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PREPARATION AND CHARACTERIZATION OF NANO-STRUCTURED ZnS THIN FILMS GROWN ON GLASS AND N-TYPE Si SUBSTRATES USING A NEW CHEMICAL BATH DEPOSITION TECHNIQUE

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Abstract. Nano-crystalline zinc sulfide thin films were prepared by a new chemical bath deposition (CBD) technique onto glass and n-type (111)-oriented silicon substrates. Deposition took place at a temperature of 70 °C and a pH of 6.0, from an aqueous solution containing zinc acetate, thioacetamide, and ethylenediamine. Structural analysis using atomic force microscopy shows that the films deposited on silicon substrates contain 28-30 nm clusters, whereas much larger clusters (around 80-120 nm), comprise the films deposited on glass substrate. X-ray diffraction analysis indicates that both the film and powder formed in the reaction bath have cubic zincblende structure and the clusters in microstructure images are coalescences which they compose of nano-crystallites of about 4.5-13 nm in diameter. UV-Vis spectrophotometry measurements give an average transparency of around 70-80% in the visible range (400-700 nm) for the films with different thicknesses and deposition times. Direct band gap energy of these samples was measured to be in the range of 3.97-4.00 eV. Fourier transform infrared spectrum of the films reveals no peak due to any impurity.

1. INTRODUCTION

Recently, the II-VI compounds semiconductor thin films (e.g. CdS, ZnS, CdSe, ZnSe) have received an intensive attention due to their application in thin film solar cells, optical coatings, optoelectronic devices, and light emitting diodes [1-4]. Among these metal chalcogenides, ZnS is an important semiconductor material because of its broad, direct band gap energy (~3.6 eV) at room temperature [5]. Various techniques have been employed to fabricate ZnS thin films, such as, electrodeposition [6], pulsed-laser deposition [7], chemical vapor deposition (CVD) [8], molecular beam epitaxy (MBE) [9], spray pyrolysis [10], and chemical bath deposition (CBD) [11]. Among these, the CBD method is much more attractive since the technique possesses a number of advantages over the conventional thin film deposition methods including the simplicity in experimental set up. It does not require an expensive vacuum system. The chemical bath deposition process uses a controlled chemical reaction to deposit a thin film by precipitation. This technique is based on controlled release of the metal and sulfide ions [12]. The main advantages of the CBD method are low cost, low deposition temperature, easy coating of large surfaces, and having the capacity to deposit optically smooth, uniform, and homogeneous layers [13]. In addition, the method is free of some inherent problems associated with high-temperature

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techniques. These problems involve increasing the point defect concentration, evaporation, and decomposition of metal chalcogenide thin films. Polycrystalline or amorphous ZnS thin films have been grown via chemical bath deposition (CBD) method by many research groups [14-17]. Most of these works are based on the use of an alkaline solution of ammonia or hydrazine as a complexing agent for zinc ions.

In this work, we report the deposition of nanocrystalline zinc sulfide thin films on the glass and n-type crystalline Si substrates using a weak acidic bath in which ethylenediamine acts as a complexing agent and thioacetamide acts as a source of sulfide ions. Atomic force microscopy (AFM), X-ray diffraction (XRD), and UV-Vis spectrophotometery techniques are used to investigate the surface morphology, structural, and optical properties of the nano-structured ZnS thin films. We have shown that, the morphology and surface roughness of the ZnS thin films depend on the type of the substrate.

