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Phase controlled synthesis and optical properties of ZnS thin films by pulsed laser deposition

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ABSTRACT

Both zinc-blende and wurtzite ZnS thin films have been successfully synthesized on uncoated and Au-coated sapphire substrates by pulsed laser deposition (PLD). Structure phase transitions from zinc-blende phase to the mixture of zinc-blende and wurtzite have been observed with increasing temperature from room temperature to 500 °C for the ZnS thin films deposited on uncoated sapphire substrate, while only the wurtzite phase has been identified for the ZnS thin films deposited on Au-coated sapphire substrate. The SEM images show that the ZnS thin film deposited on Au-coated sapphire substrate has a high crystallinity over that of uncoated sapphire substrate. For all the prepared samples room-temperature photoluminescence (PL) measurements with a 325 nm excitation show two emission bands at ~405 nm and ~520 nm, respectively.

1. Introduction

Zinc sulfide, an important wide-bandgap semiconductor, possesses two distinct structures, namely, the wurtzite-type hexagonal structure with a stacking sequence of ABAB··· along the [0 0 0 1] direction and the zinc-blende-type cubic structure with a stacking sequence of ABCABC··· along the [1 1 1] direction [1]. ZnS thin films are mostly important in the production of devices such as short wavelength emitting laser diodes [2], photodetectors [3], flat-panel displays [4], thin-film electroluminescent devices [5]. For those applications, phase controls of ZnS thin films were critical to tune their physical properties to the appropriate ones. However, much more stable ZnS structure in nanoscale is the zinc blende structure [6,7], some groups have explored various synthesis methods of the wurtzite structure of ZnS thin films, such as chemical vapor deposition (CVD) [8], molecular-beam epitaxy (MBE) [9], atomic layer epitaxy (ALE) [10], sol–gel method [11], RF magnetron sputtering [12] and metal–organic chemical vapor deposition [13]. Nevertheless, there are currently no effective experimental approaches that provide a good method to control the crystal phase of ZnS films.

Pulsed laser deposition (PLD) has emerged as a potential technique for the fabrication of well-defined nanostructures and surface morphologies of various materials because of the ability to control the dimensions and the crystalline phase by varying the laser parameters and the deposition conditions. In previous works, some researchers had prepared ZnS thin films by PLD method. For instance, Xin et al. [14] reported firstly the epitaxial growth of high ZnS films on sapphire and silicon substrates using pulsed laser deposition. Yano et al. [15] prepared the ZnS thin film by PLD on quartz and studied its absorption and photocurrent properties. Chalana et al. [16] deposited ZnS thin films on quartz substrates using PLD and investigated the influence of argon ambience on the microstructural, optical and luminescence properties of ZnS thin films.

In this paper, using PLD method, we have achieved controllable growth for the crystalline phase of ZnS thin films through appropriate adjustment of substrate temperature during the growth process or coating an Au-layer on sapphire in advance. Furthermore, photoluminescence spectra of the ZnS thin films were investigated with a 325 nm excitation, and green emission bands related to S vacancies and other defects were observed for all the samples which is consistent with that of our prepared ZnS ceramics targets [17].

2. Experimental details

In this work, ZnS thin films were synthesized by ablating stoichiometric home-made target using pulse laser deposition technique. Depositions were carried out with a KrF excimer laser operating at 248 nm. The laser beam of energy density 8.8 J/cm^2 with a repetition rate of 5 Hz was used to ablate from the sintered ZnS target. Before deposition, the chamber was pumped down to a base pressure of 1.0×10^{-5} Torr. The distance between the target and substrate was maintained at 4 cm. During deposition, argon

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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 time of ZnS thin films is 60 min and the substrate temperature is varied from room temperature to 500 °C.

Structural and morphological characterization of ZnS thin films were carried out using X-ray diffraction (Shimadzu XRD-7000), and FESEM (Hitachi S-4800) equipped with an X-ray energy dispersive spectrometer (EDS). Absorption spectra and photoluminescence emission spectra were recorded at room temperature with UV-Vis-NIR spectrophotometer (Varian Cary-5000) and luminescence spectrophotometer (Edinburgh EPL-375), respectively.

3. Results and discussion

3.1. Micrographs and structural analysis

The surface morphologies of ZnS thin films were characterized by FESEM, as shown in Fig. 1. Fig. 1a–c shows the SEM surface morphologies of the samples deposited on uncoated sapphire with the substrate temperature at room temperature (RT), 300 °C and 500 °C, respectively. It can be seen that ZnS thin films are consisted of small grains and with some pores inside. Besides, the grain sizes of ZnS thin films become larger with the substrate temperature increasing. Fig. 1d is the SEM surface morphology of ZnS thin film deposited on Au-coated sapphire, it showed more uniform and compact microstructures with bigger grains.

