Enhancement in the photoluminescence of ZnS nanowires by TiO_2 coating and thermal annealing

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ABSTRACT

Influences of the TiO_2 coating and thermal annealing on the photoluminescence (PL) properties of ZnS nanowires were investigated. ZnS nanowires were synthesized by thermal evaporation of ZnS powder and then coated with TiO_2 by using the sputtering technique. The PL emission of ZnS nanowires can be significantly enhanced without nearly changing the wavelength of the emission by coating them with a TiO_2 layer with an appropriate thickness and then annealing them in an Ar atmosphere. The optimum TiO_2 coating layer thickness for the highest PL emission enhancement was found to be about 6.5 nm. The PL emission of the ZnS-core/TiO_2-shell coaxial nanowires is degraded by annealing in an oxygen atmosphere whereas it is enhanced by annealing in an argon atmosphere.

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1. Introduction

Zinc Sulfide (ZnS) is an important II–VI semiconductor with a wide direct band gap (3.7 eV) at room temperature having received significant attention over the past few decades. ZnS has potential applications in flat panel displays, infrared windows, ultraviolet light-emitting diodes and injection lasers, phosphors in cathode-ray tubes, electroluminescent thin film devices, and sensors owing to its intense luminescence, high refractive index, and high transmittance properties in the visible range [1,2]. ZnS is also promising for room temperature exciton devices because of the large exciton binding energy (38 meV) in comparison with room temperature thermal energy (25 meV) [3].

The core/shell 1-D nanostructures may realize various tailor-made functions by assembling different features of both nanowires (cores) and nanotubes (shells) with different compositions in the radial direction [4]. To make core/shell coaxial 1-D nanostructures by coating ZnS nanowires with another material can modify or improve the properties of the as-synthesized ZnS nanowires. For example, the intensity and the wavelength of the photoluminescence (PL) emission of the ZnS nanowires can be enhanced and shifted, respectively, by TiO_2 coating.

Various visible PL emission bands of ZnS nanostructures have been reported before [5–13]. These emission bands can largely be classified into five different kinds in terms of the

wavelength range or the mechanism of the emission: a near-band edge (NBE) emission band in the range of 320–370 nm, a violet emission band in the range of 390–400 nm, a blue emission band in the range of 430–470 nm, a green emission band in the range of 510–550 nm, and an orange emission band at 640 nm. The NBE emission is known to originate from band to band transitions since the band gap of ZnS (3.66 eV) corresponds to 330 nm [5]. The mechanism of the emission could be due to the quantum size effect [6]. The violet emission has been reported to originate from deep levels like sulfur vacancies and interstitial lattice defects [7]. The blue emission is known to be associated with the trapped luminescence arising from surface states [5–9]. The green emission is attributed to dopants or impurity atoms, i.e. transitions from the conduction band of ZnS to the different levels of excited impurity atoms in the ZnS band gap [10,11]. On the other hand, the orange emission has also been reported to be due to deep levels [8].

On the other hand, three kinds of PL emissions of anatase TiO_2 nanostructures have been reported [14–23]: a violet emission band centered at in the wavelength range of 410–420 nm, a blue emission band in the range of 460–500 nm, and a green emission band in the range of 510–550 nm. Besides these, an orange emission band centered at 650 nm has been reported for Pr^{3+}-doped TiO_2 incorporated in silica matrix [24]. The violet emission is known to be attributed to self-trapped excitons localized on TiO_6 octahedra [14,15], while the blue emission originates from oxygen (O) vacancies [15,16] or surface states [17,18]. The green emission has been reported to be associated with impurities, O vacancies, or F^+ color centers on the surface of TiO_2 nanowires

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[19,20]. The orange emission band is associated to $3P_0 \rightarrow 3F_2$ transitions [24].

