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Surfactant and template free synthesis of porous ZnS nanoparticles

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HIGHLIGHTS

- ZnS thin films composed of porous nanoparticles have been deposited.
- Methodology is based on a combination of three techniques.
- Cubic phase ZnS nanoparticles deposited onto glass substrates.
- Films characterized by UV/Vis, PL, XRD, SEM, TEM, AFM and XPS.

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ABSTRACT

ZnS thin films composed of porous nanoparticles have been deposited on to glass substrates by combining three simple synthesis methodologies *i.e.* chemical bath deposition, co-precipitation and spin coating. The XRD results reveal the cubic phase of ZnS thin films crystallized at nano scale. The crystallite size estimated by Scherrer formula was 3.4 nm. The morphology of the samples was analyzed through scanning electron microscopy (SEM) and is evident that thin films are composed of porous nanoparticles with an average size of 150 nm and pores of 40 nm on almost every grain. Crystallinity, phase and morphology were further confirmed *via* transmission electron microscopy (TEM). The stoichiometry and phase purity of thin films were determined by energy dispersive X-ray (EDX) spectrum and X-ray photoelectron spectroscopy (XPS) analysis, respectively. The surface topography and homogeneity of thin films were analyzed by atomic force microscopy (AFM) and obtained root mean square roughness (4.0326 nm) reveals the morphologically homogeneous growth of ZnS on glass substrates. The UV–Vis spectroscopy and photoluminescence (PL) were carried out to estimate the band gap and observe the emission spectra in order to speculate the viability of ZnS porous nanoparticles in optoelectronic devices and sensors.

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1. Introduction

In the recent years, extensive studies have been carried out on the synthesis/deposition and characterization of large band gap semiconductors due to their applications in photovoltaic, photo-electrochemical energy conversion and photoconductors [1,2]. ZnS is an important II-VI semiconductor with large band gap and have been studied extensively regarding its viability in above mentioned applications. Porous nanoparticles, thin films and structures have attained focus of research since they exhibit novel properties and have many applications in photo-catalytic, luminescent and sensing devices [3–5]. Several methods have been employed to synthesize ZnS thin films including: chemical spray

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pyrolysis [6,7], solvothermal synthesis [8,9], sol-gel [10], successive ionic layer adsorption and reaction (SILAR) [11], pulsed laser deposition (PLD) [12], metal-organic chemical vapor deposition (MOCVD) [13], RF-mganetron sputtering [14,15], electrodeposition [16,17], thermal evaporation [18], electron beam evaporation [19], aerosol assisted chemical vapor deposition (AACVD) [20,21] and chemical bath deposition (CBD) [22–30]. Amongst all, CBD is a simple and cost effective method to deposit high quality thin films at relatively low temperatures without need of ultra-high vacuum and sophisticated instrumentation. Synthesis of un-doped and doped ZnS nanoparticles by various methods has also been reported previously. Most recently, Zhu et al. [31] reported the sonochemical synthesis of mesoporous ZnS nanocrystals without using template/surfactant. The prepared nanomaterials exhibit higher photo-degradation activity of Rh under UV irradiation than that prepared in absence of sonochemistry or in an aqueous system. Pathak et al. [32] reported the synthesis of un-doped and cobalt doped ZnS nanoparticles by co-precipitation method. However literature suggests that the study and growth of porous ZnS nanoparticles is lacking. To the best of our knowledge, the deposition of porous ZnS nanoparticles on glass substrates without use of surfactants or templates by any of the chemical technique or combination of them has not been reported yet. However, few reports have been published on study of luminescent properties of ZnS thin films deposited on porous substrates (Si) by different techniques [33].

We have reported the deposition of uniform ZnS thin films by an optimized CBD method [34]. Herein, we report a novel approach to deposit thin films composed of porous ZnS nanoparticles by simple CBD/co-precipitation and spin coating method. The observed green PL emission of the ZnS nanoparticles and their porosity are important factors for the development of novel luminescent devices and sensors.

