Synthesis of Germanium Nanocubes by a Low-Temperature Inverse Micelle Solvothermal Technique

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We present a low-temperature inverse micelle solvothermal approach for the synthesis of germanium nanocubes using the surfactant heptadecaethylene glycol monododecyl ether as a capping agent. X-ray diffraction results indicate that the as-prepared nanocubes are diamond-type pure germanium. Transmission electron microscopy observations show that the as-prepared germanium nanocubes have an edge length of 100 ± 20 nm, highly crystallized.

Introduction

Recently, one of the frontier fields in nanometerial research has been morphology-controlled synthesis of nanocrystals, since novel optical and electronic properties were observed for special particle sizes and shapes.1,2 Consequently, considerable efforts have been made for the controllable synthesis of nanomaterials with a desired structure and morphology. Numerous nanomaterials with an interesting morphology or a specific structure have been successfully prepared, such as nanowires,3 nanobelts,4 nanotubes,5 nanonails,6 nanoflowers,7 nanocubes,8 and nanospheres.9 Germanium (Ge) is an important semiconductor and has been studied extensively. In recent years, there have been many reports on the study of photoluminescence, especially the visible photoluminescence of Ge nanocrystals at room temperature10,11 because of the potential applications in devices such as electronics and optoelectronics.12,13 Up to date, a few methods have been used to prepare Ge nanoparticles, including both physical14–18 and chemical19–24 methods. However, either a high temperature, a high pressure, laser annealing, or complicated reactions are required for these methods. In addition, it is difficult to fully characterize the nanoparticles because all these methods yield a small amount of Ge nanoparticles. Although solution-phase chemical methods have been used widely for the preparation of free-standing colloidal nanocrystals, it has been particularly challenging to synthesize Ge nanocrystals by solution-phase chemical methods, primarily due to their strong covalent bonding and the need of a high temperature to promote crystallization. Recently, it has been reported that Ge nanocrystals can be synthesized by high-temperature decomposition of tetraethylgermanium in organic solvents25 and high-temperature supercritical fluid solvents.26 However, the Ge nanocrystals prepared by these methods have a poor crystallinity and monocrystalline nature. Although there has been significant progress in the size and shape control of II–VI and III–V semiconductors,27 there has been very little work done on the shape-controlled synthesis of Ge nanocrystals. Therefore, it is still a challenge to develop a new synthetic method for the shape-controlled synthesis of Ge nanocrystals. Pileni28 reported that the shape of the surfactant micelles can provide control over particle morphology during crystal growth. It has been reported that the selective adsorption of surfactant molecules and their respective counterions on certain crystallographic facets during crystal growth is believed to affect nanocrystal shape.29 Here, we report a simple low-temperature inverse micelle solvothermal method for the preparation of Ge nanocubes using the surfactant heptadecaethylene glycol monododecyl ether (C_{22}H_{47}O) as a capping agent.

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Experimental Section

The synthesis of Ge nanocubes was performed in a 125 mL Parr reactor (model 4750, Parr Company, Moline, IL). A typical synthesis procedure of Ge nanocubes is as follows: 80 mL of hexane, 0.6 mL of GeCl₄, 0.6 mL of phenyl-GeCl₃, 1.8 mL of C₁₂E₇, and 5.6 mL of Na (25 wt % dispersion in toluene) were added to a 200 mL flask. The mixtures were stirred in a magnetic stirrer for 30 min before being transferred to a Parr reactor. The Parr reactor was kept at 280 °C for 72 h in a furnace without any stirring or shaking and then cooled to room temperature. A black powder was collected and washed with excess amounts of hexane, alcohol, and distilled water to remove any NaCl byproduct and hydrocarbon residue and then dried at 60 °C for 12 h in an oven. X-ray diffraction (XRD) and transmission electron microscopy (TEM) measurements were used to characterize the nanocubes.

Results and Discussion

Figure 1 is the XRD pattern of the as-prepared Ge nanocube powder. The XRD spectrum undisputably exhibits strong and clear characteristic crystalline peaks of the pure diamond-type Ge. By refinement of the XRD data, we found that the lattice constant of the Ge nanocubes is $a = 5.655$ Å, which is consistent with that ($a = 5.657$ Å) of the bulk Ge (JCPDS no. 4-545, Fd3m).

