O U R N A L O F

Ceramic Processing Research

Fabrication, structure, and photoluminescence of GeO₂/ZnO core-shell nanorods

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We have fabricated GeO_2 -core/ZnO-shell nanorods using the atomic layer deposition technique to shell-coat the GeO_2 nanorods. The samples were characterized by scanning electron microscopy, X-ray diffraction, transmission electron microscopy, energy-dispersive X-ray spectroscopy, and photoluminescence spectroscopy (PL). The coated product showed a rod-like morphology, in which the shell layer comprised a hexagonal ZnO phase. PL measurement of GeO_2 -core/ZnO-shell nanorods exhibited emissions from the ZnO shell layer, in addition to those form the GeO_2 -core nanorods.

Key words: Nanostructures, ZnO, GeO₂.

Introduction

There have been a variety of nanostructures for application to nanodevices [1-20]. Among them, onedimensional (1D) materials have been the focus of intensive recent studies because of their wide application in electronics, optics, and mechanics [21,22]. Since the formation of heterostructures is believed to be of importance in tailoring optical, electronic, electrical, magnetic, and chemical properties of two-dimensional thin-film structures, the heterostructure formation in 1D nanostructures is equally important for their potential applications. Not only does a protective shell made of thermally and chemically stable materials on core nanorods enhance their performance, but also nanoscaled devices with a variety of functions may be realized by combining different types of nanosructures.

Germanium dioxide (GeO_2) is one of the dielectric oxides that are promising for optical devices such as optical waveguides for integrated optical systems [23]. GeO₂ is a luminescent material, and germanium oxidebased glass is thought to be more refractive than the corresponding silicate glass so that the GeO₂ 1D nanostructures may be used for nanoconnections in future optoelectronic communication devices. On the other hand, zinc oxide (ZnO) is one of the most remarkable materials, for it has the large band gap of 3.3 eV as well as a free exciton energy of 60 meV at room temperature [24]. Owing to its versatile physical properties, ZnO presents substantial interest for practical applications such as in transparent electrode [25], light emitting diodes [26], ultraviolet lasers [27], piezoelectric devices [28], acoustic devices, solar cells, and gas

sensors [29].

In this paper, for the first time we have synthesized GeO₂/ZnO core-shell nanorods and investigated their structural and photoluminescence (PL) properties. Since both GeO₂ and ZnO are important oxides for industrial application and of scientific interests with the shell layers being deposited with a well-controllable atomic layer deposition (ALD) process, this novel approach will be a step toward the potential applications of core-shell nanostructures. We expect that the formation of GeO₂/ZnO heterostructures may help to obtain tailored optical properties. In addition, by subsequent thermal annealing, we are able to obtain Zn_2GeO_4 compounds or Ge-doped ZnO, which are supposed to have useful properties [30,31]. In spite of their technological and scientific significance, there are few reports on coaxial nanostructures with ZnO shell layers, such as SnO₂/ZnO [32] and Zn/ZnO [33] core/ shell structures. Furthermore, to our knowledge, there has been no report on GeO₂-cored core-shell nanostructures.

Experimental

A two-step process was used to fabricate the coreshell structures. First, GeO₂ nanorods were synthesized by heating Ge powders in a tube furnace [34]. 99.9%pure Ge powders and the Au-coated Si substrates, respectively, were placed on the lower and the upper holder in the center of the quartz tube furnace. The reaction was carried out at 900 °C for 1 h in a flow of nitrogen (N₂) gas. The gas flow rate of N₂ was 2 standard litre per minute (slm). Subsequently, we have carried out the ZnO coating experiments on the asgrown GeO₂ samples using the ALD technique. A schematic diagram of the deposition system was previously outlined [35]. Diethylzinc (DEZn) and H₂O were kept in bubblers at 10 °C. The number of ALD cycles was set to 50, in which one cycle for the ZnO

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Fig. 1. XRD pattern of (a) uncoated and (b) ZnO-coated products.



