The influence of deposition temperature on the structure and optical band gap of zinc sulphide thin films deposited from acidic chemical baths
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ABSTRACT
Nanocrystalline zinc sulphide (ZnS) thin films have been successfully deposited on silica glass substrates from acidic chemical baths containing tartaric acid and hydrazine as complexing agents, thioacetamide as a sulphur source and zinc acetate as the source of zinc ions. The influence of temperature on the structural-, optical-, morphological properties and elemental composition of the films were investigated by a variety of techniques. Powder x-ray diffraction patterns of the films exhibited the cubic structure. The deposition temperature had a significant influence on the lattice parameter and crystallite size. Scanning electron microscope and energy dispersive x-ray investigations have shown an improvement in morphology and stoichiometry of the films with increasing deposition temperature. The band gap of the thin films obtained by optical absorption spectroscopy showed a decrease from 3.88 eV to 3.75 eV as the deposition temperature increased. Transmittance of the films increased with decreasing deposition temperature.

1. Introduction
ZnS is an important group II-VI semiconductor with a large direct band gap which is about 3.67 eV [1]. It has generated a lot of interest among scientists because of its extensive use in the fabrication of solid state devices especially, photovoltaic or optoelectronic devices [2, 3]. Various techniques have been employed to prepare thin films of ZnS. Among these techniques, chemical bath deposition (CBD) has been widely used [4] because of its simplicity, cost-effectiveness and conducive for applications involving large area deposition such as fabrication of solar cells [5]. CBD technique is sensitive to deposition parameters which include bath temperature, deposition time, type of precursors and their concentrations, and bath pH. The deposition is usually carried out in alkaline chemical baths [6, 7]. The deposition of pure ZnS films appears to be remarkably difficult to achieve in alkaline solutions due to the stability of the hydroxyl species [8]. There is a much wider range of conditions in which the concurrent deposition of zinc sulfide and oxide can occur [9], and this may have a deleterious effect on the properties of the films [10]. Deposition of ZnS films in acidic chemical baths can minimize this problem and improve film quality [4]. In this work, we report on the deposition of ZnS thin films from acidic chemical baths using tartaric acid and hydrazine as complexing agents, thioacetamide as a sulphur source and zinc acetate dihydrate as the source of zinc ions. The effect of deposition temperature on the optical and structural properties is also investigated and discussed. The combination of tartaric acid and hydrazine is rarely reported for the deposition of ZnS in alkaline bath [3]. However, as far as the authors are aware, there is no report on the deposition of ZnS thin films in acidic chemical baths using a combination of tartaric acid and hydrazine as complexing agents.

2. Experimental Details
Silica glass substrates were used for the deposition of the ZnS thin films. In a 100 ml reaction vessel, 20 ml (0.1 M) zinc acetate dihydrate was mixed with 5 ml of 60% hydrazine hydrate and stirred for few minutes. 17.5 ml of de-ionized water was added. An appropriate amount of (1 M) tartaric acid solution was added to the solution and the pH adjusted to the required value of 3.8 by the drop wise addition of HCl. 7.5 ml of (1 M) thioacetamide solution was added to the mixture under continuous stirring. Finally, the pH was adjusted again to the required value by adding a few drops of HCl. The substrates, which had been cleaned using the procedure reported in [11], were then immersed vertically in the stock solution. The vessel was sealed with a special cover which also served as a substrate holder. The reactant mixture, placed in a water bath, was continuously stirred. The deposits were carried out at temperatures of 55°C, 65°C and 75°C for one hour. After deposition the slides were removed from the bath, washed in de-ionized water and dried under ambient conditions before characterization. The as-deposited films were grey-white in color, smooth, transparent and well adherent to the substrate.

Different techniques were used for the characterization of the thin films. Structural characterization of the ZnS thin films was carried out by using a Panalytical X’Pert PRO x-ray diffractometer with Cu Kα monochromatic radiation (λ=0.15406 nm) operating at (45 kV, 40 mA). Optical properties were studied by measuring the absorbance of the thin films using Shimadzu UVmini-1240 UV/Vis single beam spectrophotometer.

The surface morphology and composition of the thin films were investigated using field emission scanning electron microscopy (FESEM, Zeiss, sigma) attached with energy dispersive x-ray (EDX).
3. Results and discussion

3.1. Structural Analysis

Double depositions were carried out to increase the thickness of the thin films in order to obtain good X-ray diffraction patterns. Three XRD peaks were observed around the 2θ values of 28.5°, 47.5° and 56.5° for all samples (Fig. 1). Comparing the results with JCPDS data file number 01-077-8756, the three peaks were indexed to (111), (220) and (311) planes of the cubic structure of ZnS, respectively.

The relative intensity of the (220) and (311) planes were found to increase with deposition temperature, FWHM and the background effect of the ZnS samples decreased with deposition temperature indicating an improvement in crystallinity. Similar observations were reported by different workers [14, 15].

