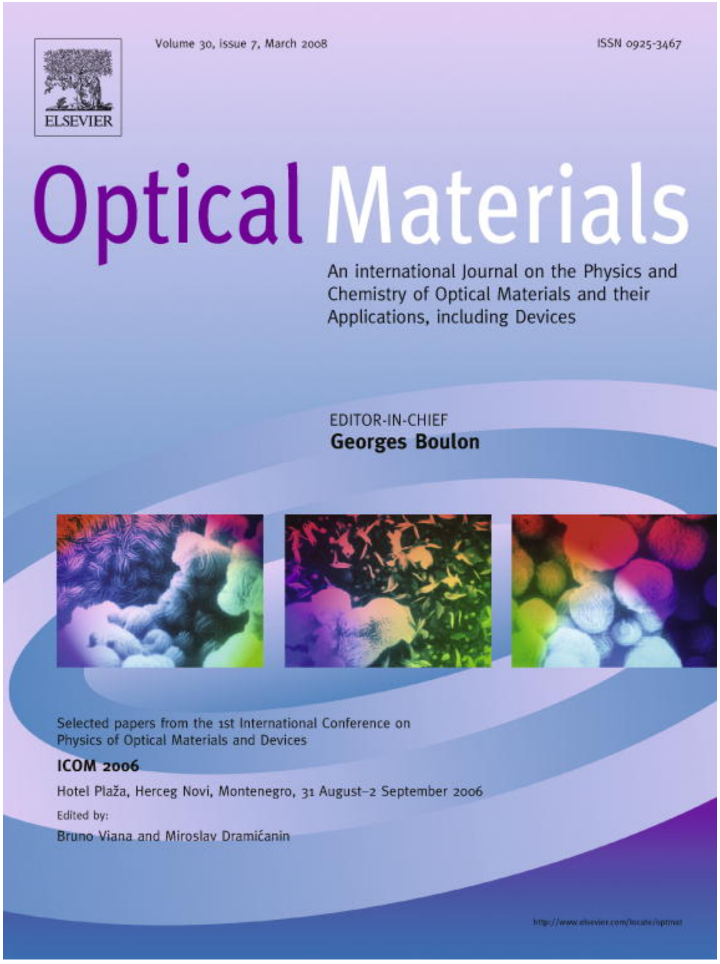
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ZnO-sheathed SiO_x nanowires: Annealing effect

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Abstract

This study reported the preparation of ZnO-coated SiO_x nanowires and investigated changes in the structural and photoluminescence (PL) characteristics resulting from application of a thermal annealing process. While X-ray diffraction (XRD) analysis revealed the annealing-induced transformation of ZnO to Zn_2SiO_4, transmission electron microscopy (TEM) observation suggested that shell layer tended to be transformed to nanoparticle-like structures by thermal annealing. Thermal annealing induced the changes in the shape of the PL emission spectrum.

Keywords: ZnO; Nanowires; Thermal annealing

1. Introduction

Since the discovery of carbon nanotubes [1], one-dimensional (1D) nanoscale materials have drawn much attention due to their peculiar and interesting physical properties and potential device applications [2–4]. Recently, coaxial nanocable-like 1D structures comprising different kinds of materials have been successfully synthesized for a variety of purposes. Notable applications include the fabrication of nanometer scale electronic devices with a variety of functions and the protection of 1D structures from contamination or oxidation [5–13]. Furthermore, as demand for fabricating special nanowire structures increases, development of a method not only for synthesizing a wide variety of nanowires but also for modifying or improving the properties of as-synthesized nanowires is becoming increasingly important.

Zinc oxide (ZnO) is of considerable interest because of its attractive optical functions based on the large binding energy of excitons and biexcitons (60 and 15 meV, respectively) as well as its multi-functional physical properties. Si and SiO_x nanostructures have attracted considerable attention due to their unique properties and promising application in mesoscopic research, nanodevices and opto-electronics devices [14–16]. Particularly, SiO_x is an important material for photoluminescence (PL) [17,18]. Therefore, the synthesis of SiO_x nanostructures is important not only for scientific interests but also for future industrial applications.

