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Synthesis of crystalline and amorphous germanium nanorods

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Abstract

Crystalline and amorphous germanium nanorods have been synthesized by PVD of germanium powders in flowing Ar/H_2 atmospheres. TEM images show diameters of the nanorods ranging from 20 to 200 nm and length up to 5 μm. Selected area electron diffraction indicates that the crystalline nanorods have tetragonal structure. Their growth process has been considered as VLS mechanism.
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1. Introduction

Nanoscale materials have unique properties in comparison to the bulk material owing to quantum confinement effects, for example, as the diameter of the Si nanowire approaches the de Broglie wavelength, visible photoluminescence is induced [1,2]; silica nanowires at a diameter of about 15 nm emit stable and intense blue light at 2.65 and 3.9 eV. The intensity of the emission is two orders of magnitude higher than that of porous silicon [3]. Lately special attention has been paid to one-dimensional structures, such as nanotubes and nanowires owing to their contribution to understanding fundamental concepts in mesophysics, and potential applications in nanoelectronic devices [4,5]. For instance, semiconductor CdS nanowires have been used in laser

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light-emitting diodes and optical devices based on nonlinear properties [6,7]. Zinc oxide nanowires grown on sapphire substrates have been fabricated into nanolasers [8].

Ge has especially interesting properties because the direct gap is about 741 meV above the indirect gap [9]. Nanocrystallite Ge embedded in a SiO_2 matrix shows broadband photoluminescence (PL) spectra in the visible wavelength range at room temperature [10]. The synthesis of crystalline semiconductor nanowires, such as Si and Ge holds considerable technological promise for device applications, and for improving the optical properties of these indirect gap materials but has been difficult to achieve. Ge whiskers [11,12] were once synthesized, but their diameter was larger, and their structure was not analyzed. Single crystal Ge quantum wires synthesized by organic solvothermal method [13] and laser ablation [14] were of cubic structure (with lattice constant: $a = 0.5656$ nm).

In this communication, we reported the synthesis of crystalline and amorphous Ge nanorods. The crystalline nanorods reveal a tetragonal structure, which is the high-pressure phase of germanium at 30°C under 25 kbar [15]. Amorphous Ge nanorods have not been reported so far. Crystalline and amorphous heterojunction in the nanorod was observed, which may be used in optoelectronic nanodevice.

2. Experimental

High-pure GeO_2 powders (Speciality products, Johnson Matthey Chemicals Ltd., England) were placed at the center of conventional horizontal furnace with a quartz tube and reduced into Ge powders at 700°C for 2 h in flowing hydrogen atmosphere. The Ge powders were placed in alumina crucible, and then an alumina ceramic plate was placed on top of the crucible. Finally, the crucible was pushed into the hot zone inside the quartz tube. As Ge powders were calcined at 1050°C in flowing Ar (40 ml min^{-1})/H_2 (80 ml min^{-1}) atmospheres for 2.5 h, a black product was deposited on the alumina plate. The sample structure was analyzed by X-ray diffractometer (XRD, Philips PW 1700) with Ni-filtered Cu Kα radiation, transmission electronic microscopy (TEM, JEM-200CX), and high-resolution electronic microscopy (HREM, JEOL-2010). The chemical components of the nanorods were estimated by OXFORD-6498 energy dispersive X-ray spectrometer attached HREM.

3. Results and discussion

Fig. 1 shows the XRD pattern of the products. It was identified as a mixture of tetragonal lattice unit cell dimensions of constants: $a = 0.593$ nm, $c = 0.698$ nm (ASTM card: 18–549), and a cubic unit cell with $a = 0.5656$ nm (ASTM card: 4–545) Ge. The tetragonal structure reveals (0 0 3) and (0 0 2) peaks, compared with the bulk material. Fig. 2 indicates the coexistence of nanorods and nanocrystallites. The nanorods have a diameter ranging from 20 to 200 nm and lengths up to 5 μm. Fig. 3(a) shows the morphology of single nanorods. Selected area electronic diffraction

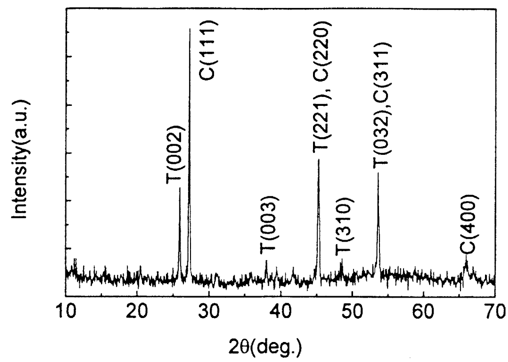

Fig. 1. XRD pattern of Ge nanorods.