2. EXPERIMENTAL DETAILS

The commercially available glass (Microscope Slides, Hirschmann, Techcolor, Germany) and n-type crystal silicon (MaTecK Gmbh Co., Germany) were used as the substrates. Before the deposition, the glass slides were placed in sulphochromic acid solution for 12 hours, washed with de-ionized water and finally dried in an oven at 90 °C. The as-received (111)-oriented n-type Si wafers were etched with HF (10%) for two minutes, washed with de-ionized water, cleaned with acetone and finally dried. Zinc acetate dehydrate [$Zn(CH_3COO)_2,2H_2O$], thioacetamide (CH_3CSNH_2), and ethylenediamine ($NH_2CH_2CH_2NH_2$) of analytical reagent grade were purchased from Merck Chemical company. All the reagents were used as received. Aqueous solutions of 1 M zinc acetate dehydrate, 0.5 M thioacetamide (TAA), 2 M HCl, and 1 M ethylenediamine (En) were used for ZnS thin films deposition. First, 5 ml zinc acetate and 10 ml Ethylenediamine were mixed in a beaker and stirred for several minutes to get a clear and homogeneous solution. The pH value of the obtained solution was measured to be 8.4, and then some small amount of HCl was added to the solution in order to reduce the pH to 6.5. Thereafter, 40 ml TAA was added under stirring condition. Finally, a few drops of HCl were added to fix the solution pH at the value of 6.0. The glass or Si substrates were then immersed vertically in the solution. The beaker was sealed with a teflon tape and was placed in a thermostat bath set at a desired temperature (70±0.5 °C). The depositions were carried out in the time intervals of 4 hours. The deposition process was then repeated in order to obtain the films with different thicknesses. After each deposition stage, the samples were taken out from the beaker and cleaned with de-ionized water. The powdery and less-adherent ZnS particles were removed by washing the sample with distilled water. The films, as they were grown appeared to be in a gray-blue color -exhibit a good uniformity and adherence and they can be used as new substrates to deposit thicker films.

X-ray diffraction (XRD) patterns were recorded in the thin film grazing angle mode with an automated X' pert Philips instrument with Cu Kα radiation (40 kV and 30 mA) for 2θ values over 20–60°. The optical absorption studies were carried out with a Cam Spec M350 double beam spectrophotometer. In order to investigate the surface morphology and surface roughness, the atomic force microscopy (AFM) observations were performed using an AFM Auto Probe CP from Park Scientific Instruments in the contact mode with a high resolution scanner (1×1 μm^2). The AFM images were analyzed with the Pro Scan software (Park Scientific Instruments), calculating the root mean square surface roughness value. Infrared spectrum was recorded on BRUKER EQUINOX 55 Fourier transform infrared (FTIR) spectrometer in the range of 200–6000 cm^{-1} with a resolution of 0.5 cm^{-1}. For Rutherford backscattering (RBS), 2.3 MeV He^+ ions were used as incident ions and the backscattered particles were detected by a silicon surface barrier detector at a 165º scattering angle relative to the incident beam. The chemical composition of the thin films was also determined by RBS measurements.

3. RESULTS AND DISCUSSION

3.1. Reaction mechanism

Chemical bath deposition refers to the deposition of films on a solid substrate from a reaction occurring in an aqueous solution. In the CBD of ZnS, the trick is to control the rate of these reactions so that they occur slowly enough to allow the ZnS molecules to form gradually on the substrate or to diffuse there and adhere either to the substrate itself or the growing film, rather than to aggregate into larger particles in the solution and to precipitate out. In this technique, a soluble salt of the required metal is dissolved in an aqueous solution to release cations. Non-metallic element is provided by suitable source compound. The anions and cations then react and form the compound. The ZnS thin film can be pre-

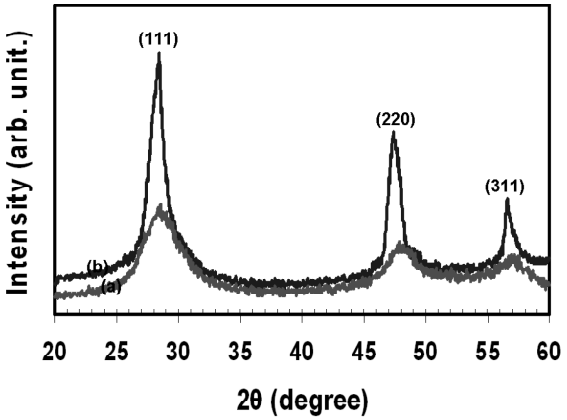


Fig. 1. X-ray diffraction patterns of the ZnS film deposited on; a) glass substrate, and b) the precipitated ZnS collected from the same reaction bath.