Figure 2a shows a representative low-magnification TEM image of the Ge nanocubes. The TEM image reveals that the Ge nanocrystals prepared using the surfactant C₁₂E₇ as a shape-controlling agent have a cubic morphology. A careful TEM survey of the nanocubes from different areas on the copper grid indicates that most of the nanocubes have an edge length of 100 ± 20 nm, although some small-sized nanocubes were also observed. Figure 2b shows a TEM image of an individual nanocube, and Figure 2c shows the corresponding SAED pattern that exhibits the hexagonal symmetry of the {111} lattice plane of the diamond-type Ge, indicating the high crystallinity of the nanocubes. The different contrast in the bright field images (Figures 2a and b) is caused by the strain-induced misorientation under the irradiation of electron beam. The different intensity and morphology of the diffraction spots indicates that the crystal is not orientated exactly to its [111] zone axis.

Figure 3a shows a high-resolution TEM (HRTEM) image of a nanocube, in which the clear lattice fringes further confirm that the nanocubes are single crystals. The interplanar spacing is 3.25 Å, corresponding to the {111} planes of the diamond-type Ge. The chemical composition of the as-prepared nanocubes was analyzed by energy-dispersive X-ray spectroscopy (EDS), which is shown in Figure 3b, indicating that the as-prepared nanocubes are pure Ge, since the Cu and C peaks come from the copper grid and carbon film support, respectively.

Figure 1. XRD pattern of the as-prepared Ge nanocubes.

Figure 2. (a) Low-magnification TEM image of the as-prepared Ge nanocubes. (b) High-magnification TEM image of an individual Ge nanocube. (c) SAED pattern of the Ge nanocube shown in part b.

To understand the growth mechanism of the nanocubes, the structure of the as-prepared nanocubes was further investigated by HRTEM. Figure 4a shows a HRTEM image of a Ge nanocube, indicating that this nanocube is probably formed by four smaller nanocubes (indicated by arrows) that grow separately first and then form a big nanocube. Figure 4b shows a low-magnification TEM image of the nanocubes, in which we observed that the contrast of some nanocubes (indicated by arrows) changed and the surfaces of these nanocubes began to melt under electron beam irradiation for an extended period of time. Under our experimental conditions, the sample was irradiated on the high-resolution transmission electron microscope with an accelerating voltage of 200 kV and a maximal dose of $2 \times 10^8$ e/cm$^2$·s at room temperature. During the irradiation by electron beam, the temperature of the
nanocubes would increase. However, it is very difficult to estimate the increased temperature under our present experimental conditions. The contrast change in the micrographs across the nanoparticles is likely due to changes of surface morphology. The melting of the surface and changes of the particle surface morphology caused by electron beam irradiation result in the pattern distortion of the small nanocubes, which is believed to contribute significantly to the formation of big crystalline nanocubes when these small nanocubes aggregate together. On the basis of the above investigations, we propose the following growth mechanism for the nanocube formation. First, during the reduction process, chlorogerma- niums are reduced to small-sized cubic Ge nanocrystals. The small cubic particles aggregate together through assistance of the surfactant C{sub 12}E{sub 7}, which serves as a cohesive agent in the aggregating process. Finally, these aggregated cubic particles grow into nanocubes with the crystallinity being improved. Figure 5 is a scheme that illustrates the growth process of the nanocubes.

It has been reported that the micelles formed by the surfactant in solvent and the selective adsorption of the surfactant on the crystal faces during the crystal growth play important roles in controlling the size and shape of the nanocrystals. In our present case, we propose that the surfactant C{sub 12}E{sub 7} played important multiple roles in the formation of Ge nanocubes. First, the surfactant C{sub 12}E{sub 7} formed the inverse micelles in the hexane solvents. These micelles directed the nucleation and growth of Ge nanocrystals. Second, the selective adsorption of the surfactants and their respective counterions on the germanium crystal faces played a critical role in the formation of cubelike Ge
nanocrystals. Third, the surfactant C_{12}E_{7} stabilized the Ge crystals to form nanosized crystals. Fourth, it acted as a cohesive agent during the formation of bigger nanocubes. The control of the shape of the nanocrystals is a real challenge. Therefore, a detailed study is needed to understand the growth mechanism of the Ge nanocubes.

**Conclusions**

In summary, a low-temperature inverse micelle solvo-thermal route has been developed for large-scale synthesis of Ge nanocubes. These nanocubes are either highly crystallized pure Ge single crystals or aggregates of polycrystals. This method does not require a complex apparatus, sophisticated techniques, or high-temperature conditions. It has the potential to be applied to the synthesis of other semiconducting nanocrystals, too.

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