



Charge transfer and optical properties of wurtzite-type ZnS/(CdS/ZnS)_n (n = 2, 4, 8) superlattices



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ABSTRACT

ZnS/(CdS/ZnS)_n (n = 2, 4, 8) superlattices were deposited on sapphire substrate by pulsed laser deposition (PLD) with alternate cadmium sulfide (CdS) and zinc sulfide (ZnS) crystals at 100 °C. The prepared samples with an average thickness of ~30 nm for ZnS layer and ~60 nm for CdS layer have a wurtzite-type structure. Surface phonon of ZnS and multiple phonons modes for ZnS and CdS were observed from Raman spectra. PL spectra show a strong green emission at ~496 nm, two weak emission bands at ~400 and ~577 nm, where the emission band at 400 nm was attributed to the recombination of surface defects states to valence, the emission band at 577 nm as the recombination of Cd_i-V_{Cd} centers, and the strong emission at ~496 nm is from the charge transfer of electrons from CdS electron to ZnS holes by excitation energy.

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1. Introduction

Thin films of II–VI semiconductors such as CdS and ZnS are technologically important for their potential applications in optical coatings [1] and optoelectronic devices [2,3]. Hexagonal ZnS and CdS with room temperature bandgaps of about 3.7 eV [4] and 2.4 eV [5] respectively, are promising materials for optoelectronic applications in this spectral range. Particularly, the core-shell CdS@ZnS structures [6–8] and multilayer structures of CdS and ZnS (CdS/ZnS) [9–12] have attracted much attention in recent years, since the optical properties can be enhanced and the band gap can be tuned by the surface chemical bonds and charge transfer in the surface/interface region of heterostructures and core-shell structures. The hierarchical heterostructures with unique properties can be prepared by a chemical or physical process, and some new and enhanced physical properties were found due to the interface effects [13,14].

On the other hand, the wurtzite ZnS nanocrystal fabrication at room temperature is still a big challenge, as the most stable ZnS structures in nanoscale is the zinc blende (cubic) structure, therefore, people try many efforts to explore the room-temperature synthesis of the wurtzite structure of ZnS nanocrystals. For example, Banerjee et al. [15] reported the wurtzite ZnS nanocrystals realized by controlling their unfolding peptide structures, Zhao

et al. [16] displayed the results of low-temperature synthesis of hexagonal (wurtzite) ZnS nanocrystals, Chai et al. [17] reported the synthesis of wurtzite ZnS nanowire using a solvothermal technique, and Zhou et al. [18] reported the wurtzite nanoplate-like ZnS at low temperature via solvothermal route. From the industrial point of view, the wurtzite ZnS film is more practical for the application to optical devices. But, it is not easy to obtain the high-quality heterostructure with the increase in the film thickness due to the lattice parameter misfits of different materials and interfacial stress as well as the dislocations. For example, the zinc-blende ZnS films [19] grown by MBE on GaN and Al₂O₃ substrates have a highly lattice mismatched structure with a lattice mismatch of 20% and –20%, respectively. Dinger et al. [9] reported the CdS/ZnS strained layer superlattices by MBE with lattice mismatch of 7%, and Yokoyama et al. [20] synthesized the ZnSe/ZnS strained quantum well structures by low-pressure metalorganic atomic layer epitaxy (ALE) with lattice mismatch of 4.5%. All of these structures are characterized by concomitant growth enabling mutual lattice tuning of the constituents and thus reducing the hardship of interface electron scattering and enhancing device performances. Till now, there are rarely reports on wurtzite ZnS film grown at lower temperature, therefore, it is very necessary to explore the growth technique for the high quality wurtzite ZnS film at lower temperature, because it is very helpful to the manufacture of optoelectric device. At the same time, there is no report on the charge transfer for the ZnS/CdS heterostructure.

In the paper, we firstly successfully synthesized wurtzite ZnS/(CdS/ZnS)_n (n = 2, 4, 8) superlattices by pulsed laser deposition

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(PLD) technique at low temperature of 100 °C, where wurtzite ZnS and CdS multilayer structures were clearly visible by using a field emission scanning electron microscope. And the mismatch between their lattice parameters is only $\sim 3.0\%$ from XRD measurements. In addition, comprehensive studies on resonant Raman scattering were presented, and the surface optical phonon for ZnS and multiphonon processes of CdS and ZnS were resolved, indicating high crystalline ZnS/(CdS/ZnS)_n ($n = 2, 4, 8$) superlattices. Furthermore, photoluminescence spectrum of the ZnS/(CdS/ZnS)₄ superlattices shows a strong green emission centered at ~ 496 nm, and two weak emissions centered at ~ 400 and ~ 577 nm, where the emission band at 496 nm is originated from the charge transfer of electrons from CdS electron to ZnS holes by excitation energy, and the emission band at 400 nm is ascribed as the recombination of surface defects states to valence, emission band at 577 nm as the recombination of Cd_i-V_{Cd} centers.

The highlights in our work are the successful growth of high quality wurtzite ZnS/(CdS/ZnS)_n films at very low temperature and the origin of the strong green emission at 490 nm, which is from the charge transfer of electrons from CdS electron to ZnS holes by excitation energy. Those results are reported for the first time. As the green emission at 490 nm is steady, it can be used as a green optoelectric device. It provides a practical procedure to obtain the wurtzite ZnS film at lower growth temperature via using CdS film as a buffer layer.