In this paper, we report influences of the TiO_2 coating and thermal annealing on the PL properties of ZnS nanowires synthesized by thermal evaporation of ZnS powders. We investigated the influences of the TiO_2 coating layer thickness and the thermal annealing atmosphere on the photoluminescence properties of ZnS nanowires and determined the optimum TiO_2 layer thickness for the highest PL emission intensity. The mechanism of the PL enhancement by TiO_2 coating is also discussed. Actually we tried to coat ZnS nanowires with various kinds of semiconducting materials to enhance the PL properties and found that TiO_2 was the most effective among the coating materials that we used for this purpose. Hence, we chose TiO_2 as a material to coat the ZnS nanowires with in this work. In particular, we used oxide semiconductors for this purpose in the hope that the coatings would also prevent oxidation and contamination as well as reduce surface state density abundant at the surface of ZnS nanowires. Therefore, the possible applications of the ZnS-core/TiO_2-shell nanowires may be basically the same as ZnS nanowires, i.e. fabrication of optoelecronic and electronic devices. However, we believe that ZnS-core/TiO_2-shell nanowires have optical properties and reliability superior to ZnS nanowires as follows: (1) higher PL emission intensity and (2) lower contamination, native oxides, and surface state density.

2. Experimental details

ZnS-core/TiO_2-shell coaxial nanowires were prepared by using a two-step process: thermal evaporation of ZnS powders and sputter-deposition of TiO_2. First, ZnS nanowires were synthesized on the gold (Au)-coated silicon (100) substrate by thermal evaporation of ZnS powders in a two-heating zone-tube furnace. Details of the synthesis process of ZnS nanowires are described elsewhere [25]. Subsequently, ZnS/TiO_2 coaxial nanowire samples with different TiO_2 layer thicknesses were prepared by sputter-deposition of TiO_2 thin films on the ZnS nanowire samples in a direct current (dc) magnetron sputtering system for 2–20 min at room temperature. After the vacuum chamber was evacuated to 1×10^{-6} mbar using a turbomolecular pump backed by a rotary pump. Depositions were carried out at a system pressure of 2×10^{-2} mbar and a dc power of 100 W in an argon (Ar) atmosphere. The Ar gas flow rate was 30 standard cubic centimeters per minute (sccm). Subsequently, the prepared ZnS/TiO_2 coaxial nanowire samples were annealed at 700 °C for 30 min in an Ar or oxygen (O_2) atmosphere. Next, the morphologies of the nanowires were analyzed by using transmission electron microscopy (TEM, Philips CM-200). The compositional analysis was done by using energy-dispersive X-ray (EDX) spectrometer installed in the TEM. The PL measurement was carried out at room temperature using a He–Cd laser line of 325 nm (Kimon, 1K, Japan) as the excitation source.

3. Results and discussion

The PL spectra of the ZnS-core/TiO_2-shell coaxial nanowires annealed in Ar and O_2 atmospheres are displayed in Fig. 1 along with the as-synthesized (unannealed) coaxial nanowires. The sputtering time for the TiO_2-shell layer in the coaxial nanowire samples was 8 min, which corresponds to about 6.5 nm as can be seen in the TEM image of Fig. 2. A strong emission band centered at around 515 nm and two very weak violet emission bands
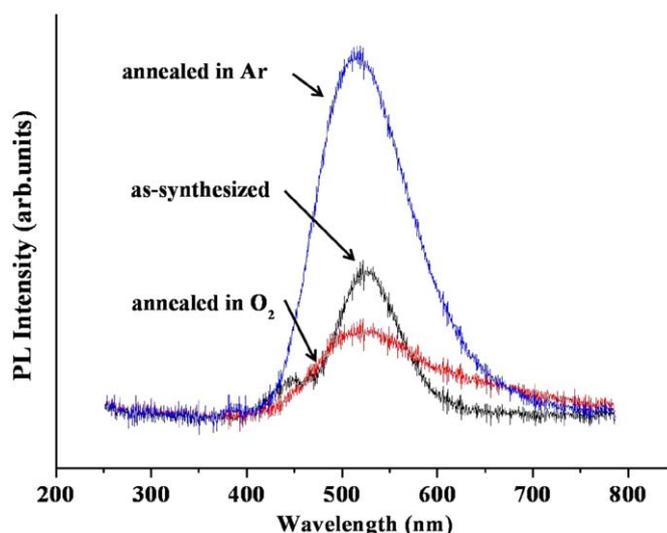