(SAED) pattern of the single nanorod, shown as an inset in Fig. 3(a), can be indexed on the basis of a tetragonal structure of Ge along $(\bar{1}\,0\,1)$ direction, which is consistent with the XRD results. This further confirms that the nanorods growth direction is (1 1 1). HREM image in Fig. 3(b) reveals the (2 0 1) lattice fringe of the single crystalline nanorods, whose spacing is 0.275 nm. Fig. 4 shows amorphous Ge nanorods, which was also confirmed by SAED (inset) and EDX quantitative micro-anlysis. However, the lattice fringe image of the amorphous nanorod cannot yet be observed by HREM. As shown in Fig. 3(a), crystalline and amorphous heterojunctions appear on the nanorod. There seems to be a eutectic droplet at the end of the

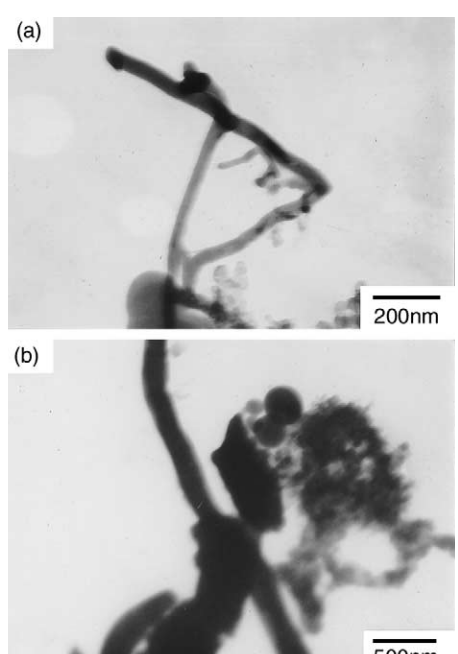

Fig. 2. TEM image of Ge nanorods.

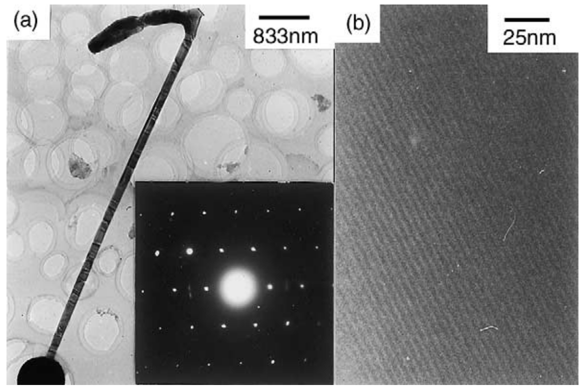

Fig. 3. (a) A magnified and SAED pattern (inset) along ($\bar{1}$ 0 1) direction; (b) lattice fringe image (HREM) of single crystal Ge (high-pressure phase) nanorods.

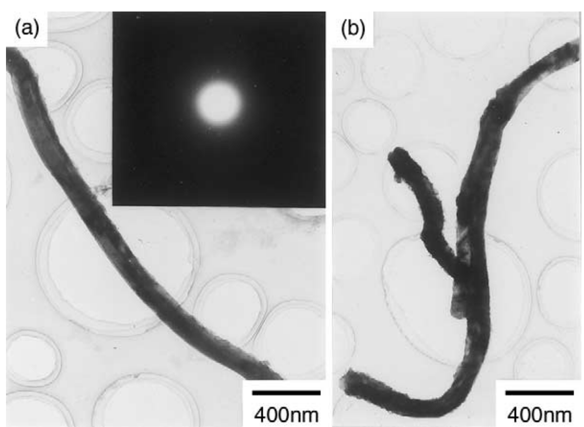

Fig. 4. TEM image and SAED (inset) pattern of a single amorphous Ge nanorod.

nanorod (in Fig. 3a), indicating that the growth process follows vapor–liquid–solid (VLS) mechanism [16].

4. Conclusions

Crystalline (high-pressure phase) and amorphous Ge nanorods have been successfully synthesized by physical-vapor-deposition (PVD) of Ge. One-dimensional heterojunctions are formed during the growth process of the nanorods, which may find its applications in optoelectronic nanodevices.

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