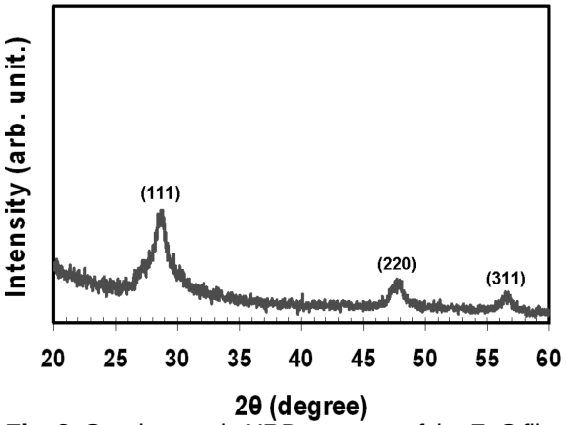
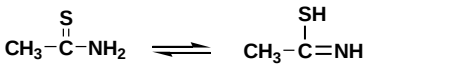
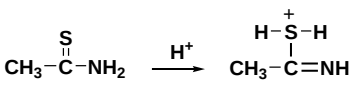


Fig. 2. Grazing angle XRD patterns of the ZnS film deposited on n-type Si substrate.

pared by the decomposition of thioacetamide in a weak acidic solution containing zinc salt. We used zinc acetate and TAA as material sources. In this technique the complexing agent plays an important role. We used ethylenediamine (En) as the complexing agent to control the slow release of Zn^{2+} ions, which reacts with HS^- ions (released from TAA) to form ZnS thin films. The chemistry of the ZnS formation from the used reagents, during the deposition process, can be written as [18]:


(1)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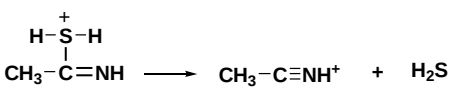
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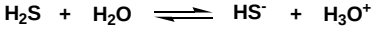
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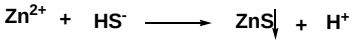
(5)


(6)

3.2. XRD studies

Zinc sulfide exists in sphalerite, cubic (zincblende) and hexagonal (wurtzite) forms. The cubic form is stable at room temperature, while wurtzite, the less dense hexagonal form, is stable only above the temperature of 1020 °C at atmospheric pressure [19]. In the present experiment, the X-ray diffraction pattern of ZnS films after a single deposition process (for 4 hours) did not exhibit any peak, suggesting that the deposited film is very thin. In order to get thick enough films, multiple depositions therefore were performed on existing ZnS film. Figs. 1a and 1b, respectively show the X-ray diffraction patterns of the ZnS film grown on glass substrate and, the ZnS powder formed in the same reaction bath. Comparing these two patterns indicates that the film has lower X-ray intensity and higher full-width at half-maximum (FWHM) than the precipitate powder, suggesting that only relatively small size nano-crystalline ZnS particles have enough energy to deposit on to substrate. The XRD patterns of the precipitated ZnS powder and the ZnS film exhibit three distinguished peaks corresponding to diffraction of the (111), (220), and (311) planes of the cubic phase [20]. The average nano-crystalline size (D) was calculated using the Debye-Scherrer formula [21].

$$D = \frac{0.9\lambda}{\beta \cos\theta}, \qquad (7)$$

where λ is the X-ray wavelength ($CuK\alpha_1$ radiation and equals to 0.154 nm), θ is the Bragg diffraction angle, and β is the FWHM of the XRD peak appearing at the diffraction angle θ. The average crystalline size is calculated from X-ray line broadening using (111) peak and Debye-Scherrer equation to be about 4.5 nm.

Fig. 2 shows the XRD patterns obtained by scanning 2θ in the range of 20-60°, with a grazing angle of 1.5° for a deposited ZnS film (~ 1 μm thick) onto

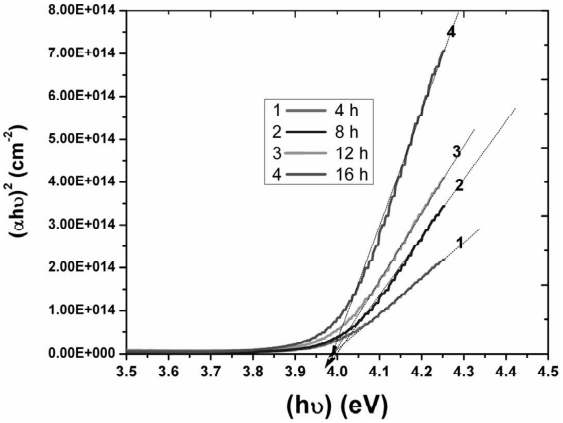


Fig. 3. UV-Visible transmission and reflection spectra of the ZnS films on glass substrate deposited at pH 6.0 and 70 °C as a function of the number of 4-hours deposition cycles.

