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The photoluminescence properties of TiO_2-sheathed ZnSe nanowires

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ABSTRACT

ZnSe nanowires have been synthesized by thermal evaporation of ZnSe powders on gold-coated Al_2O_3(0 0 0 1) substrates and then sheathed with TiO_2 by sputtering. Our results show that sheathing Zn nanowires with thin TiO_2 layers can significantly enhance the photoluminescence (PL) emission intensity. XPS analysis results suggest that the PL enhancement is attributed to increases in the concentrations of deep levels such as oxygen and titanium interstitials as well as the density of interface states. The PL emission of ZnSe nanowires is also enhanced by thermal annealing. Annealing in an argon atmosphere is more efficient in enhancing the PL emission than annealing in an oxygen atmosphere.

1. Introduction

ZnSe is a wide direct band gap compound semiconductor which has received much attention for their potential applications in optoelectronics and electronics. ZnSe is particularly suitable for applications for blue-green laser diodes [1] and tunable mid-IR laser sources for remote sensing [2]. Recently one-dimensional (1D) nanostructures of ZnSe such as nanowires, nanorods, nanobelts, nanoribbons, and nanoneedles, have been synthesized using various techniques including thermal evaporation [3], metal-organic chemical vapor deposition (MOCVD) [4], molecular beam epitaxy (MBE) [5], pulsed lased deposition (PLD) [6], and atomic layer deposition (ALD) [7].

We can give nanowires various functions that can be used effectively for nanoscale electronic or optoelectronic devices by making coaxial nanowires [8]. Furthermore, as demand for fabricating special one-dimensional nanostructures increases, development of methods 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. For example, the PL emission intensity of the light emitted from coaxial nanowire structures can be significantly increased or the wavelength of the emission can be controlled by selecting a proper coating material and a proper coating layer thickness.

The photoluminescence properties of ZnSe nanowires have been reported recently by many researchers. The optical properties of anatase TiO_2 materials have also been widely investigated because of its key role in the injection process of a photochemical solar cell with high conversion efficiency [9]. Anatase TiO_2 nanowires have been intensively synthesized for the same reason. However, there has been no report on the synthesis or the PL properties of ZnSe/TiO_2 coaxial nanowires yet. In this paper, we report on the influence of TiO_2 coating and thermal annealing on the PL emission of the ZnSe nanowires.

2. Experimental procedure

We prepared ZnSe/TiO_2 coaxial nanowires on Al_2O_3(0 0 0 1) substrates to investigate influence of TiO_2 sheathing and thermal annealing on their PL properties. Firstly, ZnSe nanowires were synthesized on 3 nm gold (Au) layer-coated c-plane sapphire (Al_2O_3(0 0 0 1)) substrates by thermal evaporation of ZnSe powders. The heating furnace used for this thermal evaporation process is schematically shown in Fig. 1. A quartz tube was mounted inside a horizontal tube furnace. The quartz tube consisted of two temperature zones: zone A at 900 °C and zone B at 750 °C. An alumina boat loaded with pure ZnSe powders was located in zone A and the Au-coated Si or Al_2O_3 substrate was in zone B. The nitrogen gas flow rate was 100 standard cubic centimeters per minute (sccm) and the chamber pressure was 0.5 Torr. The synthesis was performed for 1 h. Next, the nanowires were annealed at 300 °C for 5 min in a vacuum furnace (base vacuum level = 10^{-3} Torr).

Secondly, ZnSe/TiO_2 coaxial nanowire samples with different TiO_2 layer thicknesses were prepared by sputter-deposition of TiO_2 thin films on the as-synthesized ZnSe nanowires for 0.5–10 min. The sputtering process parameters for TiO_2 deposition used in these sputtering processes are as follows: radio frequency

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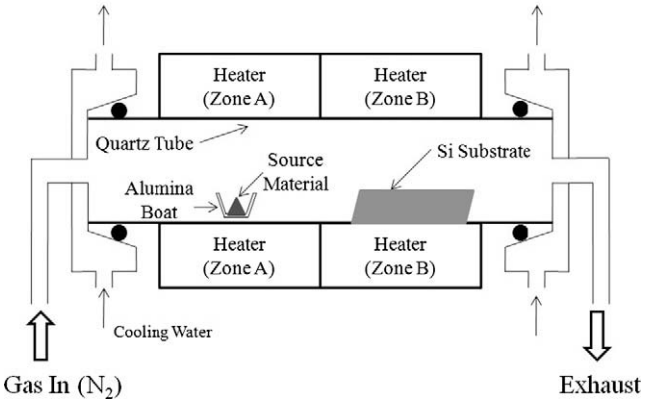

Fig. 1. Schematic of the thermal evaporation system with two heating zones used for ZnSe nanowire synthesis.