Fig. 1. PL spectra of ZnS-core/TiO_2-shell coaxial nanowires annealed at 700 °C for 30 min in Ar and O_2 atmospheres along with as-synthesized ZnS-core/TiO_2-shell coaxial nanowires.
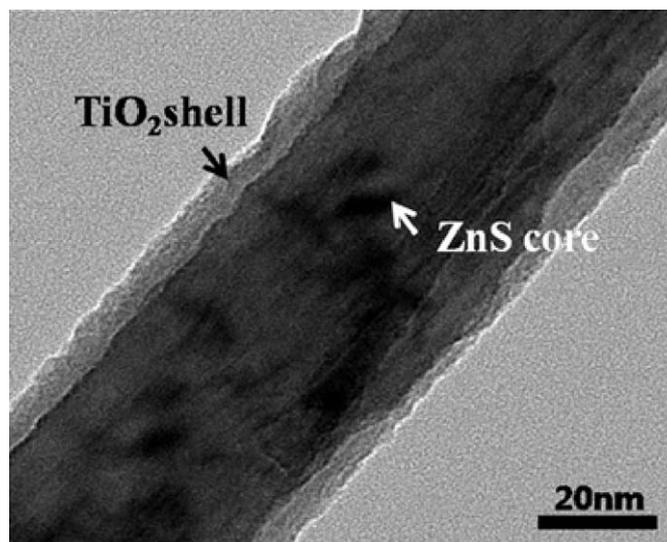

Fig. 2. High-magnification TEM image of a ZnS-core/TiO_2-shell coaxial nanowire.

centered at around 390 and 450 nm are observed on these spectra. The PL emission of the coaxial nanowires is enhanced by annealing in an Ar atmosphere whereas degraded by annealing in an O_2 atmosphere. It is well known that the PL emission is generally enhanced by thermal annealing since the thermal energy excites the atoms in the lattice to facilitate formation of point defects. In addition to the generation of point defects, interdiffusion of ZnS and TiO_2 between the core and the shell occurs during annealing in an Ar atmosphere, leading to an increase in the concentrations of Ti and O impurities in the ZnS cores and the concentrations of Zn and S impurities in the TiO_2 shells. Fig. 3a and b respectively present the EDX concentration profiles of Zn, S, O, and Ti along the line drawing across the diameter in a typical ZnS-core/TiO_2-shell coaxial nanowire before and after annealing as shown in the TEM images. A careful comparison of the O concentration profiles before and after annealing clearly indicates that the O and Ti concentrations in the ZnS-core region have been increased, which is a good evidence of the interdiffusion. Besides the interdiffusion, migration of the Au
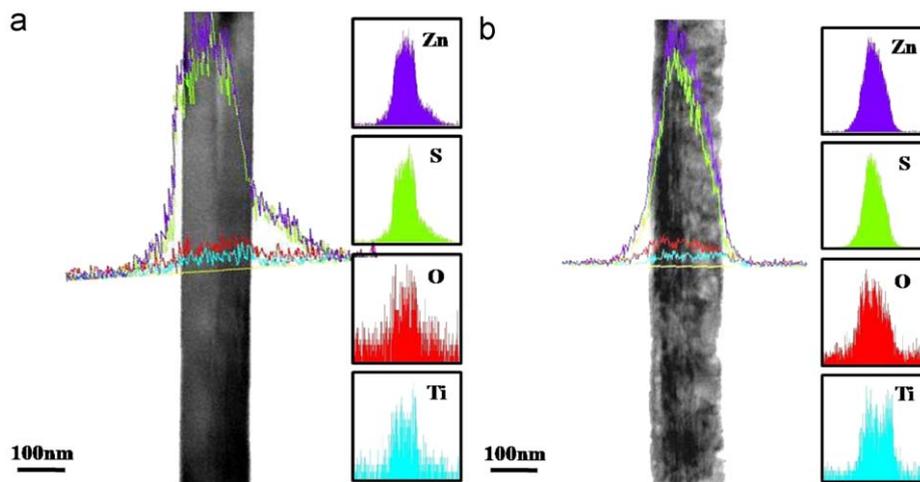
Fig. 3. EDX concentration profiles of Zn, S, O, Ti along the line drawing across the diameter in a typical ZnS-core/TiO$_2$-shell coaxial nanowire (a) before and (b) after annealing at 700 °C for 30 min in an Ar atmosphere.
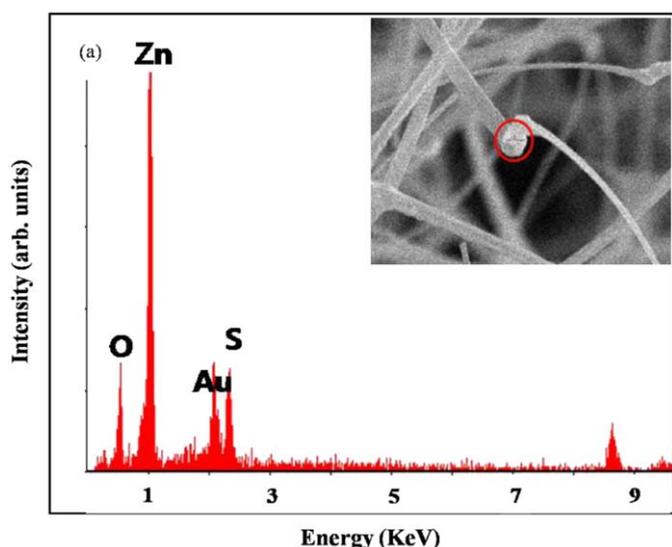