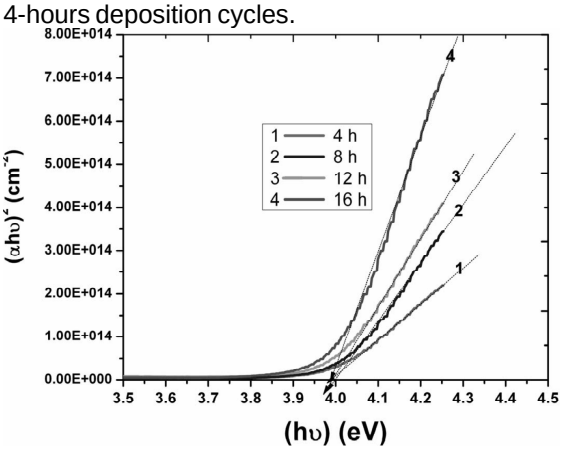


Fig. 4. Plots of $(\alpha h\nu)^2$ versus $h\nu$ for the ZnS films using 1-4 hours deposition cycles.

(111)-oriented Si substrate. The three distinguished peaks at the angles of 28.6°, 47.7°, and 56.5° reveal a cubic lattice structure and can be assigned to the (111), (220), and (311) plans, respectively. Broadening of diffraction peaks in the XRD pattern of the ZnS film is attributed to the nanometer-sized crystallines. The calculated average size of nanocrystallines, using Debye-Scherrer equation is found to be about 8 nm.

3.3. Optical properties

The optical transmission measurements of ZnS thin films deposited on glass substrates were determined in the wavelength of 250–900 nm. Fig. 3 shows the optical transmittance and reflectance spectra for a series of ZnS films deposited for 4, 8, 12, and 16 hours from a chemical bath at pH of 6.0 and the temperature of 70 °C. The average transmittance of these films- in the visible wavelength region -is calculated to be 84%, 78%, 74%, and 71%, respectively. This result is comparable to one which reported by Cheng *et al*. [22], who measured the optical transmittance of 70% in the visible region. As it is clear from spectra, the films have a steep optical absorption feature, indicating good homogeneity in the shape and size of the nano-crystallines and low defect density near the band edge [23]. The optical absorption coefficients (α) were calculated using the following equation [24]:

$$T = (1-R)\exp(-\alpha t), \tag{8}$$

where T is transmittance, R is reflectance, and t is the film thickness. The absorption coefficients (α) were analyzed using the well-known relation for near edge optical absorption of semiconductors [25]:

$$\alpha h\nu = K\left(h\nu - E_g\right)^{\frac{n}{2}}, \tag{9}$$

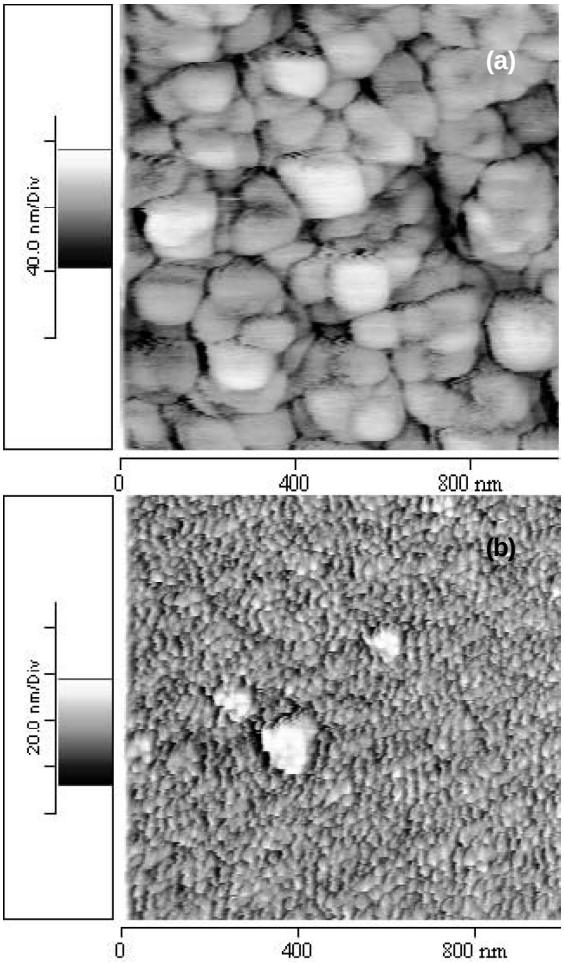


Fig. 5. Two-dimensional AFM images of ZnS thin films deposited on a) glass, and b) Si substrate.

