carbon produced from polyvinyl alcohol. The present work indicates that the pyrolysis of polymer materials with clusters is a useful fabrication method for the mass-production of carbon nanocapsules and onions at low temperatures compared to the ordinary arc discharge method.

Keywords: HREM; carbon nanocapsule; cluster; SiC nanoparticle; interface; carbon onion

INTRODUCTION

Nanoclusters encapsulated within the carbon hollow-cage-structures have a potential of studying materials in the low dimensions with the isolated environment, and are intriguing for both scientific research and future device applications such as cluster protection, nano-ball bearings, nano-optical-magnetic devices, catalysis, and biotechnology[1-6]. Although the arc discharge method[7] is an ordinary method for the formation of the hollow-cage-structures, separation of these cages from carbon soot is difficult because of the coexistence of various carbon by-products and of high-temperature

process.

The purpose of the present work is to prepare the carbon nanocapsules with nanoclusters at low temperatures by ordinary annealing and electron-beam irradiation without using the arc discharge method. In the present work, various clusters with polyvinyl alcohol were selected for the nanocapsule formation. The polyvinyl alcohol is easy to decompose at elevated temperatures, and produces carbon-based materials. To understand the formation mechanism of the nanocapsules, high-resolution electron microscopy (HREM) was carried out for microstructure analysis, which is a powerful method to determine atomic structures[8-12]. These studies will give us a guideline for designing and synthesis of the carbon nanocapsules, which are expected as the future nanoscale devices.

EXPERIMENTAL

In the present study, the following nanoparticle materials were used; β-SiC nanoparticles (Sumitomo Cement Co. Ltd.), Ge nanoparticles (10 nm, produced by He gas condensation method), Fe nanoparticles (10 nm, ULVAC Co. Ltd.), Co nanoparticles (10 nm, ULVAC Co. Ltd.), Au clusters (in toluene, ~10 nm, ULVAC Ltd.) and GeO_2 (in H_2O, Wako Pure Chemicals Industries Ltd.). These nanoparticles were dispersed in the de-ionized water with polyvinyl alcohol (PVA-706, Kuraray Co., Ltd.) at 60℃. This polymer is copolymer of polyvinyl alcohol and polyvinyl acetate. The solution with clusters and polyvinyl alcohol was dried in a drying oven prior to loading into the vacuum chamber. The annealing camber was first evacuated to 1×10^{-5} Pa, and the samples were annealed at 400~800℃ for 30 min in Ar gas atmosphere of 0.12 MPa.

Samples for HREM observation were prepared by dispersing the materials on holey carbon grids. HREM observation was performed with 1250 kV electron microscope (ARM-1250) having a point-to-point resolution of 0.12 nm. To compare observed images with calculated ones, HREM images were produced by the multi-slice method using the MacTempas software (Total Resolution, CA, USA). The parameters used in the calculations are as follows: accelerating voltage = 1250 kV, radius of the objective aperture = 8.8 nm^{-1}, spherical aberration C_s = 2.28 mm, spread of focus Δ = 15 nm, semi-angle of divergence α = 0.85 mrad, defocus values Δf = -49 nm, and crystal thickness t = 2.0 nm.

RESULTS AND DISCUSSION

A HREM image of SiC nanoparticles prepared with polyvinyl alcohol annealed at 500℃ in Ar gas atmosphere is shown in Fig. 1(a). The particle size of SiC is 10~50 nm. All the SiC particles are surrounded by graphite sheets, and the number of the graphite sheets are in the range of 1~6. An enlarged HREM image of a carbon nanocapsule is shown in Fig. 1(b).

