

Preparation and Studies of Nickel Sulfide Thin Films in the Presence of Sodium Tartrate as a Complexing Agent

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Cathodic electrodeposition in the presence of tartrate ions in aqueous solution was used to prepare nickel sulfide thin films deposited on titanium substrates. The effect of deposition potential and bath temperature was studied to determine the optimum condition for electrodeposition process. The thin films are characterized using X-ray diffractometry. The surface morphology studies were performed using scanning electron microscope. The photoactivity of the deposited films and their conduction types were evaluated using photoelectrochemical technique. The bandgap energy and type of optical transitions were determined from optical absorbance data. The film was found to exhibit direct transition in the visible spectrum with a bandgap value of about 1.30 eV.

Keywords: thin films, nickel sulfide, electrodeposition, photoelectrochemical cell, metal chalcogenide.

1. INTRODUCTION

Efforts have been made in finding new materials for solar energy conversion. Two important factors that should be considered in producing these materials are the band gap energy matching solar spectrum and the competitiveness of production cost [1]. Metal chalcogenides and their mixtures are attractive and useful systems for solar energy conversion studies by photoelectrochemical means [2–11]. These compounds are also used as sensor and laser materials, thin films polarizers and thermoelectric cooling materials. They possess certain criteria to make them potential candidates in the photoelectrochemical (PEC) solar cells.

Thin-film technologies are being developed as a means of substantially reducing the cost of photovoltaic (PV) or photoelectrochemical systems using electrodeposition method. The rationale for this is that thin-film modules are expected to be cheaper to manufacture owing to their reduced material costs, energy costs, handling costs and capital costs [12]. Reduction of cost for the thin film cells is achieved by minimization of the amount of material used, the possibility of inexpensive materials, processing methods and the use of inexpensive mounting arrays [13, 14].

Electrodeposition could be a cost-effective technology for the production photoelectrochemical (PEC) cells [15]. This technique is a perspective competitor because of several advantages such as the possibility for large-scale production, minimum waste of components and easy monitoring of the deposition process. This technique is generally less expensive than those prepared by the capital-intensive physical methods. The presence of complexing agents in the solution during the electrodeposition process of metal chalcogenide thin films was found to improve the lifetime of the deposition bath as well as the adhesion of the deposited film on the substrate [16, 17]. The use of

additives in aqueous electroplating method is extremely important. The potential benefits of additives include: brightening the deposit, increasing grain size, changing mechanical and physical properties, reducing stress and reducing pitting. We report here the electrochemical deposition of nickel sulfide thin films using sodium tartrate as a complexing agent for photoelectrochemical cells.

2. EXPERIMENTAL PROCEDURE

Electrodeposition was performed in a conventional three-electrode cell. Ag/AgCl was used as the reference electrode to which all potentials were quoted. The working and counter electrodes were made from titanium (Ti, 99.99 %) and platinum, respectively. The Ti substrates and counter-electrode was polished and cleaned with distilled water before the deposition process. Cyclic voltammetry (CV) test was carried out between two potential limits (500 to –1600 mV) for the solutions prepared (mixture Ni-tartrate and $\text{Na}_2\text{S}_2\text{O}_3$) to probe the prospective potentials for deposition.

An EG & G Princeton Applied Research Potentiostat (Versastat model) driven Electrochemical Analysis System software (model 270) was used to control the electrodeposition process and to monitor the current and voltage profiles. The electrolytes were prepared using analytical grade reagents and deionised water. Sodium tartrate was used to chelate with Ni^{2+} to obtain a Ni-tartrate complex. Nitrogen gas was flowed into the solutions prior to mixing to remove any dissolved O_2 . HCl was added to prevent the formation of hydroxyl species and insoluble compound [18].

The deposition was carried out at room temperature by varying deposition potentials and solution temperature in order to determine the optimum condition for the deposition of nickel sulfide thin films. Immediately after deposition, the deposits were tested for adhesion by subjecting it to a steady stream of distilled water.