where K is a constant, which is usually taken to be unit, E_g is the separation between valance and conduction bands of semiconductor (band gap energy), and n is a constant. n for direct band gap semiconductor materials is taken to be unit. Variation of $(\alpha h\nu)^2$ as a function of photon energy ($h\nu$) is plotted in the Fig. 4. As observable, $(\alpha h\nu)^2$ varies linearly with ($h\nu$) after a certain amount of photon energy, confirming the direct nature transition mode in the ZnS films. The band gap energy is obtained by extrapolating the straight portion of the curve to zero absorption coefficients. In this work the band gap energy (E_g) was determined to be in the range of 3.97-4.00 eV for the ZnS films with deposition times varying from 4 to 16 hours. These values are rather larger than the literature value for the bulk ZnS (~ 3.6 eV) [19]. The result could be attributed to the quantum size effects as expected from the nanocrystalline nature of the ZnS thin films [26, 27].

3.4. Surface morphology

Atomic force microscopic (AFM) allows us to get microscopic information on the surface structure and to plot topographies representing the surface relief. This technique offers digital images which allow quantitative measurements of surface features, such as root mean square roughness, R_q, or average roughness R_a, and the analysis of images from different perspectives, including three-dimensional simulation [28]. Figs. 5a and 5b illustrates two-dimensional AFM images of the ZnS thin films deposited on a commercial glass slide and (111)-oriented Si substrates, respectively. The thin film deposited on glass substrate is made of aggregates (clusters) with a square-like surface morphology, whereas much finer aggregates with an isosceles triangular surface morphology comprise the film deposited on Si substrate. As observable, the films deposited on the Si substrate contain smaller clusters (average grain size of around 28-30 nm in diameter) and have more surface aggregates than those deposited on glass substrate (average grain size of around 80-120 nm in diameter). Smooth and regular surfaces are observed on thin films deposited on the Si substrate. The root mean square roughness (R_q) and the average roughness (R_a) were found to be 2 nm and 3 nm, respectively. For the thin films deposited on glass substrate, it is obvious that the surface of the thin films is rough and irregular with calculated R_q and R_a values of 5.2 nm and 4.6 nm, respectively. It is important to note that these obtained values are averaged and there is a statistical variation associated with them, which depends on the location of the measurements that are performed on the samples [29]. To minimize these errors, we have performed many measurements of each parameter in different locations on the surface of samples.

3.5. FTIR Characterization

In order to investigate the presence of organic compounds as impurities in the ZnS films, we considered the Fourier transform infrared (FTIR) spectrum of the zinc sulfide powder collected by scraping the surface of the ZnS films deposited in the same conditions. The existence of isothiocyanate groups (-N = C = S), Zn-O, Zn-OH, and absorbed H_2O in chemically deposited ZnS thin films have been reported by many research groups [30-32]. The analysis of absorption spectrum for the ZnS powder shows two very weak peaks at 737 and 1427 cm^{-1} which can be attributed to C=S bending mode and C-Cl stretching mode, respectively [32]. We did not observe any peaks corresponding to impurities, such as Zn-O, Zn-OH, and -N = C = S in FTIR spectrum of the ZnS powder and observed only a broad and weak peak at 3260-3600 cm^{-1}. This peak can be assigned to the presence of a trace amount of adsorbed water in the films which disappears by annealing. Therefore the bands appearing in the 3200-3600 cm^{-1} region can be attributed to the O-H stretching modes of water [33].

4. CONCLUSION

We have successfully deposited the nano-crystalline ZnS thin films onto glass and n-typ (111)-oriented Si substrates, from a chemical bath at the temperature of 70 °C, by using ethylenediamin as a complexing agent. The XRD measurements indicate that the structure of the ZnS thin films is cubic. In our experiment, based on the optical transmission measurements, the band gap energies are calculated to be between 3.97-4.00 eV for the ZnS films with different thicknesses. The result promises a potential application of chemical bath deposited ZnS thin films for the solar cells. Morphology and optical properties of the ZnS films were characterized using AFM and UV-Visible spectroscopy.

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