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Influence of pH on the Properties of Chemical Bath Deposited Ni_4S_3 Thin Films

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Abstract

The Ni_4S_3 thin films were prepared by chemical bath deposition method. The chemical bath contained nickel sulphate and sodium thiosulfate which supplied the Ni^{2+} and S^{2-} ions, respectively. The structure and morphology of the films were studied using X-ray diffraction and atomic force microscopy technique, respectively. Absorbance spectra data of the films were obtained by UV-Vis spectrophotometer. The influence of pH was investigated in order to determine the best conditions for deposition process. The number of peaks attributable to cubic structure of Ni_4S_3 increased to three as the pH was increased to 2.5 according to XRD analysis. In optical absorption spectra, we found that the highest absorbance value was obtained for the films deposited at pH 2.5. Also, the AFM image revealed that the films were smooth, compact and uniform at this pH value. The band gap of films ranged from 0.85 to 1.8 eV depending upon the pH value.

Key words: Nickel sulphide, Thin films, Solar cells and Semiconductor.

Introduction

Semiconductor thin films have found extensive applications in electronic and optical devices. Among them, nickel sulphide is the most commonly used material for applications such as solar cells, sensors, photoconductors and infrared detectors. These are due to its non-toxicity, abundant in nature, cheap and possess semiconducting properties. Several techniques have been employed to prepare nickel sulphide thin films such as electrodeposition (Anuar *et al.* 2004), SILAR (Pathan and Lokhande, 2004), pulsed laser ablation (Lee *et al.* 1993), metal-organic chemical vapour deposition (Nomura and Hayata, 2001), thermal and photochemical chemical vapour deposition (Cheon *et al.* 1997). Chemical bath deposition technique is simple, low cost and convenient for large area deposition of films. In chemical bath deposition method, controlled chemical reaction plays a key role for the deposition of the thin films. The substrates are immersed in solution containing the chalcogenide source, the metal ion and a complexing agent. The preparations of various thin films using chemical bath deposition method such as ZnS (Ubale *et al.* 2007), CdS (Li *et al.* 2005), $Cu_{2-x}Se$ (Al-Mamun and Islam, 2004), $CuBiS_2$ (Sonawane *et al*. 2004) and Cu_4SnS_4 (Anuar *et al.* 2009) have reported by several authors. Up-to-date, there is no report on deposition of Ni_4S_3 thin films from aqueous solution at room temperature using triethanolamine as complexing agent by chemical bath deposition technique.

In this paper, we prepare Ni_4S_3 thin films by chemical bath deposition technique and study the effect of pH on the properties of these materials. X-ray diffraction is used to study the structural properties of films. Meanwhile, the morphological and optical properties of Ni_4S_3 thin films are investigated by using atomic force microscopy and UV-Visible spectrophotometer, respectively.

Materials and Methods

Nickel sulphide thin films were deposited onto indium tin oxide (ITO) glass substrates using chemical bath deposition method. Prior to deposition, the substrate was degreased in ethanol for 10 min, followed by ultrasonically cleaned with distilled water for another 15 min and finally dried in desiccators. An aqueous solution of nickel sulphate [$NiSO_4$], was acted as a source of Ni^{2+}, sodium thiosulfate [$Na_2S_2O_3.5H_2O$] was supplied as S^{2-} ions and tri-

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ethanolamine [$(HOC_2H_4)_3N$] was used as complexing agent for depositing nickel sulphide thin films. All these chemicals used for the deposition were analytical grade. All the solutions were prepared using deionised water (Alpha-Q Millipore). Deposition of thin films was carried out at room temperature in the following manner. 25 ml of $NiSO_4$ (0.075 M) was complexed with 5 ml of concentrated triethanolamine solution. 25 ml of $Na_2S_2O_3$ (0.075 M) was added slowly to the mixture. The cleaned ITO glass substrate was immersed vertically into beaker. The deposition was carried out at different pH solutions (pH 1.5, 2.5 and 3.5) in order to determine the best conditions for the deposition of thin films. Hydrochloric acid solution was added to the chemical bath to adjust the pH under the control of a pH meter. After the completion of deposition (3 hours), the glass substrate was taken out of the beaker, washed with distilled water and dried in desiccators for further characterization.

The XRD data were obtained by means of Philips PM 11730 diffractometer using CuK_α (λ=1.5418 Å) radiation source. The accelerating voltage and current were 40 kV and 30 mA, respectively. Data were collected by step scanning from 20° to 60° with a step size of 0.05° (2θ). The surface morphology was studied by atomic force microscopy. The AFM was carried out with a Q-Scope 250 (Quesant Instrument Corporation) in a contact mode. The optical absorption measurement was carried out in the wavelength range from 300 to 800 nm by using a Perkin Elmer UV/Vis Lambda 20 Spectrophotometer. The film-coated glass substrate was placed across the sample radiation pathway while the uncoated glass substrate was put across the reference path. The absorption data were man ipulated for the determination of the band gap energy.