(R.F.) power = 100 W, base vacuum = 1.0×10^{-6} Torr, chamber pressure = 1.2×10^{-2} Torr, Ar gas flow rate = 30 sccm, and substrate temperature = room temperature. The ZnSe/TiO_2 coaxial nanowire samples to see the influence of the TiO_2 sheath layer thickness on the PL properties were then annealed at 300 °C for 5 min in a vacuum furnace. On the other hand, another set of ZnSe/TiO_2 coaxial nanowire samples to see the effect of the annealing atmosphere on the PL properties were annealed in an oxygen (O_2) or argon (Ar) atmosphere.

Next, the prepared nanowire samples were characterized by using the field emission scanning electron microscope (FESEM, Hitach S-4200). PL spectroscopy and X-ray diffraction analyses were performed at room temperature on the ZnSe nanowire and ZnSe/TiO_2 coaxial nanowire samples using a 325 nm He–Cd laser (Kimon, IK, Japan) and a diffractometer (Philips X'pert MRD) with Cu Kα radiation, respectively. XPS analyses (model: K-alpha, Thermo Fisher Scientific) were performed to investigate the compositions and bonding states of the elements in the surface region of ZnSe nanowires and the interface region of the ZnSe core and the TiO_2 shell in the ZnSe/TiO_2 coaxial nanowires. X-ray photoelectron emission spectroscopy (XPS) depth profilings were also performed to understand the redistribution of the elements in the ZnSe/TiO_2 coaxial nanowires during annealing. ZnSe thin films for XPS analyses were prepared on Al_2O_3(0 0 0 1) substrates by evaporating ZnSe powder at 500 °C for 1 h since XPS analyses and particularly XPS depth profilings were very difficult to be performed directly on nanowire samples. ZnSe/TiO_2 thin film samples were also prepared on Al_2O_3(0 0 0 1) substrates for the same purpose by evaporating ZnSe powders at 500 °C for 1 h and then sputter-depositing TiO_2 thin films at 100 W for 5 min. Subsequently, all these XPS samples were annealed at 300 °C for 5 min in a vacuum furnace (base vacuum level = 10^{-3} Torr). The etch rate in the depth profiling was about 0.1 nm/s.

3. Results and discussion

The PL spectra of the ZnSe nanowires are dominated by the deep level emission and the near-band edge (NBE) emission is negligible. A room temperature PL spectrum of ZnSe nanowires is typically dominated by two characteristic emission peaks [10–15]: (1) an NBE emission peak at around 465 nm and (2) a broad deep level emission peak in the wavelength range of 500–680 nm. The NBE emission is generally known to be due to bound excitons and donor–acceptor pairs. On the other hand, the deep level emission is generally known to be mainly due to deep levels such as vacancies, interstitials, and stacking faults. Shalish et al. [16] reported that the intensity ratio of NBE emission to the deep level emission in the luminescence spectrum almost linearly decreases as the average nanowire diameter increases, although this conclusion was made on the hypothesis that the deep level emission solely originates from surface states. Fig. 2 shows the PL spectra of ZnSe/TiO_2 coaxial nanowires with different TiO_2 sputtering times (corresponding to TiO_2 layer thicknesses). The diameters and the lengths of the ZnSe nanowires grown by thermal evaporation of ZnSe powders on Au-coated Al_2O_3(0 0 0 1) substrates are in a range of 100–200 nm and a few tens of micrometers, respectively as shown in the SEM images of Fig. 3. The PL spectra of the ZnSe/TiO_2 coaxial nanowires are dominated by a broad deep level-related emission band centered at around 630 nm, which may be attributed to the average diameter of the ZnSe nanowires synthesized in this work relatively larger than those in the previous works. In this regard our results seem to agree well with the previous report [16].