Fig. 4. EDX spectra of the particle, marked "circle" in the inset, at the tip of a typical ZnS-core/TiO$_2$-shell coaxial nanowire. The inset is the SEM image of the coaxial nanowires.

Fig. 5. PL spectra of ZnS-core/TiO$_2$-shell coaxial nanowires with different sputter-deposition times for TiO$_2$ coating, i.e. different TiO$_2$-shell layer thicknesses. All the coaxial nanowire samples were annealed at 700 °C for 30 min in an Ar atmosphere prior to the PL measurement. The inset shows the peak intensity ratio, I/I_0 as a function of the TiO$_2$ sputtering time, where I and I_0 represent the emission peak intensities of TiO$_{2-}$ coated and uncoated ZnS nanowires, respectively.

atoms in the particle at the tip of each nanowire along the length direction of the nanowire can occur during the annealing process, resulting in the increase in the concentration of the Au impurity in the ZnS core. The EDX spectra in Fig. 4 indicate existence of Au in the particle at the tip of a ZnS-core/TiO$_2$-shell coaxial nanowire, which suggests that the ZnS nanowires were grown by vapor-liquid-solid (VLS) mechanism. Hence, enhancement in the green emission during annealing in an Ar atmosphere is caused by the increase in the concentration of metallic impurities such as Ti and Au in the ZnS core, which is in a good agreement with the previous reports [10,11] on the origin of the green emission from ZnS nanowires.

On the other hand, regarding the cause of the degradation of the PL emission by annealing in an O$_2$ atmosphere, further detailed investigation is necessary, but we surmise at the moment as follows: During O$_2$ annealing the O atoms migrate from the annealing atmosphere or the TiO$_2$ shell into the ZnS core and then make bonds with Zn and Ti interstitials leading to a decrease in the concentration of deep levels such as Zn and Ti interstitials in the ZnS-core region. Hence, the green emission is degraded by O$_2$
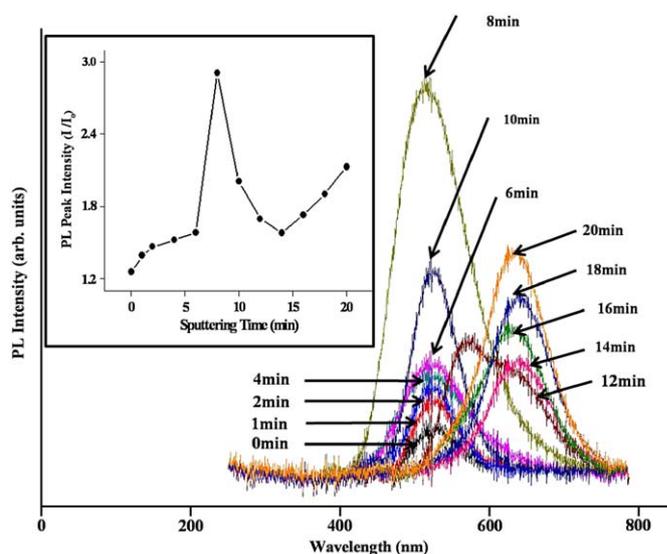
annealing. Zn interstitial have formed penetration of Ti atoms into the ZnS core during the TiO$_2$ sputter-deposition process,

