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# Studies on Electrodeposited NiS Thin Films

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***Abstract:*** *Thin films of NiS have been deposited on indium doped tin oxide coated conducting glass substrates using electrodeposition technique. Structural studies revealed that the deposited films exhibit hexagonal structure with preferential orientation along (002) plane. Structural parameters such as crystallite size, strain and dislocation density are calculated for films with different thickness values obtained at various deposition time. The film composition and surface morphology have been analyzed using scanning electron microscopy and energy dispersive analysis by X-rays. Optical absorption analysis showed that the deposited films possess band gap value around 0.7 eV.*

*Keywords: Thin Films, NiS, Electrodeposition, Semiconductor*

## 1. INTRODUCTION

Thin films of transition metal chalcogenides have been received considerable interest due to their unique optical and electrical properties along with their wide variety of potential applications in nonlinear optical devices, semiconductors and electroluminescent devices, industrial catalysts and solar energy conversion devices etc., [1,2]. Besides, these are non-toxic and abundant in nature, inexpensive and possess semiconducting properties. Transition metal chalcogenides and their mixtures are attractive and useful systems for solar energy conversion through photoelectrochemical route [3-5]. Nickel Sulphide (NiS) is a direct band gap semiconductor with band gap value in the range between 0.45 and 1.2 eV, which make them interesting for electrochromic and solar cell devices **[**6-8**]**. Thin films of NiS are usually crystallized in hexagonal structure (JCPDS ICDD, PDF File No.77 0624) with lattice constants (a = 3.439 Å; c = 5.324 Å). Various techniques have been attempted to prepare NiS thin films, such as electron beam evaporation [6], chemical bath deposition [9], pulsed laser ablation [10], metal organic chemical vapor deposition [11], SILAR [12] etc. When compared to the deposition techniques used for the preparation of NiS thin films, electrodeposition come into picture, because of its low cost of synthesis, low temperature processing, no need of vaccum facility, no contamination to the surrounding, control of film growth and morphology by readily adjusting the deposition parameters as well as composition of the electrolytic bath [13-18].

In the present investigation, we have reported our work on the preparation and characterization of NiS thin films on indium doped tin oxide coated conducting glass (ITO) substrates from an aqueous acidic bath containing $NiCl_2$ and $Na_2S_2O_3$. Thickness of the deposited films has been measured using Stylus Profilometer. X-ray diffraction analysis has been carried out to determine film structure and microstructural parameters such as crystallite size, strain and dislocation density. Scanning electron microscopy and energy dispersive analysis by X-rays have been carried out to determine the surface morphology and film composition of the depo-

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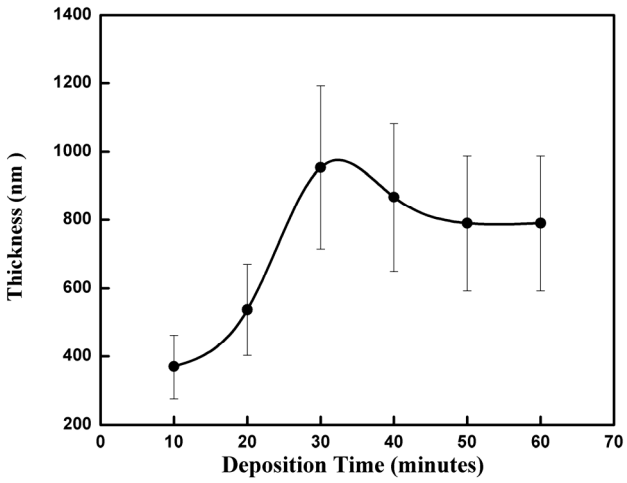


Figure 1. Variation of film thickness with deposition time for NiS thin films prepared at bath temperature 80ºC

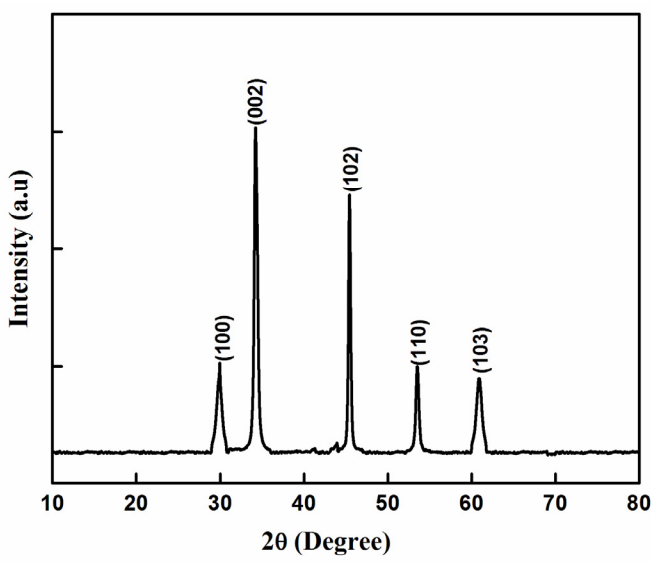


Figure 2. X-ray diffraction pattern of NiS thin films obtained at bath temperature 80ºC