It can be understood from Fig. 2 that the PL peak intensity strongly depends on the TiO_2 sputtering time. It is evident from the inset of Fig. 2 that the PL peak intensity of the ZnSe/TiO_2 coaxial nanowires has a strong dependence on the TiO_2 shell layer thickness since the TiO_2 shell layer thickness is proportional to the TiO_2 sputtering time. The PL peak intensity increases slightly first and then significantly as the TiO_2 sputtering time increases from 0 to 1 to 1.5 min. However, the PL peak intensity decreases with further increases in the TiO_2 sputtering time. Thus, the highest PL peak intensity of the ZnSe/TiO_2 coaxial nanowires is obtained for the sputtering time of 1.5 min corresponding to ~5 nm. The PL peak intensity of the ZnSe/TiO_2 coaxial nanowires for the sputtering time of 1.5 min is about 30 times as strong as that of ZnSe nanowires without TiO_2 coatings (equivalent to the sputtering time of 0 min).

To investigate the mechanism of the enhancement in the deep level emission of the ZnSe nanowires by sheathing them with TiO_2 we performed XPS analyses. There is one thing to mention here that all the TiO_2-sheathed or unsheathed ZnSe nanowire samples in this work were annealed at 300 °C for 5 min in a vacuum furnace (base vacuum level = 10^{-3} Torr) to enhance their PL property. Actually, we annealed the nanowire samples annealed at 300 °C for 5 min in an Ar atmosphere at first, yet they showed PL properties inferior to those of the same kind of samples annealed in a vacuum furnace against our expectation although the detailed experimental results are not shown here. Comparison of the XPS depth profiles of ZnSe/TiO_2 coaxial nanowires (Fig. 4a) with those of ZnSe nanowires (Fig. 4b) reveals that quite a bit of interdiffusion

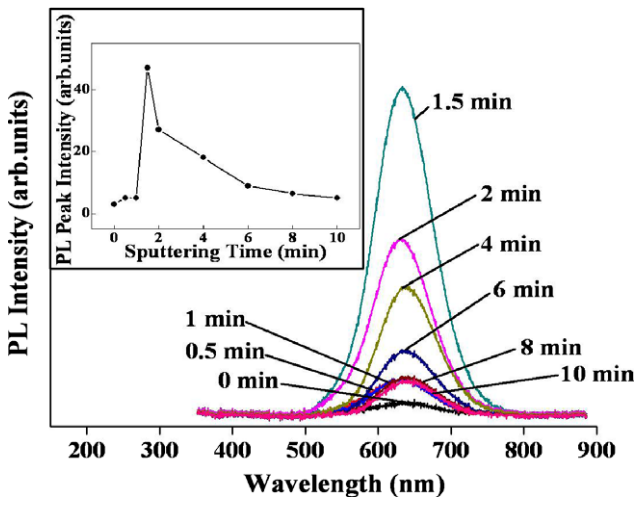

Fig. 2. PL spectra of the ZnSe nanowires sheathed with TiO_2 films with different thicknesses and then annealed at 300 °C for 5 min. Inset, PL emission peak intensity versus TiO_2 layer thickness curve.

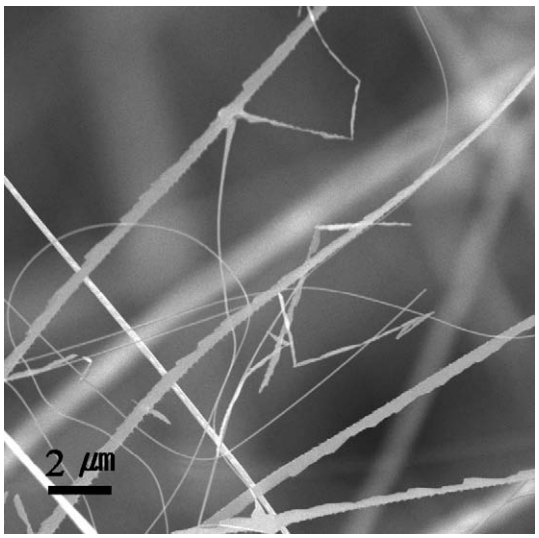

Fig. 3. SEM images of ZnSe nanowires grown on the Al_2O_3(0 0 0 1) substrate: (a) magnification: 5000 and (b) magnification: 20,000.