Although there have been some reports on the coaxial nanostructure comprising ZnO, including ZnO/SnO_2 [19] and SnO_2/ZnO [20] core/shell structures, to the best of our knowledge, there have been no reports on the synthesis of SiO_x/ZnO core–shell structures and on their annealing effects. In the present study, we coated ZnO on the surface of SiO_x nanowires in the course of preparing SiO_x/ZnO core/shell structures. Furthermore, we comparatively investigated the core/shell structures before and after thermal annealing, with respect to their structural and photoluminescence (PL) characteristics.

2. Experimental

The synthesis of SiO_x nanowires was carried out in a tube-furnace. We have employed Au (approximate

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thickness = 5 nm)-coated Si substrates. During the experiment, a constant pressure with an air flow (~2.1% O_2 in a balance of argon) was maintained at 200 m Torr. The substrate temperature was set to 1000 °C for 2 h. After the furnace was cooled naturally to room temperature, the substrates were removed from the furnace and then transferred to an atomic layer deposition (ALD) chamber. A schematic diagram of the ALD deposition system and the detailed experimental procedure, wherein diethylzinc (DEZn) and H_2O were used as Zn and O precursors, respectively, have been previously reported [21]. For the ALD growth, DEZn and H_2O were alternately fed into the chamber with the time period of purging the reactants for deposition of the ZnO outlayers on SiO_x nanowires. Following this, samples were subjected to thermal annealing in a quartz tube furnace at a temperature of 900 °C in N_2 ambient for 1 h (flow rate: 500 standard cm^3/min).

The core/shell structures were studied by X-ray diffraction (XRD) (Philips X'pert MRD diffractometer with Cu Kα radiation), field emission scanning electron microscopy (FE-SEM) (Hitachi, S-4200), and transmission electron microscopy (TEM) (Philips, CM-200) equipped with energy-dispersive X-ray spectroscopy (EDX). PL was conducted at room temperature with the 325 nm line from a He–Cd laser (Kimon, 1 K, Japan).

3. Results and discussion

Fig. 1 shows typical top-view SEM image of the as-synthesized core/shell structures prior to annealing, indicating that the product consists of 1D structures. A statistical analysis of numerous SEM images indicated that the average diameter of the 1D structures was in a range of 100–210 nm. Fig. 2a shows the XRD pattern of the as-synthesized core/shell structure. The θ–2θ scan data of deposits exhibit strong 2θ peaks at 38.18° and 44.39°, respectively, corresponding to (1 1 1) and (2 0 0) peaks from Au from the substrates (JCPDS File No. 04-0784). Although we suppose that the deposits are close to the amorphous phase due to the absence of a strong ZnO diffraction peak, a weak line is found to coincide with the (1 0 1) peak of the hexagonal structure of ZnO with lattice constants of $a = 3.249$ Å and $c = 5.205$ Å (JCPDS File No. 05-0664). In addition, it is noteworthy that a peak at around 39° can be clearly indexed to the (2 2 3) reflection of rhombohedral structure of Zn_2SiO_4 with lattice constants of $a = 13.94$ Å and $c = 9.309$ Å (JCPDS File No. 08-0492). We infer from XRD data that the deposits include a Zn_2SiO_4 phase, as well as a ZnO phase. Fig. 2b shows the XRD pattern of the annealed core/shell structure. We observe that peaks at around 31.5° and 34.0° are indexed to (1 1 3) and (4 1 0) reflections of rhombohedral Zn_2SiO_4. It is possible that considerable amount of ZnO has been transformed to Zn_2SiO_4 by thermal annealing.

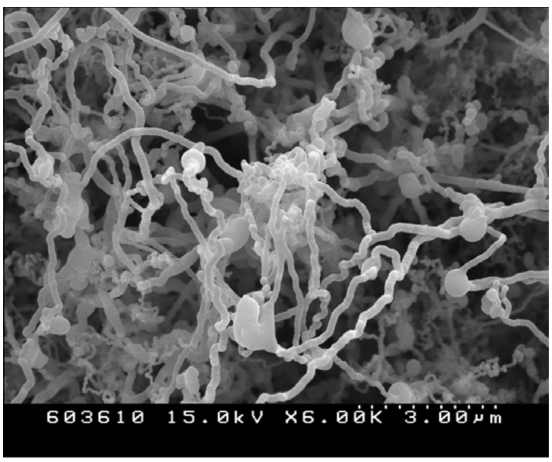

Fig. 1. SEM image of the core/shell structures.