sited films. Optical absorption analysis has been taken out to determine the band gap value of the deposited films. The effect of deposition time with film thickness on structural, morphological, compositional and optical properties of the films were analyzed. The experimental observations are discussed in detail.

## 2. EXPERIMENTAL DETAILS

Thin films of NiS were prepared on ITO substrates using potentiostatic electrodeposition technique. The chemicals used in the present work were of Analar grade (AR) reagents (Merck). The first the working solution was obtained by dissolving 0.162 g $NiCl_2$ in 250 cc double distilled water and the second working solution was obtained by liquefying 9.515 g $Na_2S_2O_3$ in 250 cc double distilled water. Each 30 cc of the two solutions forms the reaction mixture and this mixture can be used as an electrolytic bath for all depositions. The electrochemical experiments were carried out using Model SP50 scanning Potentiostat/Galvanostat (Biologic, France) applying the three-electrode cell configuration with ITO substrate as working electrode, platinum electrode as counter electrode and saturated calomel electrode (SCE) as reference electrode, respectively. The pH value of the electrolytic bath was adjusted to 3.5 ± 0.1 with the help of dilute $H_2SO_4$. Before using for film preparation, ITO substrates were immersed in a bath of isopropanol and then rinsed with acetone. The magnetic stirrer with heater set up was used to stir up the solution as well as raise the temperature of the electrolytic bath. The SCE was kept closer to the working electrode with the help of luggin capillary arrangement. The bath temperature and deposition potential were fixed as 80°C and -700 mV versus SCE for all depositions. The deposition time was varied in the range between 10 and 60 minutes to obtain films with different thickness values.

### 2.1. Characterization

Stylus profilometer (Mitutoyo SJ 301, Japan) was used to measure thickness value of the films obtained at various deposition times. An X-ray diffractometer (XPERT PRO PANalytical, Netherland) with $CuK_\alpha$ radiation ($\lambda$=1.5406Å) was utilized to identify crystalline nature and phases of the deposited films. Structural parameters such as crystallite size, strain and dislocation density were determined from observed X-ray diffraction data. The film composition and surface morphology of the deposited films were analyzed using scanning electron microscopy and energy dispersive analysis by X-rays (Philips Model XL30, USA). Optical absorption measurements was carried out using an UV-Vis-NIR spectrophotometer (Shimadzu Model 2600, Singapore).

## 3. RESULTS AND DISCUSSION

### 3.1. Film Thickness

The deposition of NiS thin films was controlled by separate variables such as film thickness, uniformity and surface morphology [16,17]. Thickness value of the deposited films could be controlled by controlling the plating current, plating temperature and deposition time. Thickness value of the deposited films is measured using stylus profilometer. Figure 1 shows the variation of film thickness with deposition time for NiS thin film obtained under bath temperature 80ºC at various deposition times in the range between 10 and 60 minutes. It is found that film thickness increases with deposition time and tends to attain its maximum value at a deposition time around 30 minutes. Initially, film thickness increases rapidly which may be due to the presence of more number of ions present in the electrolytic bath. Once the deposition is started, film thickness increases with deposition time due to effective mass transfer present in the electrolytic bath. The rate of deposition was attained its maximum value at a deposition time around 30 minutes, thereafter its value decreased slightly which is indicated in figure 1 which may be due to transfer of less number of ions to the cathode. Hence, deposition time is fixed as 30 minutes to obtain films with higher thickness values.