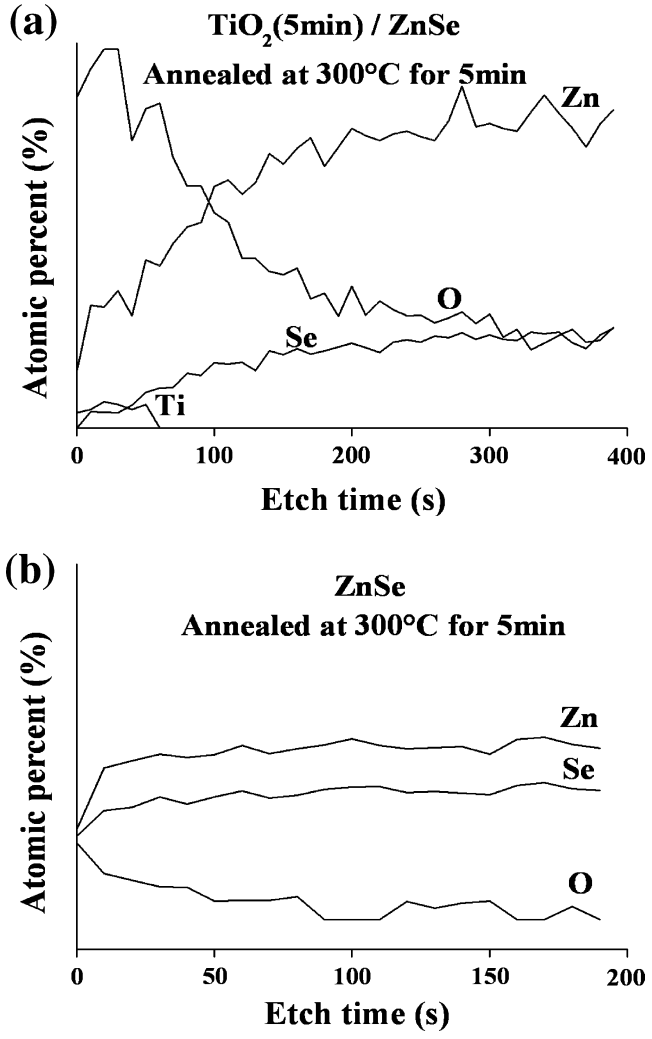

Fig. 4. XPS depth profiles of (a) the ZnSe/TiO_2 coaxial nanowires and (b) the ZnSe nanowires grown on the Al_2O_3(0 0 0 1) substrate and then annealed at 300 °C for 5 min.

of atoms has occurred between the ZnSe core and the TiO_2 shell. Particularly, significant redistribution of O is noted. The O atoms newly flowed from the annealing atmosphere into the sample as well as the O atoms preexisting in the TiO_2 sheath layer (about 5 nm thick) seems to have advanced more than 35 nm from the interface of ZnSe–TiO_2 into the ZnSe core region while Ti atoms have not nearly moved into the ZnSe core.

The XRD patterns of ZnSe/TiO_2 coaxial nanowires and ZnSe nanowires which have been annealed at 300 °C for 5 min in a vacuum furnace are shown in Fig. 5 and that of TiO_2 thin films is also shown in Fig. 5 just for comparison. All the diffraction peaks in the XRD patterns of ZnSe/TiO_2 coaxial nanowires belong to crystalline anatase TiO_2 with the tetragonal structure (JCPDS Card No. 21-1272) and crystalline ZnSe with the zinc blende structure (JCPDS Card No. 88-2345). No peaks of elemental Ti, Zn and Se are observed at all, which suggests two things as follows:

(1) The composition of the as-deposited TiO_2 layer was O-rich. The excess O atoms in the TiO_2 shell mostly have diffused into the ZnSe core during annealing treatment. The O molecules in the annealing ambient gas also have diffused into the ZnSe core through the TiO_2 shell.
(2) Fig. 4a indicates that the composition of the as-grown ZnSe nanowires is Zn-rich and that the ratio of Zn to Se in the TiO_2 shell is almost the same as that in the ZnSe core, suggesting that a part of the Zn and Se atoms in the ZnSe core have diffused into the TiO_2 shell not in a state of Zn and Se atoms but in a state of ZnSe molecules during annealing treatment.