Fig. 2. (a) SEM image of the ZnO-coated product. (b) Enlarged SEM image of coated nanorods.

deposition was composed of DEZn dosing, Ar purging, H_2O dosing, and Ar purging. The substrate temperature and pressure in the chamber were set to 150 °C and 0.3 Torr (40 Pa), respectively.

The samples were observed and analyzed using glancing angle (0.5 °) X-ray diffraction (XRD, X'pert MPD-Philips with CuK \dot{a}_1 radiation) with a contribution from the substrate minimized, scanning electron



Fig. 3. (a) TEM image of a single ZnO-coated nanorod. (b) TEM image taken in the area enclosed by the dotted box in (a). (c) Associated SAED pattern. (d) TEM image of a single uncoated GeO_2 nanorod.

microscopy (SEM, Hitachi S-4200), and transmission electron microscopy (TEM, Philips CM-200) with an energy-dispersive X-ray (EDX) spectroscope attached. The TEM samples were prepared by ultrasonically dispersing the product in acetone and a drop of the dispersion solution was then placed on a holey carbon film supported on a copper (Cu) microgrid. PL was conducted at room temperature in a SPEC-1403 photoluminescence spectrometer with the 325 nm line from a He-Cd laser (Kimon, 1K, Japan).

Results and Discussion

Figure 1(a) displays the XRD spectrum of the uncoated product. All sharp peaks can be clearly determined as from the hexagonal GeO₂ structure with lattice constants of a = 4.985 Å and c = 5.648 Å (JCPDS File No. 43-1016). No reflection peaks from impurity phases, such as unreacted Ge or other germanium oxides, were observed, indicating the high purity of the product. Figure 1(b) shows the XRD spectrum of the ZnO-coated product. While some diffraction peaks correspond to the hexagonal GeO₂ structure, other lines are found to coincide with the (100), (002), (101), (102), (110), (103), (112), and (201) peaks of the ZnO hexagonal lattice, which are in agreement with JCPDS file No. 05-0664. By comparing Figure 1(b) with Figure 1(a), we reveal that the coating structure comprised a crystalline ZnO phase.

Figure 2(a) shows a typical SEM image, indicating that the coated product consists of a large quantity of 1D structures. Furthermore, statistical analysis of many



Fig. 4. (a) TEM image of a coated nanorod and corresponding elemental maps of (b) Ge and (c) Zn. (d) EDX spectrum taken from the region A in (a).

SEM images revealed that the coated 1D structures had average diameters in the range of 50-250 nm. It is noteworthy that the nanorods have a slightly rough surface, as shown in Figure 2(b). Figure 3(a) shows a TEM image of a single coated nanorod. The coated nanorod shows a straight-line morphology with a not perfectly smooth surface, agreeing with the SEM data. Figure 3(b) is a lattice-resolved high-resolution TEM (HRTEM) image enlarging an area enclosed by a dotted square in Figure 3(a). The observed lattice fringe spacing is about 0.25 nm, which belongs to the (101) plane of hexagonal ZnO. Figure 3(c) represents an associated selected area electron diffraction (SAED) pattern taken from the shell region. The pattern shows weak diffraction rings, suggesting that the shell contains a crystalline phase. The diffuse rings from inside to outside belong to (100), (101), (110), and (112)planes of hexagonal ZnO, respectively. Accordingly, Figures 3(b) and 3(c) coincidentally reveal that the shell of the coated nanorod is poly-crystalline. Figure 3(d) shows a TEM image of an uncoated GeO₂ nanorod, indicating that the uncoated nanorod has a smoother surface than the coated one.

Figure 4(a) shows a TEM image of a coated nanorod and Figures 4(b) and 4(c) correspond to the elemental maps of Ge and Zn, respectively. The bright areas indicate a high concentration of these elements. By comparing Figure 4(b) with Figure 4(a), we reveal that the Ge is mainly concentrated in the core region of the nanorod. Similarly, Figure 4(c) indicates that the Zn mainly resides in the shell region. Accordingly, the Ge and Zn elemental maps are in good agreement with what can be expected for the ZnO-coated GeO₂ nanorods. An EDX spectrum taken from region A in Figure 4(a) indicates that the coated nanorod consist of Ge, Zn, and O, whereas the C and Cu signals were generated from the microgrid mesh supporting the



Fig. 5. PL spectra of (a) uncoated and (b) ZnO-coated GeO_2 nanorods. The light source was the 325 nm-wavelength line from a He-Cd laser.

nanorods (Figure 4(d)).

