INFLUENCE OF AN AQUEOUS/ETHANOLİC SOLUTİON ON THE STRUCTURAL AND ELECTRİCAL PROPERTIES OF POLYCRYSTALLİNE ZnS FİLMS

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Polycrystalline zinc sulfide (ZnS) films were prepared on glass substrates using a chemical bath deposition (CBD) technique in an aqueous/ethanolic solution. The films were characterized by X-ray diffraction (XRD) and electrical conductivity measurement. The XRD studies revealed that the deposited films have a polycrystalline and the hexagonal structure. The electrical measurements of the samples are performed using a dc four-probe technique on rectangular-shaped samples. The influences of various parameters such as temperature and solvent polarity (ethanol/water volume ratio) on the properties of the films were studied in detail.

(Received May 14, 2012; Accepted June 12, 2012)

Keywords: ZnS, Spray pyrolysis, Structural Properties

1. Introduction

Zinc sulfide (ZnS) films, with a wide direct band gap and n-type conductivity, are promising for optoelectronic device applications, such as electroluminescent devices and photovoltaic cells. In optoelectronics, ZnS can be used as a light-emitting diode in the blue-toultraviolet spectral region owing to its wide band gap of 3.7 eV at room temperature [1]. In the area of optics, ZnS can be used as a reflector and a dielectric filter because of its high refractive index (2.35) and high transmittance in the visible range, respectively [2, 3]. Several techniques such as molecular beam epitaxy [4], H2 plasma chemical sputtering [5], metal organic chemical vapour deposition (MOCVD) [6], metalorganic vapour phase epitaxy (MOVPE) [7] and liquid phase techniques such as electrochemical deposition [8] and chemical bath deposition (CBD) [9– 13] have been used to produce ZnS films. Among them, CBD is the least costly and is a lowtemperature technique. The CBD process uses a controlled chemical reaction to effect the deposition of ZnS film by precipitation. In the most typical experimental approach, substrates are immersed in an alkaline solution containing the chalcogenide source, metal ions, an added base and a complexing agent. The deposition of ZnS by using CBD is a more difficult proposition than the deposition of CdS. It is evident that there is a much wider range of conditions in which the concurrent deposition of ZnS and zinc oxide can occur [14]. When the ZnS film is doped with a small amount of metallic ions, it emits light in the visible region, which is characteristic of the incorporated impurity. Therefore, it forms a very important class of phosphors for the fabrication of electroluminescent devices. For example, ZnS:Cu has turned out to be a good CRT phosphor and is applied in, for example, colour TVs and oscilloscopes. Therefore, the luminescent properties of ZnS phosphors doped with metallic ions have been discussed extensively in the literature, and information on the properties of such phosphors can be found in many books dealing with luminescence [15–17]. In this work, polycrystalline ZnS films were prepared using

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the CBD technique in an aqueous/ethanolic solution. Their characterization was done by means of XRD. Electrical conductivity measurements of ZnS films were carried out in a temperature range of 300–400 K. The temperature-dependent conductivity of these films was explained in terms of the thermally activated conduction mechanism.