The wide scan XPS spectra of ZnSe/TiO_2 coaxial nanowires (Fig. 6a) and ZnSe nanowires (Fig. 6b) and the XPS survey data (the insets of Fig. 6a and b) provide us with more detailed information on the concentrations of individual elements in the surface regions of the two nanowire samples. The ratio of Zn to Se was 52.5: 40.5 by at.% in the ZnSe nanowires. The ratio of Zn to Se is 14.2: 10.2 by at.% and the O concentration is far higher than the Ti concentration in the TiO_2 shells of the annealed ZnSe/TiO_2 coaxial nanowires. Comparison of the binding energy value (1022.85 eV) of the Zn 2p peak with those of the candidates in Table 1 indicates that the detected Zn compound is ZnO. These XPS analysis results suggest that ZnO has formed by the reaction between the ZnSe molecules in the ZnSe/TiO_2 coaxial nanowires and the O molecules in the annealing ambient gas or the O atoms in the ZnSe/TiO_2 coaxial nanowires although ZnO was not detected by the XRD analysis.

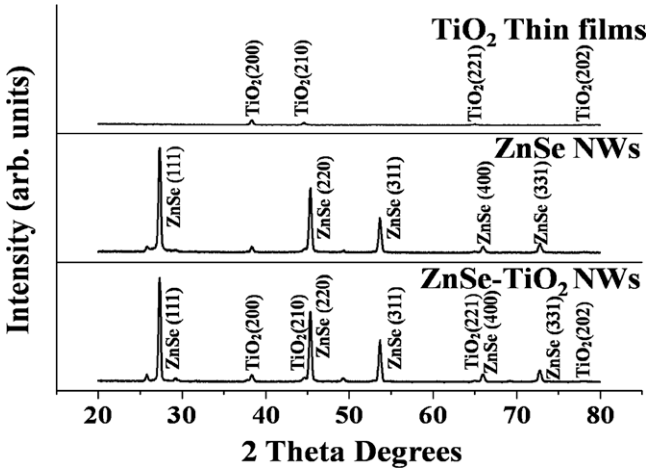

Fig. 5. XRD patterns of TiO_2 thin films and the ZnSe nanowires and the ZnSe/TiO_2 coaxial nanowires grown on the Al_2O_3(0 0 0 1) substrate and then annealed at 300 °C for 5 min.

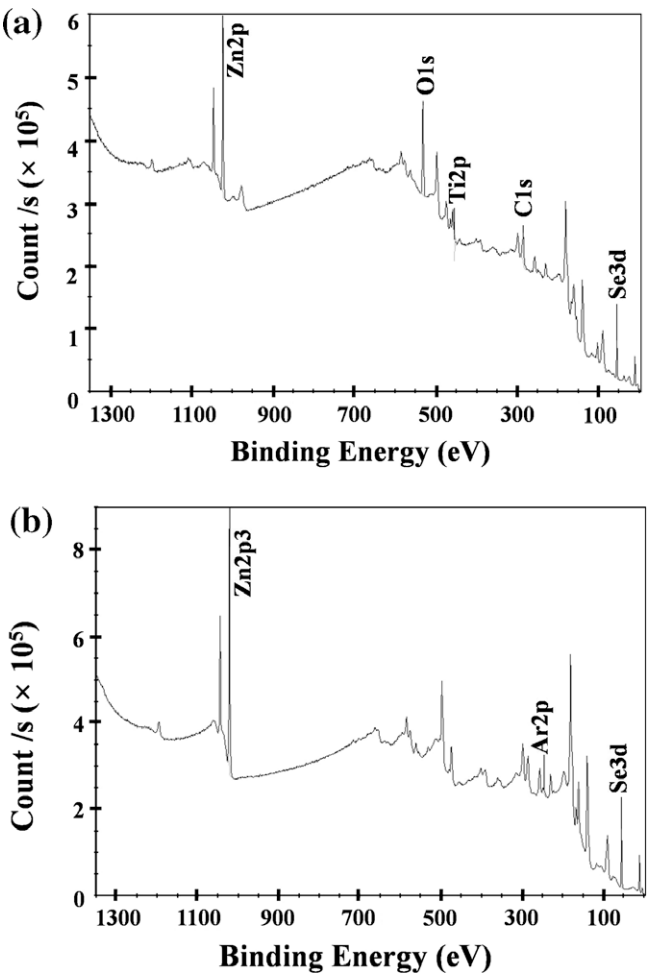

Fig. 6. Wide scan XPS spectra of (a) the ZnSe/TiO_2 coaxial nanowires and (b) the ZnSe nanowires grown on the Al_2O_3(0 0 0 1) substrate and then annealed at 300 °C for 5 min.