2. Experimental

In this work, ZnS/(CdS/ZnS)_n ($n = 2, 4, 8$) superlattices were synthesized by ablating stoichiometric home-made target using pulsed laser deposition technique. Depositions were carried out with a KrF excimer laser operating at 248 nm. Pulsed laser used for ablation was set with 380 mJ of laser energy and a repetition rate of 5 Hz. Before deposition, the chamber was pumped down to a base pressure of 5.0×10^{-6} Torr. The distance between the target and substrate was maintained at 4 cm. During ZnS (or CdS) film growth, argon gas with a flow rate of 20 sccm was fed through the mass flow controller into the chamber, and a working pressure of 0.1 Torr was maintained. The deposition process can be described as, firstly, with the interaction of incident laser, surface particles of the target is instantaneously ablated, then driving by the flow of argon gas the ablated particles reach the substrate, finally the film is formed on the substrate after the thermal equilibrium, similar to the reports [21] on Zn/ZnO core/shell structured particles obtained by laser ablation of a zinc metal target in pure water or in aqueous solution of sodium dodecyl sulfate (SDS).

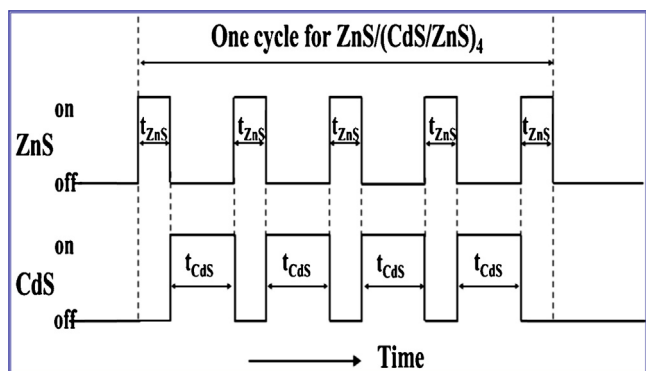


Fig. 1. The schematic diagrams of the film deposition sequence for the growth of ZnS/(CdS/ZnS)₄ by PLD.

ZnS and CdS films are alternately deposited on the sapphire substrate by PLD at a low growth temperature (~ 100 °C). Fig. 1 shows the film deposition sequence for the growth of ZnS/(CdS/ZnS)₄ superlattices, same way to the other superlattices. The film deposition intervals of the ZnS film and CdS film (labeled as t_{ZnS} and t_{CdS}) are 60 and 120 s, respectively.

Structural and morphological characterization of ZnS/(CdS/ZnS)_n ($n = 2, 4, 8$) superlattices were carried out using X-ray diffraction (Shimadzu XRD-7000), and FESEM (Hitachi S-4800) equipped with an X-ray energy dispersive spectrometer (EDS). Raman, Transmission and temperature-dependent photoluminescence emission spectra were recorded with a laser confocal Raman spectrometer (Renishaw Invia), UV-Vis-NIR spectrophotometer (Varian Cary-5000) and luminescence spectrophotometer (Edinburgh EPL-375), respectively.

3. Results and discussions

3.1. Structural and morphological characterization

The nanostructures of ZnS/(CdS/ZnS)_n ($n = 2, 4, 8$) superlattices were examined by field-emission scanning electron microscopy (FESEM). Fig. 2a–c shows the cross-sectional FESEM images of ZnS/(CdS/ZnS)_n ($n = 2, 4, 8$) superlattices deposited on sapphire substrate. Individual interfaces are very clear and smooth between ZnS and CdS layers, no other inter-diffusion layers have been observed. Besides, the film thickness of each layer can be clearly observed from the SEM image with an average thickness of ~ 30 nm for ZnS layer and ~ 60 nm for CdS layer. And apparently the film thickness deposited by PLD depends on the preparation conditions, such as deposition time, laser energy density, pulse frequency, gas pressure and target-substrate distance. Fig. 2d displays the surface FESEM micrograph of ZnS/(CdS/ZnS)₄ superlattices, where the compact film with rather smooth surface consisted with a numerous uniform grains, and no agglomeration of ZnS or CdS phases were observed.

The element quantitative analysis of EDS spectra for the samples shows the presence of Zn, Cd and S with an approximate atomic ratio of 0.353:0.164:0.483, as shown in Fig. 3a. Furthermore, crystal structure of the samples was determined by XRD, as shown in Fig. 3b. The peaks for all samples at 2θ values of 26.9° , 28.5° are indexed to (1 0 0) and (0 0 2) crystal planes of hexagonal ZnS (JCPDF no. 36-1450), and 26.5° and 28.2° match well with (002) and (101) crystal planes of hexagonal CdS (JCPDF no. 65-3414), respectively. The calculated lattice constants of ZnS/(CdS/ZnS)₄ superlattices are $a = b = 3.953$ Å, $c = 6.362$ Å for hexagonal ZnS film, and $a = b = 4.072$ Å, $c = 6.554$ Å for hexagonal CdS film, respectively. And the lattice mismatch between ZnS and CdS layer can be calculated to be about 3.0%. Combined with SEM results, the compact and uniform growth between ZnS and CdS layers is exactly due to the low lattice mismatch rate. Another notable feature observed from XRD patterns is that the intensity of diffraction peaks increases with the number of film layers increasing, indicating a better crystallinity of the superlattices with the more layers.

The microstructure of the ZnS/(CdS/ZnS)₂ superlattices can be investigated by the HRTEM, as shown in Fig. 3c–d. Fig. 3c–d are the HRTEM images of the interface of the cross-section in the sample. From Fig. 3d, the measured lattice fringes are 0.313 nm and 0.317 nm, which correspond to the {0 0 2} crystallographic plane of the hexagonal ZnS and {1 0 1} crystallographic plane of the hexagonal CdS, respectively, as indicated in the XRD powder diffraction file (36-1450 and 65-3414). Therefore, both the XRD patterns and HRTEM images show the existence of the wurtzite structure for ZnS/(CdS/ZnS)_n ($n = 2, 4, 8$) superlattices.

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