Results and Discussion

Figure 1 and Table 1 show the X-ray diffraction patterns and XRD data of nickel sulphide thin films deposited at various pH solutions ranging from 1.5 to 3.5, respectively. The XRD data for the films deposited at pH 1.5 display two diffraction peaks at 2θ values of 30.2° and 50.3° which correspond to the (111) and (220) planes, respectively. It is observed that the number of peaks attributed to cubic structure of Ni_4S_3 compound increased to three as the pH is increased to 2.5. The corresponding *d*-spacing values are in well agreement with the Joint Committee on Powder Diffraction Standard data (JCPDS reference code: 00-052-1027) belonging to the Ni_4S_3 compound (Kitakaze and Sugaki, 2001). However, beyond this point, any increase in the pH resulted in the reduction in the number of Ni_4S_3 peaks. The films prepared at pH 3.5 show only single peak at 2θ=30.2° which indicating less favourable condition for the formation of nickel sulphide thin films.

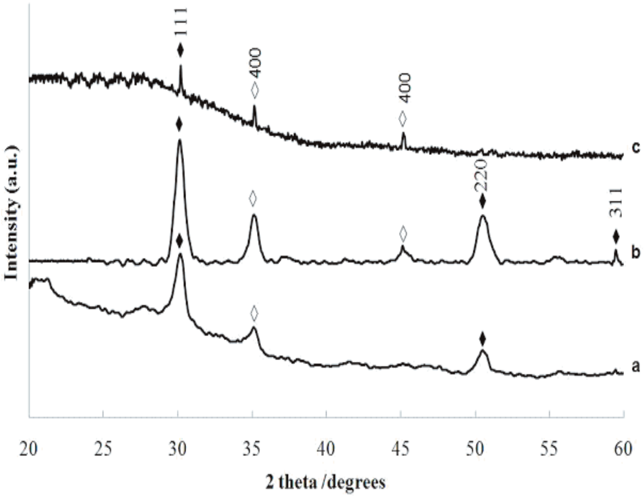

Fig. 1: **X-ray diffraction patterns of Ni_4S_3 thin films deposited at different pH solutions. (a) pH 1.5 (b) pH 2.5 (c) pH 3.5**

Table I: **Comparison of the standard and experimental *d*-spacing data for Ni_4S_3 films deposited at various pH solutions**

pH	2θ(°)	*hkl*	*d*-spacing (Å)	
			Observed value	JCPDS data
1.5	30.2	111	2.96	2.96
	50.3	220	1.80	1.82
2.5	30.2	111	2.96	2.96
	50.3	220	1.80	1.81
	59.4	3.11	1.54	1.55
3.5	30.2	111	2.96	2.96

The atomic force microscopy (AFM) images of nickel sulphide thin films prepared at different pH solutions are shown in Figure 2 for the scan area of 5µm x 5µm. The Figure 2a and 2c show the AFM images for the films deposited at pH 1.5 and 3.5, respectively. The three-dimensional images indicat that the surface of substrate is not covered completely. The discontinuous and uneven distribution of grains can be observed on the surface of the substrate. However, the uniform, continuous distribution and grains with average sizes of 0.5 µm are obtained for the films deposited at pH 2.5. The AFM results suggested that the influence of pH on the surface morphology is significant. On the other hand, the thickness of the films was measured using AFM technique. The thickness values of 25, 37 and 41 nm have been observed for samples prepared at pH 1.5, 2.5 and 3.5, respectively.

The optical properties of the Ni_4S_3 thin films were measured by UV-Vis spectrophotometer in the wavelength range 300-800 nm. Figure 3 shows the absorption spectra of Ni_4S_3 thin films prepared at different pH solutions. The films prepared at pH 2.5 showed higher absorption characteristics when compared to the films prepared at other pH solutions. The higher absorbance can be due to more materials deposited (3 prominent Ni_4S_3 peaks) and these materials are found to cover the surface of the substrate completely (as shown in Figure 2b). This is because of more atoms are present in the films, so more states will be available for the photons to be absorbed. The films produced an absorbance value in the visible region of the solar spectrum indicating possibility of these materials to be used in a photoelectrochemical cells (Anuar *et al.* 2004).