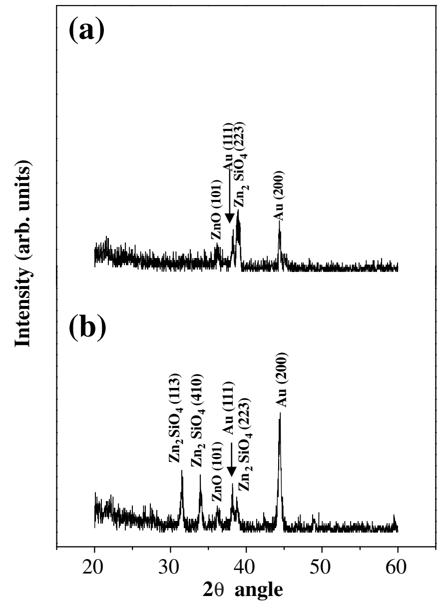

Fig. 2. XRD pattern of (a) as-synthesized and (b) annealed core/shell structures.

Fig. 3a shows a TEM image of an as-synthesized core/shell structure. As shown in the inset of Fig. 3a, the highly dispersed selected area electron diffraction (SAED) pattern indicates that the nanostructure is amorphous. An overlapping image of Si and Zn elemental maps is depicted in Fig. 3b. Green and blue points indicate high concentrations of Si and Zn elements, respectively. Si concentrates at the core region while Zn is clearly visible at the shell part, evidencing that the nanostructure is indeed a SiO_x/ZnO core–shell structure. On the other hand, Fig. 3c shows a TEM image of an annealed core/shell nanowire, indicating that there exists some nanoparticles (blackened region) in a size range of roughly 10–30 nm on the surface of the 1D structure. The inset shows an SAED pattern image taken at the area marked with the square in Fig. 3c. A halo presumably originating from the SiO_x core as well as a set of poly-crystalline electron diffraction spots corresponding to the shell layer can be seen in this image. By comparing Fig. 3c with Fig. 3a, we deduce that the as-deposited ZnO films have

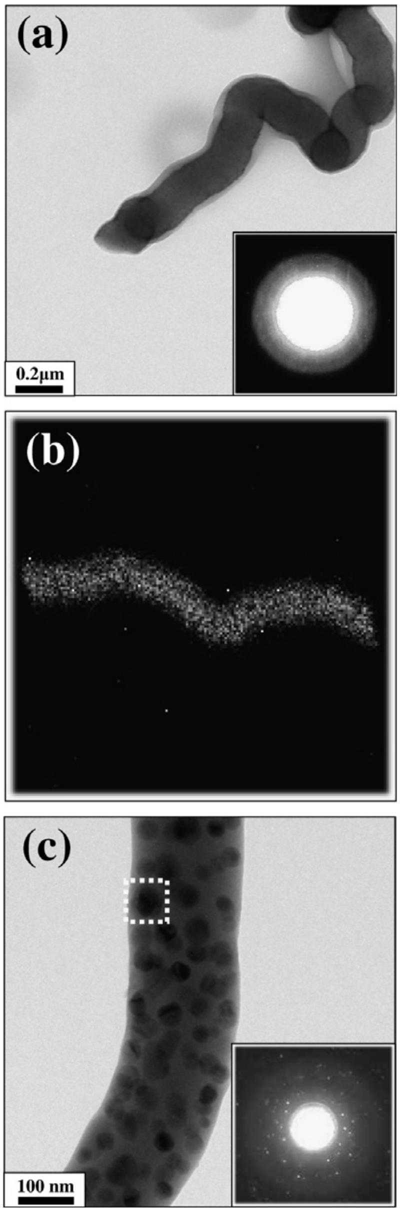

Fig. 3. (a) TEM image of an as-synthesized core/shell structure. The corresponding SAED pattern image is shown in the inset. (b) Overlapping image of elemental maps of Si (green points) and Zn (blue points) in an as-synthesized core/shell structure. (c) TEM image of an annealed core/shell structure (Inset: associated SAED pattern taken at the area marked with the square in Fig. 3c). (For interpretation of the references to colour in figure, the reader is referred to the web version of this article.)

