



## Effect of Deposition Time Towards the Properties of Nickel Sulfide Thin Films Prepared in the Presence of Sodium Tartrate as a Complexing Agent

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### ABSTRACT

Nickel sulfide thin films were deposited onto titanium substrates using sodium tartrate as a complexing agent. The presence of the complexing agent was found to improve the lifetime of the deposition bath. The deposition conditions for obtaining good quality films such as deposition period was optimized. The films were characterized and analyzed using X-ray diffractometry and scanning electron microscopy. The films deposited were found to be polycrystalline in nature. The optimum deposition time to deposit quality nickel sulfide thin films under the current condition is 60 minutes. The bandgap energy was found to be about 1.30 eV with direct electronic transition.

**Keywords :** complexing agent, electrodeposition, nickel sulfide, thin film.

### 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

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.

An EG & G Princeton Applied Research Potentiostat (Versastat model) driven by Electrochemical Analysis System software (model 270) was used to control the electrodeposition process and to monitor the current and voltage profiles. The film was deposited at a constant potential of  $-0.90$  V in an unstirred bath. The electrolytes; Ni-tartrate complex ( $0.01$  M) and sodium thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3$ ,  $0.01$  M) were prepared using analytical grade reagents and deionised water. Sodium tartrate was used to chelate with  $\text{Ni}^{2+}$  to obtain a Ni-tartrate complex. Nitrogen gas was flowed into the solutions prior to mixing to remove any dissolved  $\text{O}_2$ . HCl ( $0.1$  M) was added dropwise ( $\text{pH} = 1.5$ ) to prevent the formation of hydroxyl species and insoluble compound [18]. The deposition was carried out at room temperature by varying deposition time 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

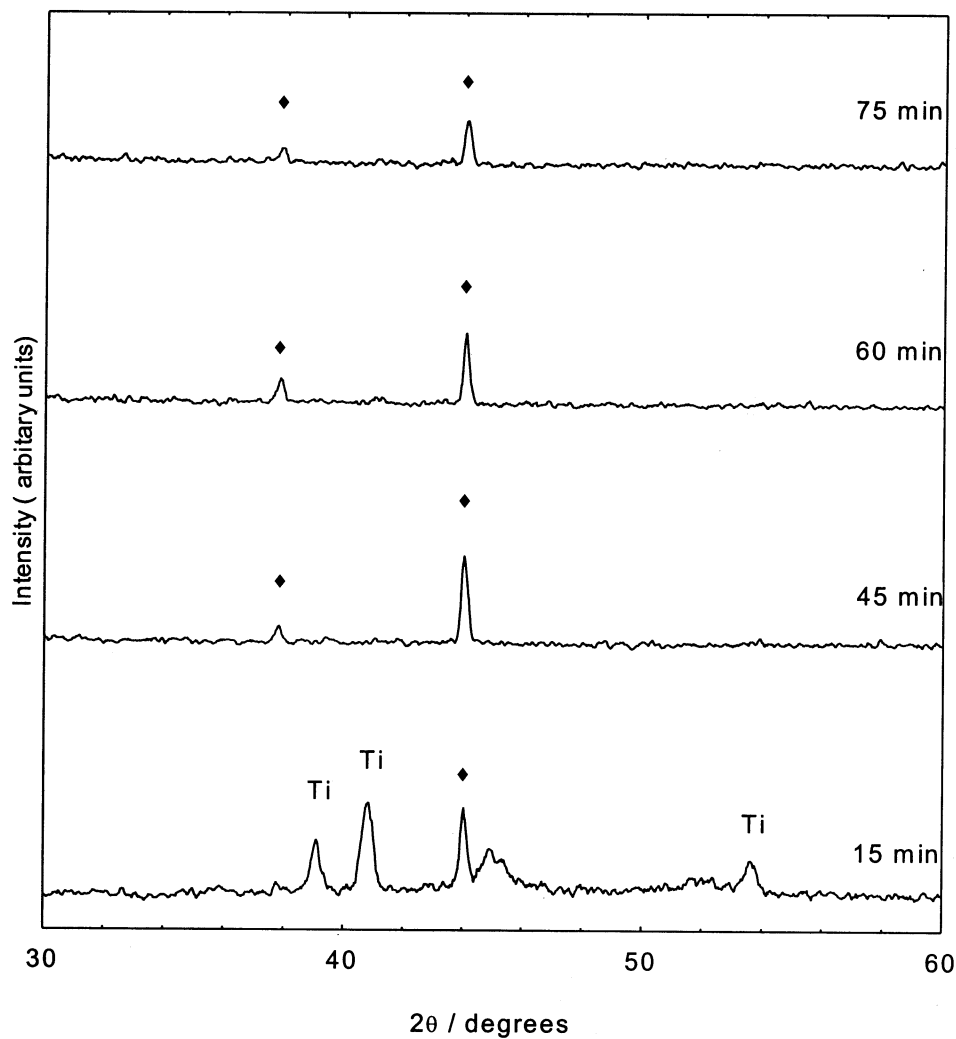
steady stream of distilled water.