Fig. 2a displays the cross-sectional SEM images of ZnS thin film deposited on Au-coated sapphire. It shows that the ZnS thin film has a uniform and dense fractural structure with a thickness of ~3 μm. The element quantitative analysis of EDS spectra for ZnS films shows the presence of Zn and S with an approximate atomic ratio of 1:1, as shown in Fig. 2b.

Fig. 3 displays XRD patterns of ZnS thin films on uncoated and Au-coated sapphire, and Fig. 3a reveals the XRD patterns of ZnS thin films on sapphire at RT, 300 °C and 500 °C, respectively. And the diffraction peaks at $2\theta = 28^\circ$ and 58° can be well indexed to the

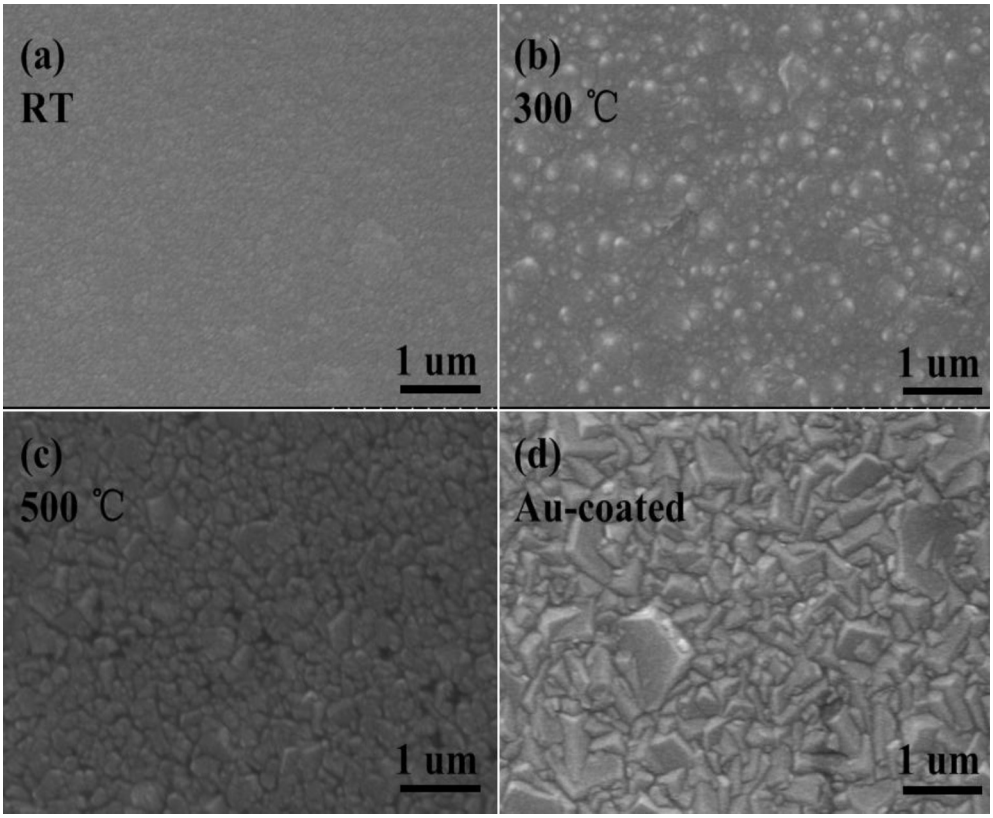

Fig. 1. SEM surface micrographs of ZnS films (a) at RT, (b) at 300 °C, (c) at 500 °C on uncoated sapphire substrate, (d) at 500 °C on Au-coated sapphire substrate.

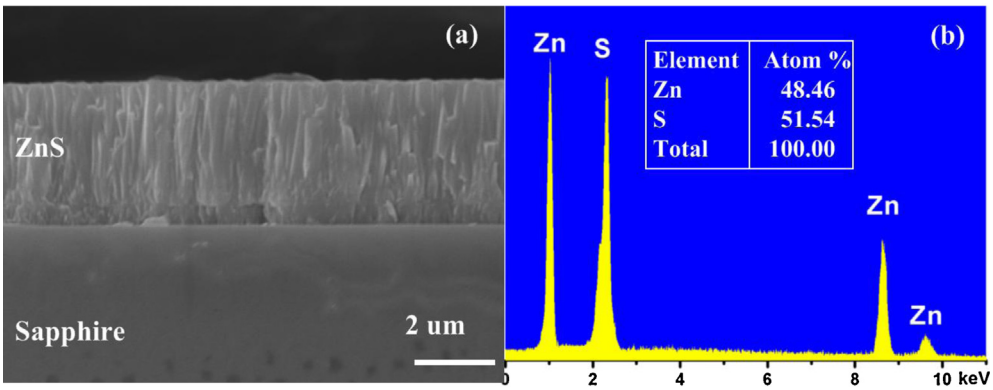

Fig. 2. (a) SEM cross-sectional micrograph of ZnS film on Au-coated sapphire substrate and (b) the localized EDS spectrums of the ZnS films.