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Influence of thickness and annealing on photoluminescence of nanostructured ZnSe/ZnS multilayer thin films prepared by electron beam evaporation

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ABSTRACT

In this paper, nanostructured ZnSe/ZnS multilayer thin films were prepared on silicon substrates by electron beam evaporation technique. This heterostructure takes advantage of the properties of ZnSe and ZnS, with ZnSe and ZnS acting as light-emitting and passivation layers, respectively. To enhance the luminescence performance, the optimal thickness of ZnS and ZnSe films and the annealing conditions were investigated. Nanostructured films with 3.5 nm ZnSe and 15 nm ZnS annealed at 660 °C for 100 min in N_2 were found to be the optimal conditions. In addition, crystal structures and surface morphologies of the films were characterized, which showed outstanding blue emission. The excellent blue emission achieved in the optimized films indicates that nanostructured ZnSe/ZnS multilayer films could be used as novel luminescence materials.

1. Introduction

In recent years, a great deal of attention has been paid to the search of high quality blue luminescent materials [1,2]. Meanwhile, there have been substantial interests in nanostructured materials due to their novel properties and extensive applications [3]. As an important II–VI semiconducting material, zinc selenide (ZnSe) has received ever-increasing attention due to its wide band-gap and high luminescence efficiency [4]. ZnSe has an optical band-gap of 2.7 eV (bulk band gap) [5] at room temperature, which is recognized as an important alternative material for blue light-emitting diodes [6–8], blue lasers [9], solar cells [10] and several optoelectronic devices [11,12]. Due to the quantum confinement effect [13,14], the emission wavelengths of nanostructured ZnSe ranges from blue to ultraviolet can be achieved by adjusting its size. Besides, unlike ZnO, ZnSe can be doped by both n and p types [15,16]. As another wide band gap II–VI semiconducting material, zinc sulfide (ZnS) owns bulk band gap of 3.66 eV [17], which is considered to be an ideal value for an inorganic passivation shell in core/shell nanostructures to improve the stability and emission properties of the semiconductor, as has been shown core/shell quantum dots [5,18,19].

Up to now, many results have been reported on photoluminescence of various forms of ZnSe with different fabrication methods. Sunghoon Park et. al. prepared ZnSe nanorods by thermal evaporation and obtained near band-edge (NBE) emission centering at about 450 nm [20]. Yaping Zhang et. al. synthesized blue-emitting ZnSe quantum dots (QDs) doped with different transition metal ions under aqueous conditions [21]. Keun-Kyu Song et. al. synthesized ZnSe/ZnS core/shell QDs with high luminescence efficiency from blue to UV emission [22]. P. Reiss et. al. synthesized colloidal ZnSe nano-crystals exhibiting size-dependent optical properties [23]. C. H. Hsiao et. al. grew single-crystalline ZnSe nanowires with an emission wavelength at 477 nm by molecular-beam epitaxy [24]. Heeyeon Park et. al. synthesized ultra-thin wurtzite ZnSe nanosheets through a chemical route [25].

Here we report fabrication of nanostructured ZnSe/ZnS multilayer thin films by electron beam evaporation. This method has the advantage of low cost and simple, but has been rarely reported. This heterostructure takes advantage of the properties of ZnSe and ZnS, with ZnSe and ZnS acting as light-emitting and passivation layers, respectively. As reported in our previous work [26], some basic features were studied, such as structural, morphological and optical properties. In order to enhance the luminescence performance, the optimal thickness of ZnS and ZnSe films and the annealing conditions including annealing temperature and annealing time were investigated in this article. Especially, we did a more comprehensive characterization, testified by the determination of the optical band gap and a temperature-dependent X-ray analysis. It was the most significant aspect of this work. Furthermore, crystal structures and surface morphologies of the films were characterized which showed outstanding blue emission. The excellent blue emission achieved in the optimized films indicates that nanostructured ZnSe/ZnS multilayer films could be used as novel

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Table 1
The deposition thickness of the ZnSe/ZnS multilayer films.

Sample name	Thickness of ZnSe film (nm)	Thickness of ZnS film (nm)	Periods of multilayer film
S1	3.5	10/12.5/15/17.5/20	10
S2	2.5/3/3.5/4/4.5	15	10

luminescence materials.

2. Experimental

High purity ZnSe particles (99.99%) and ZnS particles (99.99%) were used as starting materials for the alternate deposition of nanostructured ZnSe/ZnS multilayer thin films on silicon and quartz substrates by electron-beam evaporation (EVA450). The substrates were cleaned prior to deposition with alcohol and deionized water, and were kept at room temperature during in the deposition. The detailed deposition conditions were reported in our previous study [26]: the thickness and deposition rate of the films were monitored by quartz crystal monitor, the background pressure of the chamber was maintained at 2.0×10^{-3} Pa, the growth rates of ZnSe and ZnS were 0.5–0.6 Å/s and 0.8–1.0 Å/s, respectively. The deposition thicknesses of ZnSe and ZnS were shown in Table 1. To study the effect of the annealing temperature and time on photoluminescence, the samples were annealed in nitrogen atmosphere (N_2) at different temperatures for different times in a quartz tube. The annealing temperature ranged from 620 °C to 700 °C and the duration ranged from 40 min to 140 min, respectively.