2. Experimental details

Before developing ZnS films on glass substrates, a cleaning process was applied to the substrates. First, the glass substrates were put into a cup of distilled water and kept there for 10 min to remove contaminants such as dust on their surfaces. Then they were taken from the cup and dried. A similar cleaning treatment in an NaOH solution followed by an H₃PO₄ solution was performed to remove the remaining contaminants. After completing the cleaning processes of the substrates, solutions to be used for forming ZnS films on the surface of the substrates were prepared by using a well-known method. Commercially available, optically pure glass plates (size: $20 \times 25 \times 2$ mm) were used as the substrate to deposit films. The deposition of polycrystalline ZnS films on glass substrates was carried out by a chemical bath technique. The deposition of ZnS films by using the CBD technique in a zinc chloride-ammonia-thiourea system consisted of: complexation of zinc cations by ammonia and the consecutive reaction with the sulfide ions provided by hydrolysis of thiourea. The chemical bath solution consisted of 0.147 mol Γ^1 of zinc chloride (ZnCl₂), 0.262 mol l⁻¹ of thiourea (CS(NH₂)₂), 10 ml of 30% ammonia solution (NH₄OH) and 5.0 ml of hydrazine hydrate (N₂H₄). The deposition was carried out in a 50 ml beaker at different bath temperatures of 70, 75 and 80 °C for a deposition time of 1.5 h. The bath pH was optimized between 9 \pm 0.5 by the addition of ammonia solution. In this study, different ZnS films were developed using varying molar ratios of complexation of the zinc chloride-thiourea system to the ethanolic solution (1:10, 1:20, 1:30 and 1:40). These mixtures were poured into a beaker and heated to 80 °C with the same bath pH. After the deposition, the samples were taken out from the bath, washed in distilled water and dried at 80 °C for 15 min in a hot air oven. The structural characterization of deposited films was carried out by the X-ray diffraction (XRD) technique on a Bruker AXS D5005 diffractometer (monochromatic CuK_a radiation, $\lambda = 1.54056$ A). The electrical measurements of samples were obtained by the dc four-probe technique on rectangular-shaped samples with an area of 0.5×1 cm². A Keithley 6500 sourcemeter was used to provide constant current and the potential drop was measured by a Keithley 2700 multimeter through an interface card. These were controlled by a computer. Platinum wires with a diameter of 1 mm were employed as current and potential electrodes. The measurements were carried out in the temperature range 300–400 K. The temperature of the sample was changed by a controllable Nabertherm-type P 320 heater and measured by a standard thermocouple.

3. Results and discussions

The ZnS films obtained by this method were green and pink in colour, very compact, continuous and adhered very well. Figure 1 shows X-ray spectra obtained for ZnS films with different deposition temperatures such as 70, 75 and 80 °C. The XRD of the ZnS film (figure 1) is found to be polycrystalline with preferential orientation along the (0 0 2) plane; the other



Fig. 1. XRD spectra for ZnS films deposited at different bath temperatures.

visible secondary peaks are (1 0 0) and (1 0 1). These peaks are of much lower intensity than the (0 0.2) peak. All the peaks are associated with hexagonal ZnS and no major zinc or sulfide peaks are seen. XRD results obtained at 80 °C for 4.5 h using tri-sodium citrate agree well with that reported for ZnS [18] obtained on glass substrates at 80 °C for 4 h using tri-sodium citrate as a complexing agent by the CBD technique. The ZnS films that were prepared at different deposition temperatures have not revealed diffraction peaks, which are indicative of amorphous materials. As the deposition temperature increases, the intensity of the ZnS (0 0 2) peak increases and becomes narrower, indicating an improvement in the crystallinity. This indicates that the grain size of the films increases with an increase in the deposition temperature. The best diffraction peak was obtained at 80 °C for 1.5 h. Moreover, the full-width at half-maximum (FWHM) in the XRD diffraction peak decreases with the deposition temperature, indicating an enhancement of the crystallinity. In general, ZnS films would crystallize in both cubic (sphalerite or β -ZnS) and/or hexagonal (wurtzite or α -ZnS) structures, depending on the synthesis conditions such as the temperature and precursor concentrations. More recently, Lee et al [19] and Hichou et al [20] reported a cubic phase and a combination of cubic and hexagonal phases, respectively, for ZnS films grown by different deposition techniques. Figure 2 shows the XRD patterns of as-prepared ZnS films prepared by CBD at 80 °C for 1.5 h from ethanol-aqueous mixed solutions with different ethanol concentrations. This film is crystallized as hexagonal type (α -ZnS phase) or cubic type (β -ZnS) with a strong peak corresponding to the (002) or (111) directions, respectively. A comparison between our data and standard data from JCPDS shows that ZnS films obtained in this study have a hexagonal structure [21]. Films were analysed by XRD to investigate the effect of ethanol-aqueous concentrations on a crystalline ZnS film.



Fig. 2. XRD patterns of ZnS films with different molar ratios of aqueous to ethanol solutions containing (a) 1:10, (b) 1:20, (c) 1:30 and (d) 1:40.

The films originally consisted of mainly hexagonal crystals. Even when a high ethanol concentration was used, the same crystalline structure remained. It can be seen from figure 2 that ZnS films prepared by the CBD technique show an amorphous nature with the $(0\ 0\ 2)$ peak of very low intensity corresponding to the hexagonal ZnS structure. When the ethanol concentration decreases, the intensity of the diffraction peaks increases and the width of the

 $(0\ 0\ 2)$ plane diffraction peak becomes narrower. This behaviour is due to the fact that the starting materials (aqueous solutions) and undesired by-products (ethanolic solution) are present in the films, suggesting that the excess concentration of ethanol content may not make for completing the chemical reaction, e.g. causing a partial decomposition of the starting materials.