XRD analysis was performed using a Shimadzu XRD 6000 Diffractometer for the  $2\theta$  ranges from  $2^\circ$  to  $60^\circ$  with  $\text{CuK}\alpha$  ( $\lambda = 1.5418 \text{ \AA}$ ) radiation. Scanning electron microscope (SEM) analysis was performed using JSM-6400 JEOL Scanning Electron Microscope. 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 DISCUSSION

Figure 1 shows the XRD plot of the  $\text{NiS}_2$  thin films deposited different deposition period. At 15 minutes deposition time, a single peak at  $2\theta = 44.0^\circ$  corresponding to the interplanar distance of  $2.0 \text{ \AA}$  was obtained. As the deposition time was increased to 45 minutes, the intensity of the mentioned peak increased. Additional peak at  $2\theta = 37.8^\circ$  corresponding to the interplanar distance of  $2.4 \text{ \AA}$  was also obtained. The increase in the number of peaks due to NiS indicates that deposition time of 30 minutes was insufficient due to incomplete nucleation stage. The obtained values are well matched with the standard Joint Committee on Powder Diffraction Standards (JCPDS) data (File No: 02-1280) (Table 1). The sharp intensity of the peaks confirms the formation of polycrystalline materials. However, the intensity of these peaks decreased as the deposition time was increased to 75 minutes. This shows that deposition time beyond 60 minutes was not suitable for the electrodeposition process of NiS thin films under the current condition.

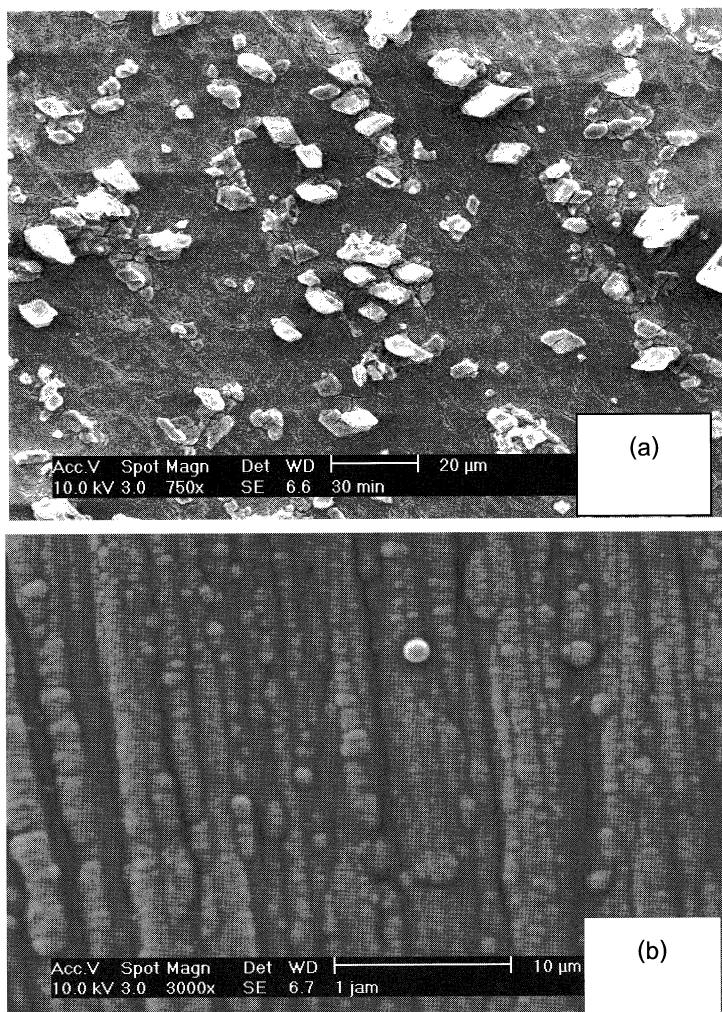
Figure 2 shows the SEM macrographs of  $\text{NiS}_2$  thin films prepared at different deposition period (30 and 60 minutes). The film prepared at 30 minutes deposition time shows an incomplete surface coverage by the polycrystalline materials. The sizes of the



**Figure 1.** XRD plot of NiS thin films deposited at different period; NiS (♦).

**Table 1.** Comparison between JCPDS d-spacing data and experimentally observed values for samples deposited at different periods.