### 3.2. Structural Analysis

X-ray diffraction analysis has been carried out to determine crys-

talline nature and phases of the deposited films. At lower bath temperature such as 40°C, adherence of the deposited film to the substrate is poor, whereas at higher bath temperatures such as 80°C and above there is peel off of the film from the substrate. As a result, the bath temperature was fixed as 80°C to obtain films with higher thickness and better crystallinity. X-ray diffraction pattern recorded for NiS thin films obtained at bath temperature 80°C is shown in Figure 2. XRD patterns showed that the deposited films are found to be polycrystalline in nature with hexagonal structure with lattice constants ( a = 3.439Å; c = 5.324Å). The diffraction peaks of NiS are observed at 2θ values of angles 30.06, 34.39, 46.37, 53.53 and 60.97 corresponding to the lattice planes (100), (002), (102), (110) and (103) respectively. The observed peaks in the diffractograms are indexed and the corresponding values of interplanar spacing "d" are calculated using Eq.(1) and compared with standard JCPDS ICDD file for hexagonal NiS [19]. It is observed that the height of (002) plane is found to be higher than all other peaks in the diffractogram indicating that the crystallites are preferentially oriented along (002) plane. Films with better quality and higher crystallinity are obtained at higher bath temperature 80°C and at a deposition time around 30 minutes. The value of lattice constants 'a' and 'c' of the hexagonal NiS films are estimated using Eq.(2). The crystallite size is defined as the size of crystallites formed on the plane of the substrate surface. The crystallite size values of the deposited films have been estimated using FWHM data with Debye-Scherrer formula given in Eq.(3) [15,16].

$$d_{hkl} = \frac{\lambda}{2\sin\theta} \tag{1}$$

$$\frac{1}{d_{hkl}^2} = \frac{4}{3}\left[\frac{h^2 + hk + k^2}{a^2}\right] + \left[\frac{l^2}{c^2}\right] \tag{2}$$

$$D = \frac{0.9\lambda}{\beta\cos\theta} \tag{3}$$

where, λ is wavelength of $CuK_\alpha$ target used (λ=1.540 Å), β is Full Width at Half Maximum of the peak position in radians, θ is Bragg's diffraction angle at peak position in degrees.

Films with different thickness value are obtained by varying the deposition time in the range between 10 and 60 minutes with constant bath temperature 80ºC. Variation of crystallite size and strain with maximum film thickness value for each film obtained with respect to corresponding deposition time is shown in Figure 3a. It is observed that the value of crystallite size increases with deposition time and reaches its maximum value of 950 nm corresponding to a deposition time of 30 minutes, afterwards its value decreases slightly. Strain is defined as the restoring force acting on the surface of the film to restrict the formation of crystallites on its surface and its value is calculated using Eq.(4). Variation of strain with maximum film thickness value for each film with respect to corresponding deposition time is indicated in Figure 3a. It is noted that the value of strain decreases with respect to deposition time and attained its minimum value for films with maximum thickness value of 950 nm obtained at a deposition time of 30 minutes, afterwards its value increases slightly. Dislocation density is defined as the number of

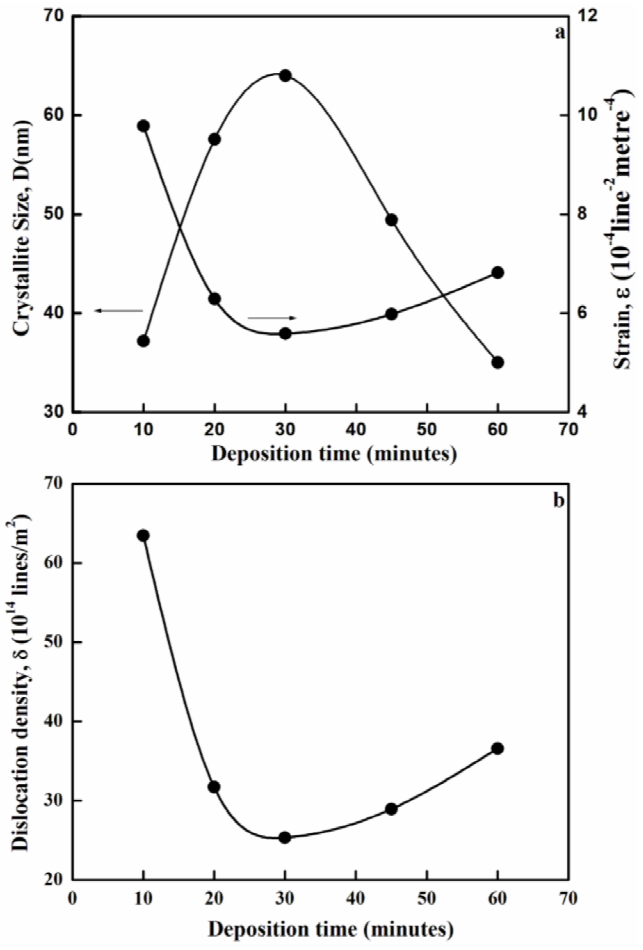


Figure 3. a. Variation of crystallite size and strain with deposition time for NiS thin films obtained at bath temperature 80ºC. b. Variation of dislocation density with deposition time for NiS thin films obtained at bath temperature 80ºC

dislocation lines per unit volume of the crystal and it can be calculated using Eq.(5) [15,18].