It can be said that ZnS films prepared with decreasing ethanol concentrations are polycrystalline materials and present a single phase with a hexagonal structure [22]. Further observation shows that a unique feature of all the diffractograms is that they contain the characteristic ZnS orientations along the preferred (0 0 2) plane. This preferred orientation remains predominant irrespective of ethanol concentration. Therefore it has been reported that the preferred orientation of the ZnS film on the glass substrate is affected by source compounds. It can be concluded that the concentration of ethanol in the reaction medium plays a crucial role in the nucleation growth and phase transformation of ZnS films during the process.

It has been found that the volume ratio of aqueous solutions to ethanol significantly affects the structure of the produced films. It is observed that the peak intensities of the hexagonal phase steadily become stronger and the width of the diffraction peak of the hexagonal phase becomes slightly narrower with decreasing ethanolic concentrations, indicating the formation of greater ZnS crystallites and an improvement of the crystallization of ZnS. The improvement in crystallinity is due to the increased ability of the atoms to move towards stable sites in the lattice. The lack of any peak shifting also supports this, since the incorporation of atoms into interstitial sites should result in some change in the overall lattice parameter of the polycrystalline structure. Liu *et al* [23] have observed the same correlation in their work. Therefore, there are two possibilities to improve the crystallinity of the films: an increase in grain size to decrease the number of grain boundaries and a decrease in barrier height at the grain boundaries.

With decreasing ethanol content, grains nucleate from the amorphous matrix and grow in size. XRD intensity is observed to increase as does grain size and the hexagonal crystallinity of the samples. This is ascribed to the fact that the lower ethanol concentration in ethanol-aqueous mixed solutions enhanced the hydrolysis of precursors, phase transformation from amorphous to hexagonal and grain growth. The appearance of larger particles at the minimum ethanol concentrations suggests that the minimum ethanol concentrations enhance grain growth via a dissolution reprecipitation mechanism (i.e. Ostwald ripening) in which larger particles grow at the expense of smaller ones [24]. Thus, at the maximum content of the ethanol, these grains are observed to decrease slightly, resulting in a decrease in XRD intensity and an increase in FWHM. The appearance of cracks in the amorphous matrix may indicate the release of lattice strain due to a lattice mismatch between the substrate and the films. Since these cracks appear concurrently with the appearance of crystallites, it is also possible that they may be due to strain relief associated with the growth of those crystals. In light of this microstructural information, the decrease in porosity with decreasing ethanol concentration is possibly due to the bridging of fine particles and formation of closed pores. There is no apparent secondary phases present in the grain interior or at the grain boundaries. And it is also known from the XRD analysis that only the hexagonal phase is present within this range of ethanol-aqueous contents.

It is known [25, 26] that there is a strong correlation between the electronic transport properties of polycrystalline semiconducting films and their structural characteristics. Particularly, both the values and the variation of the electrical conductivity of such films are in connection with their structure and its changes. On this basis, the study of the temperature dependence of the electrical properties of the films may offer useful information about possible changes of the structural characteristics of the films. The conductivity (σ) measurements were carried out in the temperature range of 300–400K using the dc two-point probe method and explained in terms of the thermally activated conduction mechanism. Since our experimental data fit the relationship

$$\sigma = \sigma_o \exp\left(\frac{-E_a}{kT}\right) \tag{1}$$

where σ is the measured electrical conductivity, *T* is the absolute temperature, σ_0 is the conductivity pre-exponential factor, E_a is the activation energy and *k* is Boltzmann's constant. Figure 3 shows the plots of $\ln \sigma$ versus 1000/T, which are linear for four representative ZnS films of different aqueous–ethanol concentrations 1:10, 1:20, 1:30 and 1:40, confirming that the conduction in the concerned range of temperature is through the thermally activated process and the increase in conductivity with temperature is exponential. Maity and Chattopadhyay [27] also made a similar observation on the conductivity behaviour in transparent conducting oxides. It is seen that conductivity increases with temperature, indicating the semiconducting nature of films. Presentations of the temperature dependence of