In the present study, no metal nanoparticles were observed at the tips of the core nanorods (Figure 3(d)). Hence, the growth of the GeO₂ structure in the present route must be dominated by a vapor-solid mechanism. It is generally agreed that the GeO₂ forms in the initial stage of oxidation of Ge vapor and that the GeO₂ further reacts with Ge vapor to form GeO. The GeO vapor (GeO sublimes at 710 °C) is driven by the flowing gas and is deposited on the substrates. The nuclei further grow, being oxidized to form GeO₂ nanorods. We believe that oxygen in the GeO_2 has been mainly come from the air leakage or the residual oxygen in the N_2 gas. Subsequently, for the ALD growth, DEZn and H₂O were alternately fed into the chamber with a time period of purging the reactants to deposit the ZnO shell layers on the GeO₂ nanorods. Since most the of coated nanorods have a uniform diameter along the length direction, we realize that a uniform coating of the shell layer has been attained. However, coated nanorods were found to have a rougher surface than uncoated ones (Figures 3(a) and 3(d)). Although surface roughness may be attributed to uneven (i.e., island-type or three-dimensional) growth, possibly because a homogeneous distribution of the active species was not attained throughout the surface area in the ALD process, a further systematic investigation is underway.

The PL spectrum of GeO₂ nanorods prior to the ZnO coating is shown in Figure 5(a). Gaussian fitting analysis showed that the broad emission band was a superimposition of two major peaks at 423 nm and 490 nm, respectively. Similar blue-green emission and blue emission were observed in the PL spectra, respectively, from GeO₂ fibers prepared by an electrospinning method [36] and from GeO₂ nanorods fabricated by a carbothermal reduction reaction [37]. It has been suggested that blue and blue-green light emissions originated from radiative recombination in regard to defects in GeO₂, including oxygen vacancies and oxygen-germanium vacancy centers. In the present study, GeO₂ nanorods were synthesized at a high temperature (900 °C), so that oxygen vacancies and oxygen-germanium vacancy pairs easily exist in the product. Therefore, the broad PL peak from the core GeO₂ nanorod is mainly attributed to the abovementioned radiative recombination.

Figure 5(b) shows the PL spectrum of ZnO-coated GeO₂ nanorods. The best fit of the emission was obtained with four Gaussian functions, which are centered at 378, 422, 494, and 549 nm, respectively. While the two peaks at 422 nm and 494 nm evidently originated from the GeO₂ core nanorods, there exist two additional peaks: First, there exists an ultraviolet (UV) emission band peaked at an energy of 378 nm, which corresponds to the near band edge peak, resulting from an emission mechanism associated with excitons in ZnO [38, 39]; second, the broad green emission band centered at around 549 nm may also originate from ZnO [40], being known to be related to the emission from deep trapping sites from possible defects such as oxygen vacancies [38, 39, 41, 42]. Accordingly, we reveal that the PL emission of GeO₂core/ZnO-shell nanorods comprises emissions from the ZnO shell as well as those from the GeO2-core nanorods.

Conclusions

We reported the first fabrication of GeO_2 -core/ZnOshell nanostructures, in which the shell was made using an ALD method. While the XRD spectrum, a latticeresolved TEM image, and an SAED pattern reveal that the coating process generated a hexagonal ZnO phase, an SEM image indicates that the coated product consists of a large quantity of 1D structures. Elemental maps are in good agreement with what can be expected for the ZnO-coated GeO₂ nanorods. The ZnO coating significantly changes the shape of the PL spectrum. While blue and blue-green emissions are attributed to the GeO₂ core, UV and green emissions originate from the ZnO shell layers.

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