XRD analysis was performed using a Philips PM 1730 Diffractometer for the 2θ ranges from 2° to 60° with $\text{CuK}\alpha$

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($\lambda = 1.5418 \text{ \AA}$) radiation. Scanning electron microscope (SEM) analysis was performed using JSM-6400 JEOL Scanning Electron Microscope. Photoelectrochemical (PEC) experiments were performed in 0.01 M $\text{Na}_2\text{S}_2\text{O}_3$, by running linear sweep voltammetry (LSV) between 0.00 V to -1.00 V. A tungsten-halogen lamp (100 W) was used for illuminating the electrode. Optical absorption study was carried out using Perkin Elmer UV/Vis Lambda 20 Spectrophotometer. The film-coated indium tin oxide (ITO) glass was placed across the sample radiation pathway while the uncoated ITO glass was put across the reference path. From the analysis of absorption spectra the band gap energy (E_g) was determined.

3. RESULTS AND DISCUSSIONS

Fig. 1 shows the cyclic voltammogram (CV) of Ti electrode in the presence of Ni-tartrate and $\text{Na}_2\text{S}_2\text{O}_3$ solution. During the forward scan, a cathodic current increase could be observed as the potential was extended to -0.50 V and above. This current increase is due to the formation of nickel sulfide compound on the surface of the substrate. As the potential was forwarded to more negative potential (-1.20 V and above), a drastic increase in the current profile confirms the hydrogen evolution process that usually occurs at higher negative potentials [18]. During the reverse scan, co-deposition of nickel sulfide compound occurs as the potential was scanned to lower potential values. However, at -0.50 V, a small stripping peak indicates the dissolution of the compound into the solution.

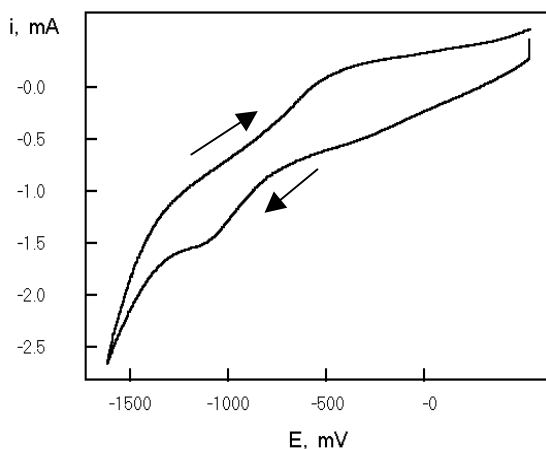


Fig. 1. Cyclic voltammetry of Ti electrode in presence of Ni-tartrate and $\text{Na}_2\text{S}_2\text{O}_3$ solution

From the data obtained through CV, we can conclude that the deposition of nickel sulfide compound occurs as the deposition potential is forwarded to values more than -0.50 V. The electrodeposition of nickel sulfide thin films was carried out at different potentials to determine the optimum deposition potentials.

Fig. 2 shows the XRD plot of the nickel sulfide thin films deposited at different potentials. At lower potentials (-0.60 and -0.70 V) only single peak attributable to NiS_2 could be obtained. The peak corresponding to $2\theta = 35.2^\circ$ was well matched with the Joint Committee on Powder Diffraction Standard (JCPDS; File No: 11-0099) data (Table 1). At higher potentials (-0.80 to -1.00 V), two

peaks at about $2\theta = 35.2^\circ$ and 44.6° due to NiS_2 , which matched, the standard JCPDS data was obtained. The XRD data also indicate the formation of polycrystalline materials.

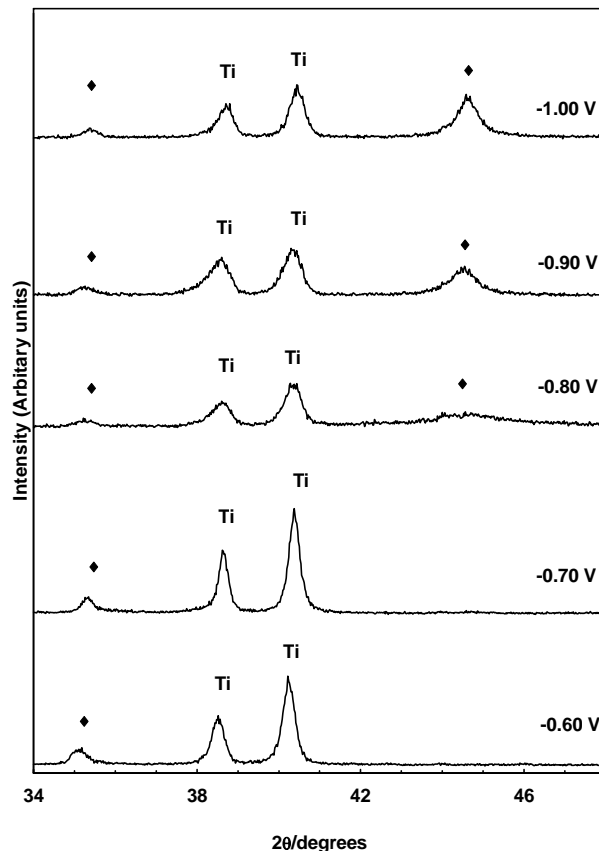


Fig. 2. XRD plot of nickel sulfide thin films deposited at different potentials

Table 1. Comparison between theoretical d-spacing data and experimentally observed values for samples deposited at different potentials

