Chemical bonding studies of silicon nanotubes by 3D nano-ESCA

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Silicon-based hollow structures such as silicon nanotubes and nanocapsules (SiNCs) have received considerable attention because of their potential applications to the encapsulation and immobilization of catalyst materials, thermal insulation, and drug delivery, for example. Hollow structures have conventionally been prepared by chemical deposition with templates such as emulsion droplets and metal nanoparticles. Monomers such as tetraethyl orthosilicate are usually used for starting materials. After the deposition of SiO on templates to build core-shell structures, cores are dissolved to obtain capsules. It has been pointed out that the shell is damaged during this dissolving process. The shell prepared by this method is not dense enough to capture guest materials. It is thus required that the preparation of templates and the formation of robust shells be combined into one step.

It has recently been demonstrated that hydrothermal synthesis is promising for preparing a wide variety of nanomaterials. In this method, starting materials and water are heated in a high-pressure container. It is possible to dissolve the poorly soluble starting materials in water under high temperature and pressure in order to synthesize novel materials. The materials prepared by the hydrothermal technique are dense and robust. Intrinsic properties of products such as silicon nanotubes and carbon nanotubes have been investigated, since templates are not used in this method.

In the present study, we have performed the one-step preparation of silicon-based hollow structures by hydrothermal synthesis and investigated their structures by transmission electron microscopy (TEM) and X-ray photospectroscopy (XPS).

The SiO powder (0.4 g) and ultrapure water (12 ml) were placed in the reaction container made of Hastelloy C22 alloy. The container was heated to 513K in 1 h, and then gradually raised to 538K at a speed of 0.2 K/min in order to form nuclei. All water was vaporized at 523K and the pressure in the container reached 3 MPa. The temperature was then held for 1 h. The suspension was stirred with an agitating blade at a rotation rate of 200 rpm during the synthetic process. The growth rate of products was very slow without stirring. The container was then cooled gradually to room temperature, and the supernatant was collected as products. Structural and chemical analyses of the products were performed with a scanning electron microscope (SEM; JEOL JSM-7500F), a transmission electron microscope (TEM; Hitachi H-800) and a high-resolution TEM (HRTEM; JEOL JEM-3200) capable of energy dispersive X-ray spectroscopy (EDX). The XPS and photoelectron mapping were performed using 3D nano-ESCA at Spring-8 BL07LSU. Diamond coated silicon wafers were used as sample supports for the XPS measurement.

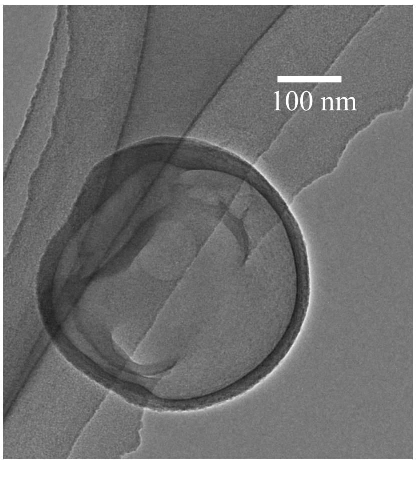

Fig.1. TEM image of a silicon nanocapsule prepared at the temperature of 538 K.

The HRTEM image of the product is shown in Fig. 1. The inner diameter of the capsule was approximately 300 nm. The thickness of the shell was approximately 20 nm. A selected-area electron diffraction (SAED) pattern exhibited only a halo pattern that indicated that the capsule was amorphous. We carried out the EDX measurement to analyze the chemical composition of nanocapsules. Elements such as C, O, Si, and Cu were detected. The Cu peak originated from the TEM grid used. C was thought to come from contaminants during the TEM observation. The synthesized nanocapsules were composed of O and Si with an atom ratio of 1:6 : 1 estimated from the EDX spectrum, indicating the existence of some oxygen vacancies. These results together with HRTEM image indicate that oxygen supply to the outer shell was not uniform. Next, we discuss the mechanism of the formation of the nanocapsules prepared. It was indicated that nanobubbles in water played an important role in the formation of silica nanocapsules [2]. The air in the container dissolved into the water and generated bubbles. It is known that nanobubbles tend to remain in the water, while typical bubbles rise to the liquid-vapor interface and collapse. These nanobubbles acted as core templates. The SiO was decomposed to form Si^{2+} below approximately 520 K [1]. Si^{2+} concentrated at the gas-liquid interface of these bubbles since the bubble surface was negatively charged owing to the existence of OH$^-$. The inner layer of the shell thus became smooth. The growth of the outer silicon oxide layer was assisted by H$^+$ and OH$^-$ in the water under the high-temperature and high-pressure condition. The recombination of Si^{2+} with oxygen occurred below 528K to form silica. Finally, we discuss about the chemical bonding status of nanocapsules from the results obtained by XPS measurements. Figures 2 (a) and (b) show the SEM image and Si2p photoelectron mapping of nanocapsules on the diamond coated silicon wafer, respectively. Aggregation of nanocapsules was observed in the SEM image. It was also clearly observed the intensity of Si2p signal increased on the aggregation in the Si2p photoelectron mapping. Figure 3 shows the XPS spectra measured on the aggregation in the Si2p region. One main peak component, centered around 103 eV, was observed. This value corresponds to the bonding energy of Si-O bonds. On the other hand, no peak corresponding to Si-Si bonds was detected.

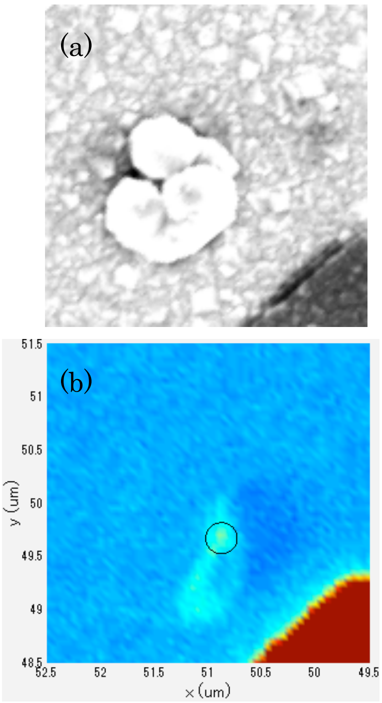

Fig.2 (a) SEM image and (b) Si2p photoelectron mapping of nanocapsules on the diamond coated silicon.

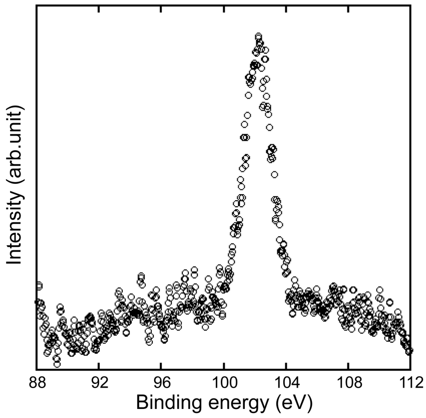

Fig.3 XPS spectra of nanocapsules on the diamond coated silicon.

In summary, we succeeded preparing nanocapsules by hydrothermal synthesis using SiO and water as starting materials. It was thought that bubbles in the water worked as core templates. It was concluded that nanocapsules consisted of amorphous silicon oxide without any Si-Si bonds from the results of TEM and XPS measurements.

References

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