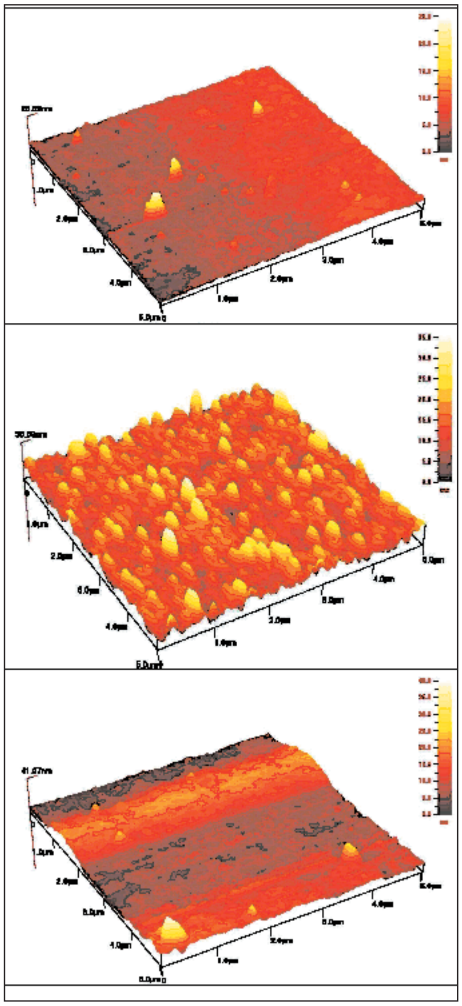

Fig. 2: Atomic force microscopy images of Ni_4S_3 thin films deposited at different pH solutions. (a) pH 1.5 (b) pH 2.5 (c) pH 3.5

In order to determine the band gap of thin films, the equation of Stern (Stern, 1963) was used.

$$A = \frac{[k(h\nu - E_g)^{n/2}]}{h\nu} \qquad (1)$$

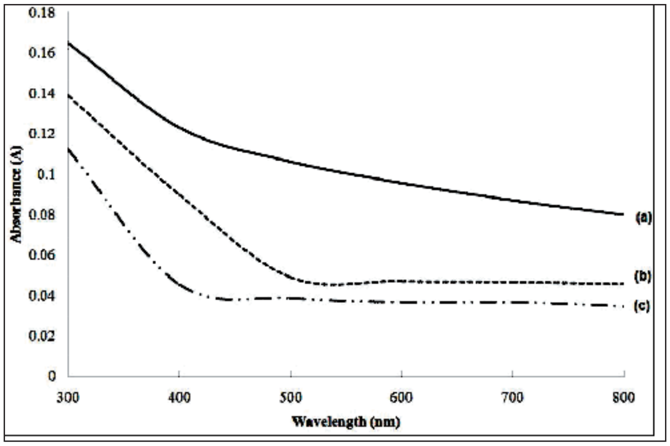

Fig. 3: Absorbance versus wavelength spectra of Ni_4S_3 thin films deposited at various pH solutions. (a) pH 2.5 (b) pH 1.5 (c) pH 3.5

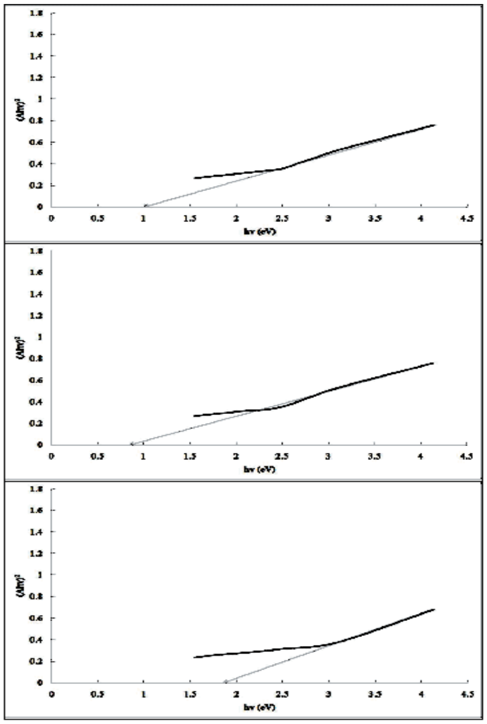

Fig. 4: The plot of $(Ah\nu)^2$ versus $h\nu$ of Ni_4S_3 thin films deposited at various pH solutions. (a) pH 1.5 (b) pH 2.5 (c) pH 3.5

where *v* is the frequency, *h* is the Planck's constant, *k* equals a constant while *n* carries the value of either 1 or 4. The *n* value is 1 for a direct gap material and 4 for indirect gap material. The plots of $(Ah\ )^2$ against *hv* are shown in Figure 4. Extrapolation of the linear portion of the curve to $(Ah\ )^2$ =0 gives the band gap energy. The straight line behaviour establishes that all the films have a direct band gap (Sartale and Lokhande, 2001). The band gap energy of the thin films initially decreases (1.0 to 0.85 eV) with increasing the pH from 1.5 to 2.5. Subsequently, as the pH is increased to less acidic medium (pH 3.5), caused increasing the band gap energy (1.8 eV). Therefore, the pH value has some influences on the band gap of the films.

Conclusion

Thin films of nickel sulphide have been deposited by chemical bath deposition technique onto indium tin oxide glass substrates at room temperature. The influence of pH value on the structure, morphological and optical properties was investigated. The deposited films indicated cubic structure of Ni_4S_3 compound according to XRD data. In this study, we found that better crystallinity, uniform surface coverage and higher absorption characteristics were achieved for the films deposited at pH 2.5. These results were consistent with X-ray diffraction, atomic force microscopy and optical properties analysis.

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