Deposition time (min)	2θ (°)	d-spacing (Å)		Compound
		Experimental values	JCPDS values	
15	44.0	2.0	1.9	NiS
45	37.8	2.4	2.5	NiS
	44.0	2.0	1.9	
60	37.8	2.4	2.5	NiS
	44.0	2.0	1.9	
75	37.8	2.4	2.5	NiS
	44.0	2.0	1.9	



**Figure 2.** SEM micrographs of NiS thin films deposited for: (a) 30 min and (b) 60 min.

crystallites were irregular indicating incomplete growth mechanism. As the deposition time was increased to 60 minutes, the surface coverage was complete thus exhibiting smooth and compact morphology. The similar growth orientation indicates constant growth mechanism. The presence of complexing agents have been reported to assist in the controlled release of metal ions into the reaction bath. The presence of smooth and well-defined grain edges in the SEM micrographs of the thin film agrees with the fact that sodium tartrate assists in the well-controlled release of  $\text{Ni}^{2+}$  ions.

Figure 3 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 opto-electric 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  $\nu$  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,  $E_g$ ,

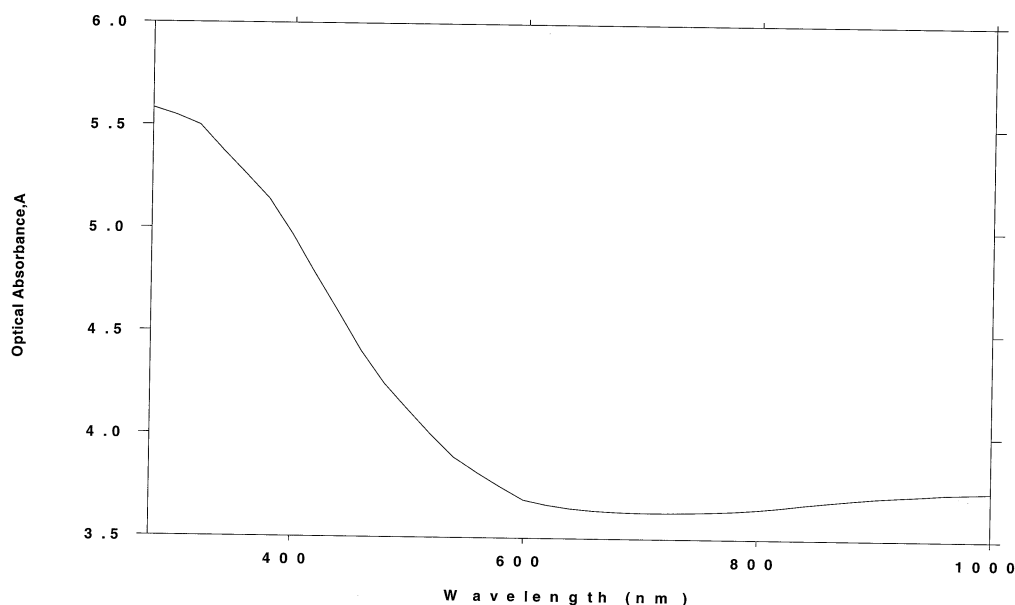


Figure 3. Optical absorbance versus wavelength of NiS thin film.

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  $n = 4$ .

A linear trend is apparent where  $n$  in the relationship (1) equals 1 (Figure 4). 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.

#### 4. CONCLUSIONS

Polycrystalline NiS thin films could be electrodeposited on Ti substrate under the presence of sodium tartrate as a complexing agent. The optimum deposition time to

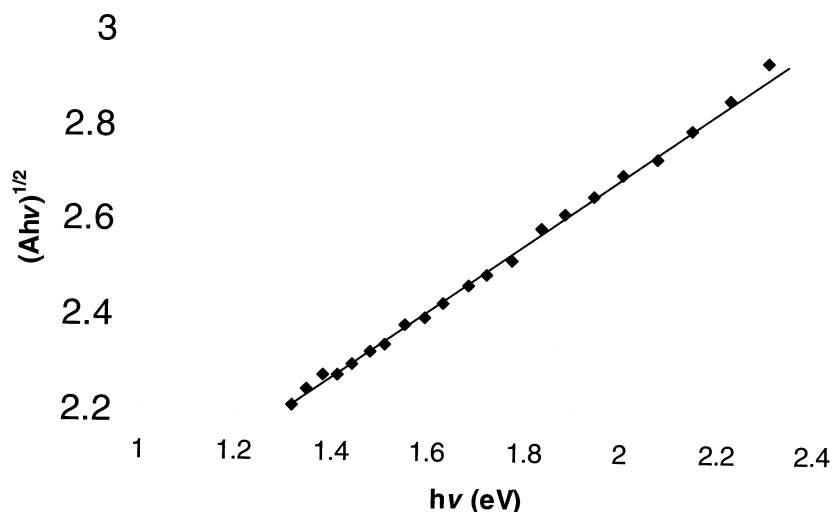


Figure 4. Plot of  $(Ah\nu)^{2/n}$  versus  $h\nu$  for the film prepared when  $n = 1$ .

deposit the film is 60 minutes. The film obtained exhibit direct transition in the visible with a bandgap value of about 1.30 eV.

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