Potential (V)	2θ ($^\circ$)	d-spacing (\AA)		Compound
		Experimental values	JCPDS values	
-0.60	35.1°	2.54	2.54	NiS_2
-0.70	35.2°	2.54	2.54	NiS_2
-0.80	35.2°	2.54	2.54	NiS_2
	44.6°	2.02	2.00	
-0.90	35.2°	2.54	2.54	NiS_2
	44.4°	2.03	2.00	
-1.00	35.3°	2.54	2.54	NiS_2
	44.5°	2.03	2.00	

Figure 3 shows the SEM micrographs of NiS_2 thin films deposited at different deposition potentials. At low deposition potential (-0.70 V), the grain size was found to be small and less visible. The structure was found to be compact and covered the surface of the substrate completely. As the deposition was increased to -0.90 V, the size of the grains was increased with the grain particles exhibiting granular morphology. The growth orientation was similar among the grain particles indicating constant growth mechanism.

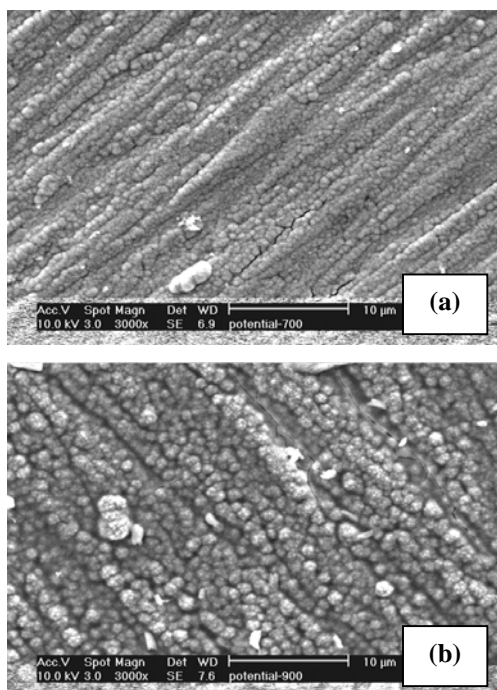


Fig. 3. SEM micrographs of nickel sulfide thin film deposited at (a) -0.70 V and (b) -0.90 V

The following deposition was carried out at different solution temperatures (15, 40 and 60 °C). Figure 4 shows the XRD plot of the sample deposited at different solution temperatures. The film deposited at low solution temperature (15 °C) produced only three peaks at $2\theta = 35.5$, 38.8 and 53.4° corresponding to interplanar distances of 2.52, 2.31 and 1.71 Å which corresponds well with the standard JCPDS (File No: 11-0099) data (Table 2). As the solution temperature was increased to 40 °C, four peaks attributable to NiS₂ were obtained. The obtained values were well matched with the standard JCPDS data (Table 2).

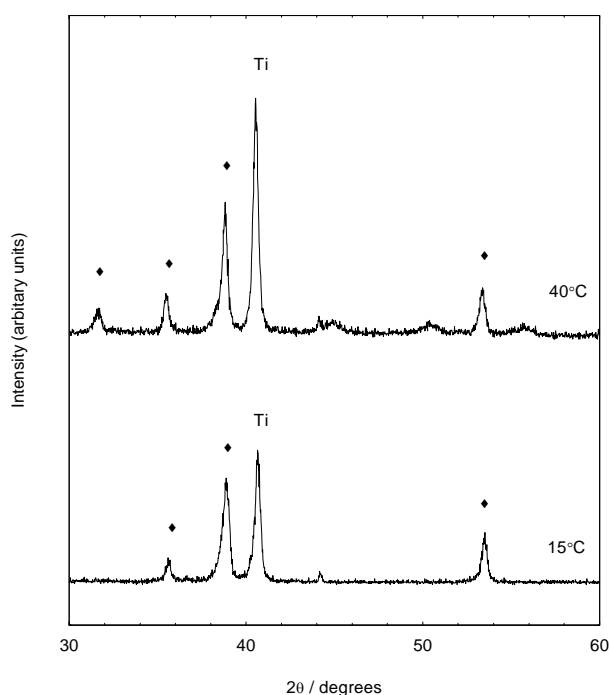


Fig. 4. XRD plot of nickel sulfide thin films deposited at different solution temperature