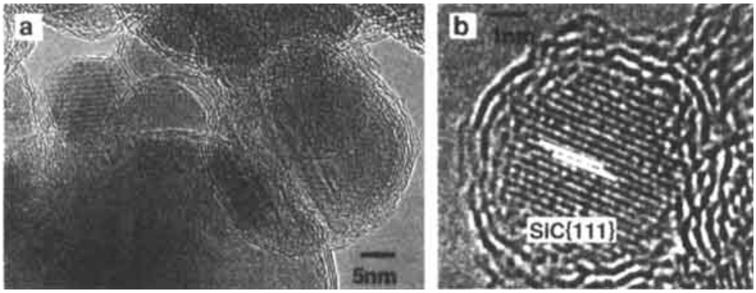

FIGURE 1 (a) HREM image of annealed SiC nanoparticles with polyvinyl alcohol. (b) Enlarged HREM image of a carbon nanocapsule.

Lattice fringes with a distance of 0.25 nm which corresponds to the distance of {111} planes of β-SiC are observed in the nanoparticle. Two {002} planes of graphite grow on the β-SiC nanoparticle.

Synthesis of carbon nanocapsules with various elements such as Au, Ge, and GeO_2, Fe, and Co, was also tried. Formation of partial carbon nanocapsules with Au was observed after annealing at 400℃. Other elements did not form good carbon nanocapsules at low temperatures, and amorphous carbon is also observed around the nanoparticle.

Table I Nanocapsule formation by pyrolysis of polyvinyl alcohol with M.

M	SiC	Au	Ge	GeO_2	Fe	Co
Annealing temperature (℃)	500	400	700	400	800	400
State of carbon	G	G+A	A+G	A	A	C
Nanocapsule formation	○	△	△	×	×	×
Particle size (nm)	10~30	~10	~10	3	~20	~20

G: graphite A: amorphous C: carbide

The formation model of carbon nanocapsules by pyrolysis of polyvinyl alcohol was proposed. In the as-prepared samples, the nanoparticle is encapsulated in amorphous polyvinyl alcohol. The polyvinyl alcohol has a basic formula of $[CH_2CH(OH)]_m$-$[CH_2CH(OCOCH_3)]_n$, which decomposes into H_2O and CO_2 at 120~170℃ in air. During annealing, the polyvinyl alcohol decomposes into H_2O and CO_2. After annealing at 400~500℃ in Ar gas atmosphere, only carbon atoms are remained, and graphite layers grow on the surface of nanoparticles. In the present work, only SiC nanoparticles formed perfect carbon nanocapsules as listed in Table I, and others produced carbon layers with amorphous structure except Co nanoparticles. This suggests that the carbide-based materials would be effective for graphite growth. Formation of the graphite layer around nanoparticles is useful for cluster protection against grain growth of nanoparticles. For various nanostructured materials, nanograins are needed to obtain the various properties such as mechanical, electronic, and magnetic properties.

Carbon hollow-structures such as carbon clusters (C_{36} ~ C_{70}) and nanocages were also formed at the surface of carbon nanocapsules. In a transmission electron microscope, carbon onions with tetrahedral, hexagonal and spherical shape were also produced by electron-beam irradiation of amorphous carbon produced from polyvinyl alcohol. The vertices consisting of pentagonal carbon bonding showed the "atom clouds", and changed into spherical structure by introducing heptagon/pentagon pairs. The atom clouds would be due to the carbon diffusion at the onion surface by the vacancy mechanism.

A HREM image of surface of a carbon nanocapsule with SiC nanoparticle prepared at 500℃ is shown in Fig. 2. (a). Although the carbon shows graphite structure on the SiC {111} (arrow A), it shows disordered structure on the other planes of SiC (arrow B). An enlarged HREM image of the surface indicated by the arrow A in (a) is shown in Fig. 2 (b). Graphite {002} planes grow epitaxially on the β-SiC {111}.