Absorption spectra of the films deposited on quartz substrates were measured by a UV–Vis–NIR scanning spectrophotometer. The crystal structures and phase composition of the films were characterized by X-ray diffraction (XRD) using an X-ray diffractometer (Bruker D8 Advance). The contents of different elements in the films were measured by energy dispersive X-ray spectroscopy (EDS). The PL spectra were measured by a fluorescence spectrometer (FLS920) with a 325 nm He-Cd laser as the excitation source. The surface morphologies of the films were studied by scanning electron microscopy (SEM). All these measurements were made at room temperature.

3. Results and discussion

3.1. Optical properties of the annealed films

In our study, the optical properties of the annealed nanostructured ZnSe/ZnS multilayer films were studied by absorption and PL spectra, as shown in Fig. 1. The absorption band edge of the films is located at about 360 nm. The fundamental absorption edge is used to analyze information about the type of electronic inter band transitions, in which the optical band gap of the annealed film is determined using Tauc's expression given by [27]:

$$\alpha h\nu = \mathrm{B}(h\nu - E_g)^m,$$

where E_g is the optical band gap of the films and B is a constant that depends on the transition probability. α is the absorption coefficient, h is Planck's constant, ν is the frequency of incident light, and m depends on the characteristic of the transition (m = ½ for direct band gap and m = 2 for indirect band gap). The extrapolating linear region of the plot of $(\alpha h\nu)^2$ versus $h\nu$ on the energy axis, as shown in Fig. 2, confirms the direct transition. The optical band-gap value is estimated to be 3.42 eV for the annealed nanostructured ZnSe/ZnS multilayer thin films, which is lower than that of ZnS (3.66 eV) and higher than that for ZnSe (2.7 eV) in bulk case.

It can be seen from Fig. 1 that the PL spectra contain two emission

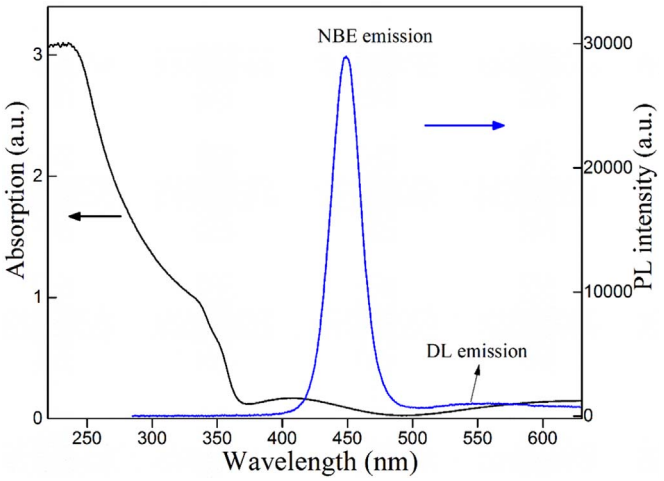

Fig. 1. Absorption and emission spectra of the film with 3.5 nm ZnSe and 15 nm ZnS annealed at 660 °C for 1 h in N_2 (λ_{ex} = 325 nm).

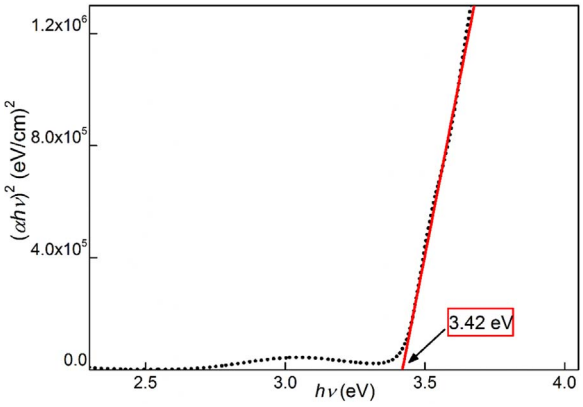

Fig. 2. Plot of $(\alpha h\nu)^2$ versus $h\nu$ of nanostructured ZnSe/ZnS thin films annealed at 660 °C for 1 h in N_2.

bands. One narrow and intense peak is located at about 446 nm with only 29 nm of the full width at half-maximum (FWHM) and another is an weak and broad peak extending from about 500–600 nm, which corresponds to the NBE emission of ZnSe and defect-related (DL) emission including vacancies, interstitials, lattice distortion, and structure defects [20,28]. The NBE emission shows a blue-shift comparing with the reported PL spectra of 452 nm in ZnSe thin films [29], which is attributed to the quantum confinement [30] in nanostructured ZnSe/ZnS thin films with thin layers of ZnSe.

3.2. Influence of ZnS thickness on the PL spectra

To study the effect of ZnS thickness on photoluminescence, samples of the S1 series were annealed under the same condition of 660 °C for 1 h in N_2. As shown in Fig. 3, the position of the NBE and DL emission peaks do not change, indicating that the emission peak originates from ZnSe to some extent. However, we find that the intensity of NBE emission increases firstly and then decreases with the increasing thickness of the ZnS layer, reaching the maximum when the ZnS at 15 nm. It has been reported that ZnS layer can act as passivation layer in quantum dots synthesis [31], here, the ZnS layer protects ZnSe nanolayer to enhance the intensity of PL. If the ZnS layer is too thin, it can not play a protective role in ZnSe NBE emission. On the other hand, if the ZnS layer is too thick, it could have a negative effect on the luminescence of ZnSe. Meanwhile, ZnS layer will also introduce some defects. Thus, the intensity of the NBE emission and DL emission changes with the increasing thickness of the ZnS layer, as shown in the