The inter-planar space (d_{hkl}) values of the ZnS particles have been calculated from Bragg’s law [16] and from which the lattice parameter, a, has been obtained using Eq. (1).

\[a = d_{hkl} \sqrt{h^2 + k^2 + l^2}\]  

where h, k and l are miller indices of the diffraction planes. The average lattice constants, a_{avabh}, were found to decrease with deposition temperature with values 5.4139, 5.383, and 5.3615 Å for samples deposited at 55°C, 65°C and 75°C, respectively. The average crystallite size of the ZnS thin films were also calculated from Debye-Scherrer’s formula [17] and the values obtained are 1.744 nm, 1.894 nm and 2.698 nm for samples deposited at 55°C, 65°C and 75°C, respectively. These results show that the deposition temperature has a significant influence on the lattice parameters and crystallite size of the ZnS samples. Similar influence of deposition temperature on the crystallites size was reported by [15]. The increase in crystallite size may be related to the rate of release of Zn²⁺ and S²⁻ ion in the solution and their rate of adsorption to form stable nucleation and growth. At higher temperatures, the decomposition of thioacetamide is faster setting more S²⁻ ions free [18]. Additionally, the zinc-complex dissociation increases to give higher concentrations of free Zn²⁺ in the solution, which in turn results in higher deposition rates for the constant deposition time [19].

3.2. Optical Properties

The optical properties of the ZnS thin films were investigated by measuring the absorption in the wavelength range of 200 to1100 nm. The optical transmittance of the ZnS thin films deposited at 65°C and 75°C was greater than 60% and for those deposited at 55°C it is more than 70% for wavelength greater than 650 nm (Fig. 2 (a)).

A good transmittance in the indicated wavelength range indicates low defect density of the ZnS films because absorption of light in the longer wavelength region (>500 nm) is usually caused by crystalline defects such as grain boundaries and dislocations [20]. Band gap energy and transition type of the thin films can be derived from mathematical treatment of data obtained from optical absorbance versus wavelength at near-edge absorption using Stern relationship [21]:

\[A = \frac{(k(n - E_g))^{n}}{hv}\]  

where \(A\) is absorbance, \(v\) is the frequency of the radiation, \(h\) is the Planck’s constant, \(k\) is a constant and \(n\) carries the value of either 1 or 4. The value of \(n\) is 1 for the direct transition and 4 for indirect transition, respectively. Since most of compound semiconductors including ZnS have direct band gap, the value of \(n\) was taken to be 1. The band gap (\(E_g\)) of the ZnS thin films were obtained by plotting the square of the product of absorbance and photon energy (\(A-hv\)) against photon energy (\(hv\)) (Fig. 2(b)). The band gap is obtained by fitting a line to the linear portion of the graph and extrapolating the fitted line to the point where it intersects the \(hv\) axis as shown in Fig. 2(b). The estimated energy band gap for the ZnS thin films deposited at 55°C, 65°C and 75°C are 3.88 eV, 3.84 eV and 3.75 eV, respectively. Similar results were reported by [15]. The values are slightly larger than the
3.3. Morphological Studies and Elemental analysis

Figure 3 shows the SEM micrographs of the ZnS thin films for different deposition temperatures. The films exhibited uniform coverage of the substrate with grains packed densely without pin holes. Some isolated and relatively large grains were observed over the compacted surface of the films.

![SEM micrographs of ZnS thin films deposited at (a) 75°C, (b) 55°C.](image)

These grains may be adsorbed to the thin films’ surface at the final stage of deposition being initially grown homogenously within the reaction solution. The homogeneity, smoothness, and transparency of the thin films can be attributed to the domination of the heterogeneous film growth process over the adsorption of homogeneously grown grains on the substrate [14]. Some cracks were observed for the thin films deposited at 55 and 65°C. Similar morphological results were reported by [23]. Elemental analysis of the ZnS thin films investigated by using EDX confirmed the formation of ZnS. The Zn/S atomic ratios of the thin films deposited at 55 and 75°C were 0.60, 0.65, and 0.75, respectively indicating an excess of sulfur for all the ZnS thin films. As the deposition temperature increased, the stoichiometry of the films improved. The result is in a good agreement to the one reported by [15, 24] for acidic bath deposited ZnS thin films.

4. Conclusion

Nanocrystalline ZnS thin films were successfully deposited on a silica glass substrate from acidic chemical bath using tartaric acid and hydrazine as complexing agents. The films were adherent to the substrate, smooth, and transparent. The influence of temperature on the structural-, optical- and morphological properties and chemical compositions of the films were investigated. The XRD studies revealed that the ZnS thin films have the cubic structure. The crystallite size increased with deposition temperature; however the lattice parameters decreased with deposition temperature. The band gap of the ZnS films decreased from 3.88 eV to 3.75 eV as the deposition temperature increased from 55°C to 75°C whereas the transmittance of the films increased with decreasing deposition temperature. The SEM and EDX investigations have shown that the films deposited at high deposition temperature had better morphology and stoichiometry. These results provide a new set of bath processes for the acidic bath deposition of ZnS and also show the importance of deposition temperature in obtaining films of good quality.

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References