Table 2. Comparison of the theoretical d-spacing data and experimentally observed values for the samples deposited at different solution temperatures

Temperature (°C)	2θ (°)	d-spacing (Å)		Compound
		Experimental values	JCPDS values	
15	35.5	2.52	2.54	NiS ₂
	38.8	2.31	2.32	
	53.4	1.71	1.70	
40	31.5	2.82	2.83	NiS ₂
	35.4	2.52	2.54	
	38.7	2.32	2.32	
	53.3	1.70	1.70	

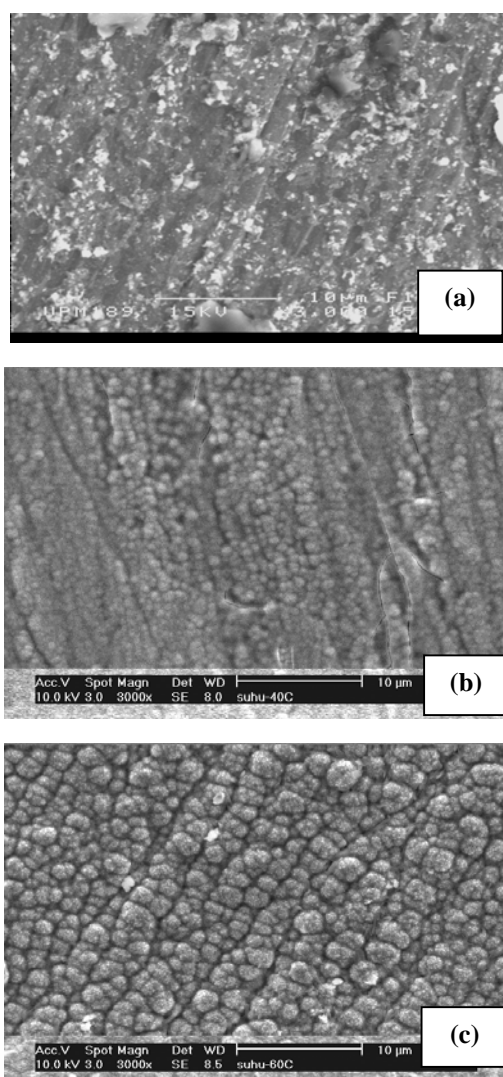


Fig. 5. SEM micrographs of nickel sulfide thin films deposited at different solution temperature; (a) 15 °C, (b) 40 °C and (c) 60 °C

Figure 5 shows the SEM micrographs of the NiS₂ thin films deposited at different solution temperature. The film deposited at 15 °C reveals incomplete growth morphology. The grains were not visible and the grain distribution was not randomly spread out over the surface of the substrate. As the solution temperature was increased to 40 °C, the

grain formation was well observed. The grains coverage was complete and the sizes varied from one another. At 60 °C solution temperature, the grains exhibit increased size morphology and compact formation. The grains were deposited in the granular form, which is common for most of the metal chalcogenide compounds.

Figure 6 shows the absorbance spectra of the nickel sulfide thin film deposited in the presence of tartrate ions. The absorbance of nickel sulfide film produced an absorbance value in the visible region of the solar spectrum indicating the possibility of this material to be used in a photoelectrochemical cell, photovoltaic and other optoelectric devices [19]. Band gap energy and transition type was derived from mathematical treatment of the data obtained from the optical absorbance versus wavelength data with the following relationship for near-edge absorption:

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

where ν is the frequency, h is the Planck's constant, k equals a constant while n carries the value of either 1 or 4. The bandgap, E_g , could be obtained from a straight line plot of $(Ah\nu)^{2/n}$ as a function of $h\nu$. Extrapolation of the line to the base line, where the value of $(Ah\nu)^{2/n}$ is zero, will give E_g . If a straight-line graph is obtained for $n = 1$, it indicates a direct electron transition between the states of the semiconductor, whereas the transition is indirect if a straight-line graph is obtained for $n = 4$.