2. Experimental

2.1. Chemicals

All reagents, zinc chloride, thioacetamide, urea and hydrochloric acid were purchased from Sigma-Aldrich and used without further purification. The de-ionized water was used as solvent. Acetone and isopropyl alcohol (IPA) were used for cleaning of the glass substrate. Glass substrates have already been established as the best substrates to study the optical properties of the thin films as compared to sapphire or MgF_2 substrates due to their negligible interaction on the optical properties of the material deposited onto them. Analytical grade ethanol was used for spin coating the films.

2.2. Instruments

X-Ray diffraction measurements were performed using Bruker D8 advance Diffractometer with Cu-Ka radiation. Data were recorded across a 2θ range of 20–80° with a step size of 0.05°. SEM and EDX analyses were carried out using Philips XL 30 microscope. TEM, HRTEM and SAED images were collected from Tecnai 20 F30 transmission electron microscope using accelerating voltage of 200 kV. An atomic force microscope (AFM) PeakForce QNM was used to measure surface roughness of the ZnS thin films. Absorbance and transmittance spectrum was acquired using Agilent HP 8453 UV–Vis spectrophotometer. Fluorolog 22 HORIBA JOBINYVON was used to obtain photoluminescence data using excitation wavelength of 340 nm.

2.3. Synthesis of porous ZnS thin films

The synthesis of porous ZnS thin films was carried out in three steps by using CBD, co-precipitation and spin coating, separately.

2.3.1. CBD/co-precipitation

Chemical bath deposition/co-precipitation of ZnS was carried out first. Chemical bath containing zinc chloride (0.2 M), urea (3 M) and thioacetamide (0.4 M) was used to synthesize ZnS. The solutions of zinc chloride (40 mL), thioacetamide (40 mL), and urea (20 mL) were mixed in a beaker to get total volume of 100 mL bath solution. The pH of bath solution was adjusted to 4.0 by drop wise addition of 1.0 M HCl. The stirred bath solution was maintained at a temperature of 80 °C. The reaction process for the formation of ZnS in CBD is based on, first the slow release of zinc and sulfur ions within the solution followed by condensation of these ions [30]. Balance between hydrolysis and condensation can be adjusted by the presence of urea in the solution [35]. Conventionally, in CBD, the deposition of thin films would be carried out under uniform magnetic stirring to avoid precipitation throughout the reaction time. After the deposition of thin films, the reaction mixture is usually disposed. In the present experiment, the mixture was stirred for 3 h at 80 °C and then the stirring was stopped while the mixture was further heated for 1 h. The heating was stopped and the white precipitate formed was centrifuged and washed three times with methanol to remove the byproducts of reaction. The precipitate was then dried under vacuum at room temperature and kept under nitrogen. The powder obtained after drying was then used to deposit the thin films of ZnS on glass substrates by spin coating.

2.3.2. Spin coating of ZnS thin films

The dried powder was aged at room temperature under nitrogen stream for 24 h to avoid oxidation. For spin coating, powder samples were dispersed in ethanol and were deposited on precleaned glass substrates. The solution was spun at 500 rpm for first 5 s and then at 3000 rpm for further 25 s in order to achieve uniform coating of material onto the substrates. Three subsequent layers were deposited to achieve workable thickness of the samples. After deposition, all the samples were annealed under nitrogen atmosphere for one hour in tube furnace at 400 °C to remove any volatile by-products and improve the crystallinity before further characterization.

3. Results and discussion

3.1. Structural studies

Fig. 1 shows the typical X-ray diffraction pattern of ZnS films. The diffraction peaks are intense and broad, suggesting the formation of crystallites with size in the nano regime. The major peaks of pure ZnS are observed. Three broad peaks corresponding to the (111), (220) and (311) lattice planes are well matched with reported data (ICSD # 01-080-0020) and can be assigned to the cubic phase of ZnS. The vertical lines on x-axis represent the standard pattern of cubic ZnS. The XRD pattern shows that the thin films are single phase since there is no diffraction peak regarding any impurity or other (hexagonal) phase of ZnS. A small but bit broader peak (hump) observed between the 2θ values of 20–25° is due to glass substrate.

From the full width at half maximum (FWHM) of most intense peak (111), the average crystallite size was estimated by Scherrer's equation as; $D = 0.9\lambda/\beta\cos\theta$, where D is the crystallite size, λ is the X-ray wavelength of Cu-Kα radiations (1.5405Å), β is the full width

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