Major point defects existing in the annealed ZnSe/TiO_2 coaxial nanowires are not only Zn interstitials and Se vacancies but also O and Ti interstitials as written earlier. Another thing worthy of noting is that the interface (or transition) region of the ZnSe/TiO_2 coaxial nanowires is far thicker than the surface region of the ZnSe nanowires, which suggests that the ZnSe/TiO_2 coaxial nanowires have higher densities of deep levels including interstitials and vacancies as well as surface or interface states. In conclusion, there are higher densities of deep levels in the ZnSe/TiO_2 coaxial nonowires than in the ZnSe nanowires, which may be the reason why the PL emission intensity of the ZnSe/TiO_2 coaxial nanowires is higher than that of the ZnSe nanowires. However, in the case of the ZnSe/TiO_2 coaxial nanowires with the TiO_2 layer thicker than a certain limit (corresponding to a sputter time of 1.5 min) the inflow of O atoms from the annealing atmosphere into the nanowires will be limited since the TiO_2 layer will act as a diffusion barrier against O atoms. Accordingly the concentrations of deep levels such as O and Se interstitials induced by the inflow of O atoms into the ZnSe core through the TiO_2 shell layer will decrease as the TiO_2 shell layer thickness increases. Therefore, the optimum TiO_2 shell layer thickness for the highest deep level emission exists and it is the one corresponding to the sputter time of 1.5 min.

The PL spectra of ZnSe nanowires and TiO_2-sheathed ZnSe nanowires annealed in an O_2 or Ar annealing atmosphere are presented in Fig. 7a and b respectively. The PL spectra of unannealed nanowire samples are also presented here for comparison. Fig. 7a and b also shows that the PL emission of ZnSe nanowires tends to be enhanced whereas that of TiO_2-sheathed ZnSe nanowires to be degraded by thermal annealing irrespective of the annealing atmosphere. Fig. 7a indicates that annealing in an Ar atmosphere is more effective in enhancing the PL emission of ZnSe nanowires than in O_2 atmosphere. Fig. 7b also suggests that either annealing in an Ar atmosphere or annealing in an O_2 atmosphere degrades the PL emission of TiO_2-sheathed ZnSe nanowires, but that the former is less harmful than the latter.

Table 1
Details of the main peaks in the XPS spectra of the interface region of the ZnSe/TiO_2 coaxial nanowires annealed at 300 °C for 5 min.

ZnSe/TiO_2		Candidates	
Elemental	Peak binding energy (eV)	Compound name	Binding energy (eV)
Zn 2p	1022.85	Zn ZnO	1021.5 1022.5
O 1s	532.13	ZnO	530.4
Ti 2p	456.08	Ti TiO_2	454.1 458.7

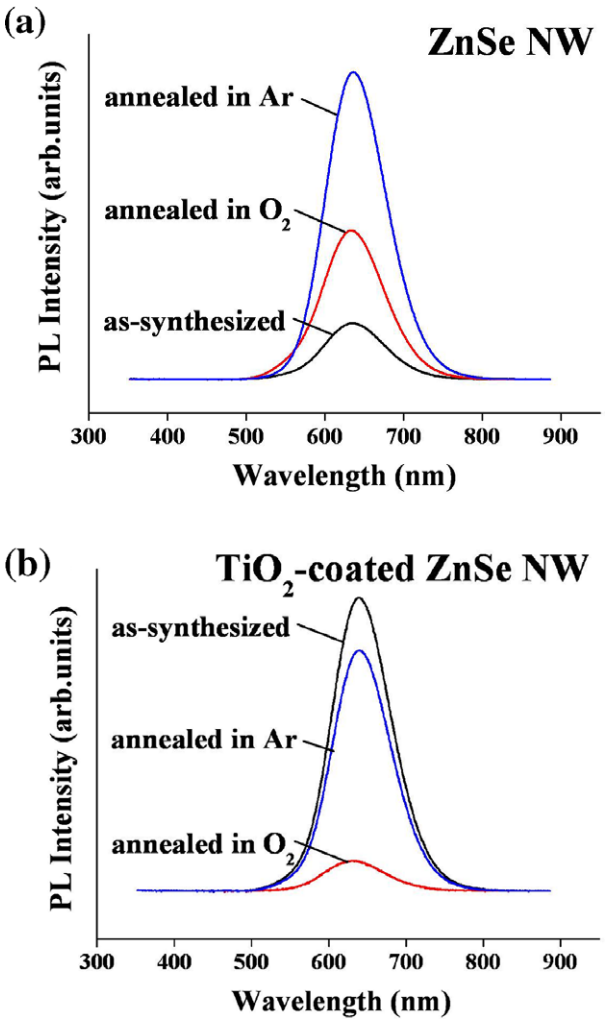

Fig. 7. Influences of the annealing atmosphere on the PL of (a) the ZnSe nanowires and (b) those sheathed with TiO_2. All the nanowire samples were annealed at 300 °C for 5 min before PL measurements.