Fig. 5 shows the influence of the TiO$_2$-shell layer thickness on the PL properties of ZnS-core/TiO$_2$-shell coaxial nanowires. All the nanowire samples have been annealed at 700 °C in an Ar atmosphere for 30 min before the PL measurement. The green emission intensity tends to increase as the TiO$_2$ sputtering time increases up to the sputter time of 8 min and then to decrease with further increases in the sputtering time. In other words, the strongest green emission can be obtained by coating ZnS nanowires with TiO$_2$ thin films 6.5 nm thick (corresponding to the TiO$_2$ sputtering time of 8 min) as clearly shown in the inset of Fig. 5. As written earlier, interdiffusion of ZnS and TiO$_2$ occurs during the thermal annealing process. The increase in the TiO$_2$-shell layer thickness seems to make two opposite effects: (1) a PL enhancing effect: to provide the coaxial nanowires with more source for Ti atoms, i.e. more metallic impurities to

diffuse into the ZnS-core region during annealing and (2) a PL degrading effect: to absorb more light emitted from the ZnS cores. Consequently, the net PL enhancing effect ((1)–(2)) is maximized for the sputtering time of 8 min, so that the green emission with the highest emission intensity is obtained for 8 min. An increase in the sputtering time from 8 to 10 min leads to a decrease in the emission intensity and further increases in the sputtering time lead to a red shift of the emission to the wavelength characteristic of TiO_2. For the TiO_2 sputtering time of 12 min, the PL spectrum has a transitional shape characteristic of both ZnS and TiO_2, i.e. displays two emission bands centered at 570 and 650 nm. For the TiO_2 sputtering times longer than 12 min only an orange emission at 650 nm is observed and its intensity increases as the TiO_2-shell layer thickness increases further. As regards the emission band at 650 nm, there are two reports: one is on that of ZnS [8] and the other on that of Pr^{3+}- doped TiO_2 incorporated in silica matrix [24], yet the orange emission in our nanowire samples seems to have an origin different from either of the two. The rapid increase in the emission intensity with an increase in the TiO_2-shell layer thickness suggests that the emission at 650 nm does not originate from deep levels in the ZnS cores but from the deep levels like Zn and S dopants generated in the TiO_2 shells by annealing.

4. Conclusions

In summary, influences of the TiO_2-shell layer thickness and thermal annealing on the photoluminescence properties of ZnS-core/TiO_2-shell coaxial nanowires were investigated. The PL emission of the coaxial nanowires is enhanced by annealing in an Ar atmosphere whereas degraded by annealing in an O_2 atmosphere. The PL emission enhancement by thermal annealing in an Ar atmosphere is mainly attributed to increase in the metallic impurities such as Ti and Au in the cores by the interdiffusion of ZnS and TiO_2 across the interface of the core and the shell and diffusion of Au from the particle at the tip of each ZnS-core/TiO_2-shell coaxial nanowire along the length direction of the nanowire. PL measurement at room temperature shows that the PL emission intensity of ZnS nanowires can be significantly increased without nearly changing the wavelength of the emission by coating them with a TiO_2 layer with an appropriate thickness and then annealing them in an Ar atmosphere. The optimum TiO_2-shell layer thickness for the highest PL emission enhancement was found to be about 6.5 nm. Further increases in the TiO_2 layer thickness, however, lead to decreases in the emission intensity as well as the red shift of the emission to the wavelength characteristic of TiO_2.

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