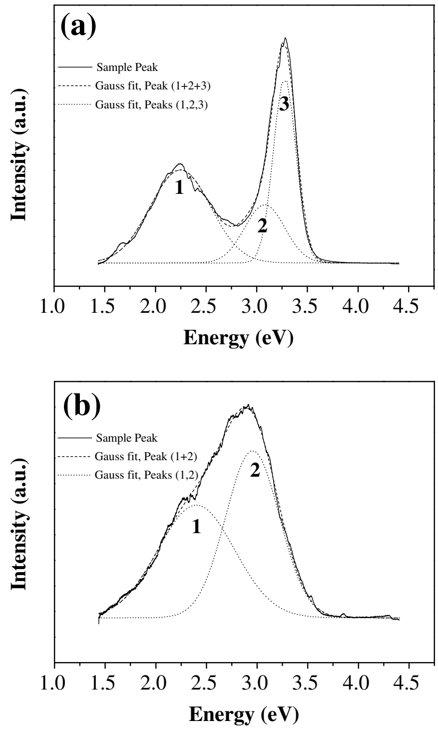

Fig. 4. PL spectrum of (a) as-synthesized and (b) annealed core/shell structures. The light source was the 325 nm-wavelength line from a He–Cd laser.

been transformed into nanoparticle-like structures as a result of thermal annealing.

Fig. 4a shows the PL emission spectrum of the as-synthesized core/shell structures upon photoexcitation at 3.82 eV. The overall feature exhibits a typical PL spectrum of ZnO nanowires reported previously [22,23] with a relatively sharp ultraviolet (UV) band in addition to a broad green emission one. In order to have more closer insights for the origin of emission, we have fitted the spectral feature with Gaussian functions. The best fit of the emission was obtained with three Gaussian functions, of which peaks are centered at 2.23, 3.04, and 3.27 eV, respectively. First, there exists a UV emission band peaked at an energy of 3.27 eV, which corresponds to the near band edge peak, resulting from the emission mechanism associated with excitons in ZnO [24,25]; second, the broad green emission band centered at around 2.23 eV may also originate from ZnO [26], being known to be related to the emission from deep trapping site by possible defects such as oxygen vacancies [22–25]. However, since a Zn_2SiO_4 XRD peak has been found in Fig. 2a and Zn_2SiO_4 is known to exhibit a green emission [27–30], there is a possibility that a Zn_2SiO_4-associated emission band has been overlapped in the broad emission peaked at 2.23 eV. The remaining peak at 3.04 eV deduced from the fitting procedure is supposed to be originated from the SiO_x core, presumably due to some intrinsic diamagnetic defect centers [31,32].

Fig. 4b shows the PL spectrum of the annealed core/shell structures, revealing that the PL spectrum is composed of two bands, peaking at about 2.27 and 2.90 eV, respectively. Being similar to the as-synthesized sample, the peak at 2.90 eV is attributed to the PL from the SiO_x core. The reduction of peak energy values by the thermal annealing may be ascribed to the formation of Si clusters in the SiO_x matrix [33]. It is noteworthy that the strong UV emission due to the presence of ZnO shell in the as-synthesized samples was suppressed after annealing process, with the SiO_x-related peak being greatly intensified. We surmise that the relative intensification of SiO_x-related peak is associated with partial exposure of the SiO_x on the surface of the annealed core/shell structure, as shown in Fig. 3c. PL spectrum of ZnO is known to consist of a UV emission band and a broad visible emission band, whereas that of Zn_2SiO_4 only reveals a green emission [27–30]. Therefore, it is possible that the suppression of the UV emission is related to the reduction of ZnO on the shell layer by the annealing-induced transformation of ZnO to Zn_2SiO_4. However, with the assumption that 2.27 eV-peak and/or 2.90 eV-peak being ZnO-originated, the other weak possibility is that the visible emission peak originated to the radiative recombination at the oxygen vacancy gains its intensity after annealing under oxygen-free condition, compared to that of UV emission from the free excitons photogenerated in ZnO shell. Although further detailed study is necessary, this result will contribute to the potential applications of coaxial 1D nanostructures to optoelectronic devices.

4. Conclusions

In summary, we have investigated the effect of thermal annealing on the structural and optical properties of core SiO_x/shell ZnO 1D structures. We employed XRD, SEM, TEM, and PL spectroscopy to characterize the samples. Thermal annealing helps the transformation of shell layer, not only generating the nanoparticle-like structures on the nanowire surface but also generating Zn_2SiO_4 phase. The overall shape of the PL spectrum has been significantly changed by the thermal annealing. This study will give an insight into the annealing studies regarding various coaxial 1D materials.

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