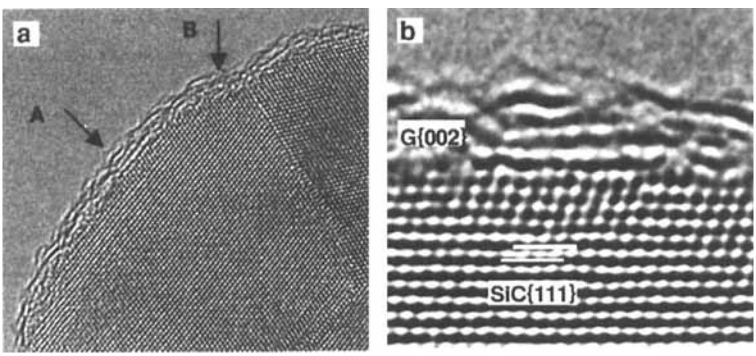

FIGURE 2 (a) HREM image of surface of carbon nanocapsule with SiC nanoparticle. (b) Enlarged HREM image of a part of (a).

Epitaxial growth of graphite {002} on the β-SiC {111} planes was often observed at the nanocapsule/nanoparticle interface in the present work,

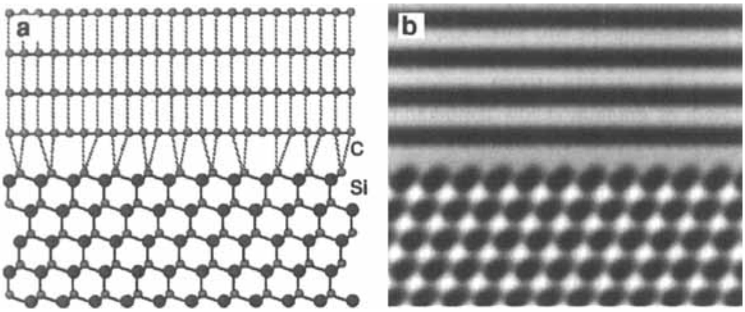

FIGURE 3 (a) Structure model of graphite/SiC interface with C-C bonding at the interface. (b) Simulated HREM image.

as shown in Fig. 2. Similar epitaxial relationship was observed at the graphite/ β-SiC in the previous works[13,14]. The information on atomic arrangement at the graphite/SiC interface was obtained from the HREM images in the present work, and a structural model of the graphite/SiC interface was constructed, as shown in Fig. 3(a). In Fig. 3(a), carbon atoms which belong to SiC structure connect directly with carbon atoms of the graphite. From the present high-resolution observation, the graphite {002} is parallel to the SiC {111}, and graphite $[1\bar{1}0]$ is nearly parallel to SiC $[01\bar{1}]$. (If the incidence is parallel to graphite [010], two dimensional lattice fringes should be observed.) Distance between the SiC crystal and graphite layer was assumed to be 0.335 nm, which is same as that of graphite {002} planes. Based on the model, HREM images are calculated as shown in Fig. 3(b). In the observed images of Fig. 2(b), the distances between the dark contrast of first graphite layer and top of the SiC crystal are almost same as those of graphite {002}, which indicates that carbon atoms of the graphite structure directly connect with carbon atoms belonging to SiC structure. Amorphous carbon might be graphitized on SiC {111} planes because of the low activation energy for graphite growth, which would result in the heterogeneous nucleation growth of graphite.

CONCLUSION

Formation of carbon nanocapsules with various clusters (SiC, Au, Ge, GeO_2, Fe and Co) by polymer pyrolysis were investigated, and nanocapsules with SiC and Au nanoparticles were produced by thermal decomposition of polyvinyl alcohol at low temperatures of 400~500℃ in Ar gas atmosphere. From the microstructure analysis, the formation mechanism of carbon

nanocapsules was described. Stable interfacial structures were often observed at the nanocapsule/SiC interface, and a structural model for the graphite/SiC interface was proposed. The SiC {111} surface might have low activation energy for graphite {002} growth, which would result in the nucleation growth of graphite at low temperatures. The present work indicates that the pyrolysis of polymer materials and the electron irradiation on amorphous carbon are effective methods for the formation of carbon nanocapsules and onions at very low temperatures compared to the conventional arc discharge methods. The former chemical process is also useful for large-scale production of nanocapsules with nanoclusters (semiconductors, metals, ceramics, and others) from solution with colloid and complex, which is expected for the application to the future nanoscale devices.

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