$$\beta = \left[\frac{\lambda}{D\cos\theta} - \varepsilon\tan\theta\right] \tag{4}$$

$$\delta = \frac{1}{D^2} \tag{5}$$

Films with different thickness value in the range between 200 and 950 nm are obtained by varying the deposition time in the range between 10 and 60 minutes and fixed the bath temperature around 80ºC. Figure 3b shows the variation of dislocation density with film thickness value for films obtained at bath temperature of 80ºC corresponding to its deposition time in the range between 10 and 60 minutes. It is observed that the value of dislocation density is found to decrease while increasing the deposition time up to 30 minutes, thereafter its value increases slightly which is noted in Figure 3b. Increase in the value of film thickness results decrease in

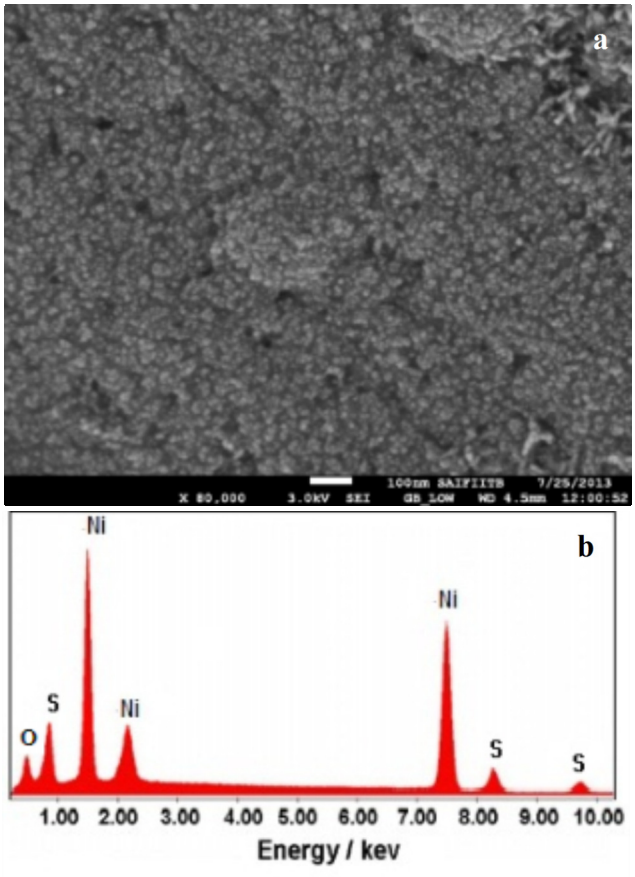


Figure 4. a. SEM image of NiS thin films obtained at bath temperature 80ºC. b. EDX spectrum of NiS thin films obtained at bath temperature 80ºC