The PL enhancement of ZnSe nanowires by Ar annealing may be attributed to the generation of Zn and Se vacancies and O interstitials during the annealing process. The O interstitials are originated from the O_2 molecules existing in the Ar atmosphere as impurities. In ZnSe nanowires various forms of intrinsic point defects such as Zn vacancies, Se vacancies, Zn interstitials, and Se interstitials may exist. Of these point defects Zn interstitials and Se vacancies are known to be dominant in the ZnSe nanowires synthesized by thermal evaporation of ZnSe powder since the ZnSe nanowires are Zn-rich, which can be clearly seen in Fig. 4b. In the case of O_2 annealing, however, decreases in the concentration of Zn interstitials also occur in addition to the increases in the concentrations of Zn and Se vacancies and O interstitials. In the case of O_2 annealing, O atoms flow into the ZnSe core region from the TiO_2 sheath layer as well as from the O_2 atmosphere during the annealing process. The O atoms migrated into the ZnSe core region make bonds with Zn interstitials to form ZnO impurities, leading to a decrease in the concentration of Zn deep levels. Hence, the deep level emission is less enhanced by O_2 annealing.

On the other hand, it is very likely that there exist high concentrations of Zn interstitials and Se vacancies in the ZnSe cores since most ZnSe nanowires synthesized by thermal evaporation have been reported to be Zn-rich. There is also a high possibility that there exist O and Ti interstitials in the ZnSe cores besides the Zn interstitials and Se vacancies. The O and Ti interstitials may have formed during the TiO_2 sputtering process. During annealing in an Ar atmosphere, O atoms migrate into the ZnSe cores mostly from the TiO_2 sheath layers or the annealing atmosphere and make bonds with Zn atoms and Ti interstitials to form ZnO and TiO_2 in the ZnSe cores, respectively, which results in decreases in the concentrations of Zn and Ti interstitials, i.e. the deep level concentrations in the cores. The vacancy concentrations in a material are commonly increased by thermal annealing. However, in the case of annealing of the ZnSe/TiO_2 coaxial nanowires in an Ar atmosphere, the deep level concentration decreasing effect in the ZnSe cores due to the inflow of O atoms seems to be dominant over the deep level concentration increasing effect due to the vacancy generation in the ZnSe cores, so that the deep level emission is degraded by Ar annealing. In the case of O_2 annealing much more O atoms migrate into the ZnSe cores than those in the case of Ar annealing because of substantial supply of O atoms from the O_2 atmosphere during the O_2 annealing. Consequently, the deep level decreasing effect is much more significant in the case of O_2 annealing than that in the case of Ar annealing. Hence, the deep level emission is further degraded by O_2 annealing than Ar annealing.

4. Conclusions

ZnSe nanowires have been grown by thermal evaporation of ZnSe powders on Si(1 0 0) and Al_2O_3(0 0 0 1) substrates coated with Au thin films. Sheathing ZnSe nanowires with thin TiO_2 layers can significantly enhance the PL emission intensity. Our results show that the PL peak intensity of the ZnSe/TiO_2 coaxial nanowires prepared by sputter-deposition of TiO_2 at 100 W for 1.5 min on ZnSe nanowires is about 30 times as high as that of ZnSe nanowires. Enhancement in the PL emission of ZnSe nanowires by TiO_2 coating is attributed to increases in the concentrations of deep levels such as O and Ti interstitials as well as the density of interface states. The PL emission of ZnSe nanowires is also enhanced by thermal annealing. Annealing in an Ar atmosphere is more efficient in enhancing the PL emission of ZnSe nanowires than annealing in an O_2 atmosphere. Enhancement in the PL emission of ZnSe nanowires by annealing is attributed to the generation of Zn and Se vacancies and O interstitials during the annealing process. In contrast, the PL emission of the ZnSe/TiO_2 coaxial nanowires is somewhat degraded by thermal annealing.

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