Fig. 3. Plot of log σ versus 1000/T of ZnS films with different molar ratios of aqueous to ethanol solutions containing (a) 1:10, (b) 1:20, (c) 1:30 and (d) 1:40.

conductivity according to equation (1) are given in figure 4 at high temperatures. This graph shows that thermally activated conduction can be found in the high-temperature part of conductivity. The experimental data on the films show a good fit with equation (1). The increase in the conductivity of the samples with temperature is due to a decrease in grain boundary concentration and an increase in ionized defects. The activation energies calculated from the local gradients of $\ln \sigma$ versus inverse temperature are found to be 0.66, 0.75, 0.82 and 0.96 eV according to the aqueous–ethanol concentrations 1:10, 1:20, 1:30 and 1:40, respectively. Further observations show that the values of E_a voltages are different due to different trapping levels, which are situated between the valence band and the conduction band.

It can be seen that the activation energy decreases with decreasing the ethanol content, which proves the semiconducting nature of films. Some structural changes caused by defects and impurities in the films may occur, causing an increase in conductivity. The high-temperature conductivity is attributed to thermal excitation of charge carriers from the grain boundaries to the neutral regions of the grains. Chourashiya *et al* [28] reported a similar behaviour for the high-temperature conduction mechanism of the gadolinium-doped ceria. The conductivity of the films increases with a decrease in ethanol concentrations. The lesser conductivity observed at the maximum value of ethanol concentration can be explained as due to the lower degree of crystallinity and the smaller grain size as correlated with XRD results.

To explain the differences observed in electrical conductivities, it must be recalled that in polycrystalline films, the transport mechanism of charge carriers is strongly influenced by grain size and the characteristics of grain boundaries. The grain sizes depend on the deposition parameters. As the ethanol concentrations decrease, we expect to obtain larger grains, with a smaller number of grain boundaries. The effect will be a decrease in carriers scattering and finally an increase in electrical conductivity, as observed.

In general, the electron transport properties are affected by the presence of a number of defects such as structural disorders, dislocations and surface imperfections. The variation of grain size could also influence the activation energy [29]. Since a polycrystalline film has crystallites joined at their surfaces via grain boundaries, the boundaries between crystallites play an important role in determining the conductivity of polycrystalline films. As the tetrabutylorthotitanate

decreases, the crystallite size decreases, leading to an increment in the trapping states at the grain boundary. Trapping states are capable of trapping free carriers and, as a consequence, more free carriers become immobilized as trapping states increase. In other words, the larger crystallite size results in a lower density of grain boundaries, which behave as traps for free carriers and barriers for carrier transport in the film. Hence, an increase in grain size can cause a decrease in grain boundary scattering, which leads to an increase in conductivity. This indicates that the crystallinity of ZnS films is improved corresponding to the samples prepared at lower molar ratios of the ethanolic solution.

4. Conclusion

The study of the structural and some physical properties of ZnS films obtained by the CBD technique shows that they are strongly dependent on the ethanol concentration. Particularly, it is observed that the best crystallinity of ZnS films is obtained at 80 °C within 1.5 h. The films have amorphous and polycrystalline structures and show a preferential orientation along (0 0 2) with well-defined microstructures.

It is observed that XRD peak intensities of the hexagonal phase steadily become stronger and the width of XRD diffraction peaks becomes slightly narrower with decreasing ethanol concentration, indicating the formation of more and greater ZnS crystallites and an enhancement of crystallization. The crystallinity of ZnS films was quantitatively evaluated via the relative intensity of the (0 0 2) diffraction peak of the hexagonal phase. It can be seen that the average grain sizes and relative crystallinity increase with decreasing ethanolic concentration. As a consequence, it was found that the ethanol concentration significantly influences the electrical properties of ZnS films. As the ethanol concentration decreases, the crystallite size increases.

Decreasing the ethanol concentration reduces both the value of the potential barrier height and the value of the density of surface states at the grain boundaries and thus increases the conductivity for the investigated samples. According to the results based on the above investigation, to eliminate effects of grain boundary and defects on the carrier transport in ZnS films, the ethanol concentration should be decreased. The results of the calculated activation energy suggests that the thermally activated conduction mechanism plays a significant role in the conduction processes. Therefore the XRD, electrical conductivity and activation energy are observed to be dependent on the ethanol contents.

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