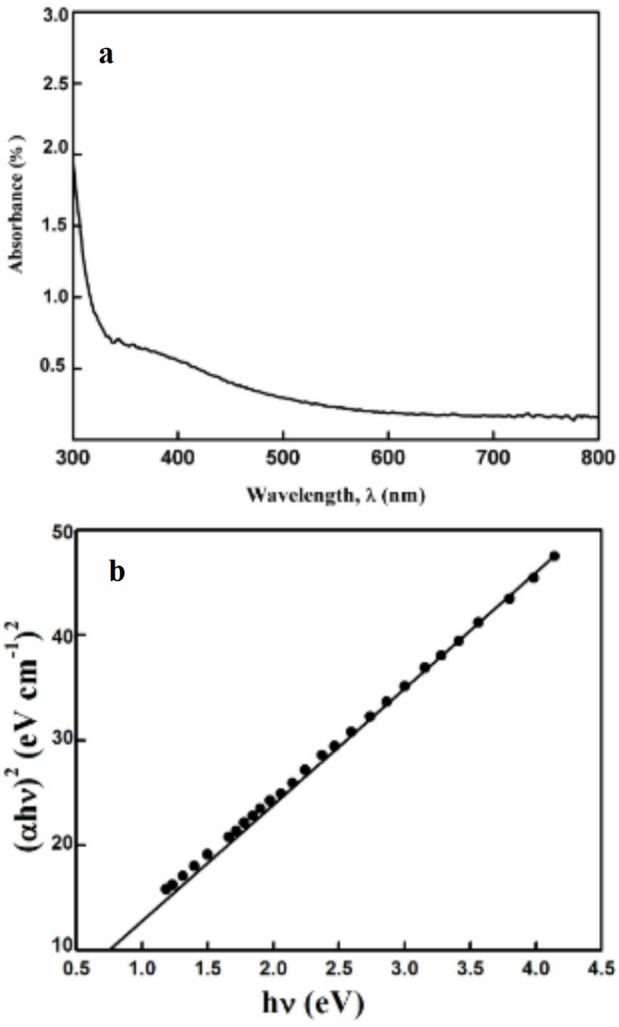


Figure 5. a. Absorption spectrum of NiS thin films obtained at bath temperature 80ºC. b. Plot of (hυ) versus $(\alpha h\upsilon)^2$ for NiS thin films obtained at bath temperature 80ºC

value of FWHM data presented in the XRD pattern leads to produce increase in sizes of the crystallites present in the deposited films. When sizes of the crystallites increased, there must be decrease in the value of restriction force present in the deposited films, thus leads to production of smaller value of strain and dislocation density present in the deposited films. It is also observed from figures 3a and 3b that maximum value of crystallite size, minimum value of strain and dislocation density are noted for films with maximum thickness value around 950 nm which has been obtained at a deposition time and bath temperature around 30 minutes and 80ºC respectively. Similar functional dependency of microstructural parameters with deposition time for CuSe and PbS have been reported earlier [20,21].

### 3.3. Morphological and Compositional Analyses

Scanning electron microscopy image of a typical NiS thin film deposited on ITO substrate at bath temperature 80ºC and at a deposition time of 30 minutes is shown in Figure 4a. It is observed that the film surface is composed of uniform size spherically shaped grains, which are strongly packed together. The grains are well covered the substrate surface without any cracks and voids. The average size of the grains is found to be 20 nm. The film composition of the deposited films has been analyzed using energy dispersive analysis by X-rays. Figure 4b shows the EDX spectrum of NiS thin films prepared at bath temperature 80ºC and at a deposition time of 30 minutes. The value of atomic percentage for films obtained at bath temperature around 80ºC is observed to be 45.24:54.76. The atomic molar ratio for films obtained at bath temperature 80ºC is found to be 0.82:1. This result is consistent with that of the X-ray diffraction analysis of the sample with phase corresponding to $Ni_{0.82}S_1$.

### 3.4. Optical Absorption Analysis

Optical absorption analysis has been carried out to determine the optical properties of the deposited films. An uncoated ITO substrate is introduced in the reference beam to correct the substrate absorption of the deposited films. The absorption coefficient (α) rises sharply on account of band-to-band transition and levels off later. An analysis of absorption spectrum in the investigated energy

indicates that (α) follows the relation in Eq. 6. The value of absorption coefficient is used to determine the type of band gap present in the deposited film [15, 22].

$$\alpha h\nu = A\left(h\nu - E_g\right)^n \quad (6)$$

where, $E_g$ is the band gap value of deposited film, hυ is photon energy, A is an energy dependent constant, substitute the value of n as 1/2, 2, 3/2 and 3 for direct allowed, indirect allowed, direct forbidden, indirect forbidden transitions. Plots are drawn for ($h\nu$) vs $(\alpha h\nu)^2$, ($h\nu$) vs $(\alpha h\nu)^{1/2}$, ($h\nu$) vs $(\alpha h\nu)^{2/3}$ and ($h\nu$) vs $(\alpha h\nu)^{1/3}$, the intercept of plot with energy ($h\nu$) axis directly gives band gap value of the corresponding transition. The optical absorption spectrum of NiS thin films prepared at bath temperature 80°C is shown in Figure 5a. Figure 5b shows the plot of ($h\nu$) versus $(\alpha h\nu)^2$ for NiS thin films obtained at bath temperature 80°C and at deposition time of 30 minutes. Extrapolation of linear portion of the graph to energy axis ($h\nu$) gives band gap value of the material. The band gap value of the material obtained in the present work is found to be 0.72 eV, which must be quite closer to the value reported earlier [6-8].

## 4. CONCLUSIONS

Thin Films of NiS were prepared on ITO substrates using electrodeposition technique. X-ray diffraction analysis showed that the prepared films possess polycrystalline in nature with hexagonal structure and preferential orientation along (002) plane. Microstructural parameters such as crystallite size, strain and dislocation density were found to exhibit monotonic variation with deposition time. Films with smooth surface and well defined stoichiometry were obtained under deposition time of 30 minutes and at optimized bath temperature around 80°C.

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