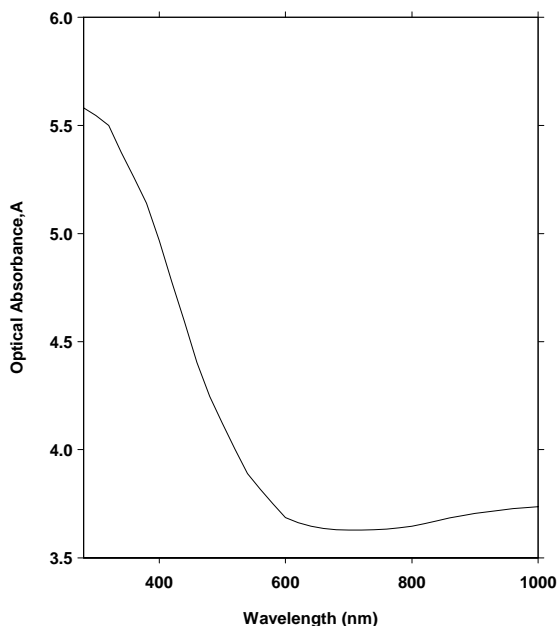


Fig. 6. Optical absorbance value of the NiS₂ thin film

A linear trend is apparent where n in the relationship (1) equals 1 (Figure 7). The straight-line behavior testifies a direct transition of the band structure. The line segments required to by pass the energy of the gap lies at about 1.30 eV for the nickel sulfide thin film.

Figure 8 shows the photoresponse of the NiS₂ film in the presence of Na₂S₂O₃ upon illumination with a halogen lamp (100 W). An increase in the current could be observed as the film is illuminated. The photoresponse upon illumination indicates semiconductor behavior of the

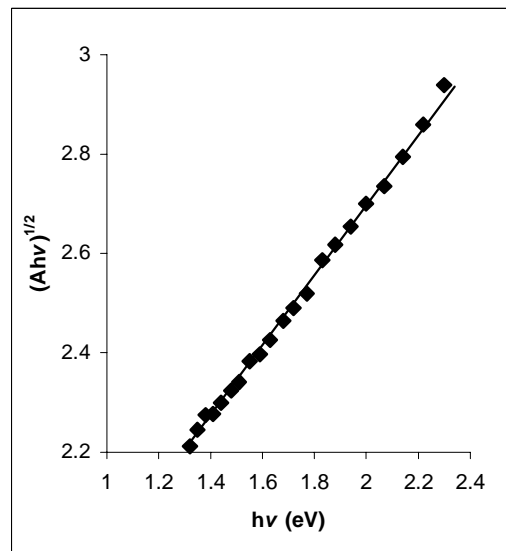


Fig. 7. Plot of $(Ah\nu)^{2/n}$ versus $h\nu$ for the film prepared when $n = 1$

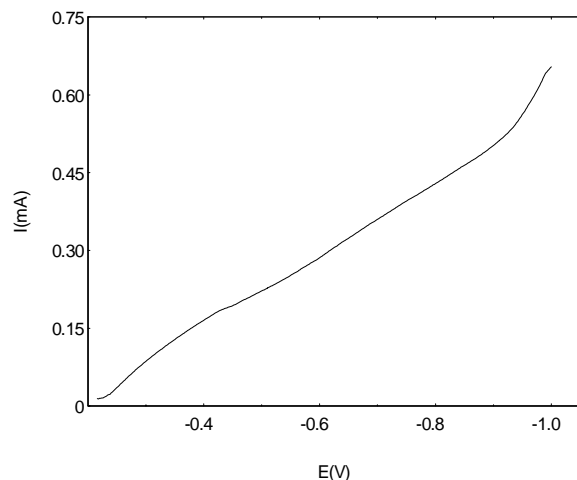


Fig. 8. Photoresponse of NiS₂ thin films upon illumination

material. The fact that the photocurrent occurs on the negative (cathode) potential area indicates that the films prepared are of p -type (positive). The films could be deployed as photo cathode in the photoelectrochemical cell application to facilitate a reduction reaction of the electro active species in the solution.

4. CONCLUSIONS

Polycrystalline NiS₂ thin films could be electrodeposited on Ti substrate under the presence of sodium tartrate as a complexing agent. The film obtained exhibit direct transition in the visible with a bandgap value of about 1.30 eV. The films displays p -type semiconductor behavior.

Acknowledgments

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