

Effect of bath temperature on the structural and optical properties of nickel sulphide (NiS) films prepared by chemical bath deposition

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Abstract - Nickel sulphide (NiS) is a promising material, which can be used in different applications such as solar cells, super-capacitors, infra-red detectors and sensors. In the present study, NiS thin films were prepared at different bath temperatures (T_b), varying in the range of 50-80°C by chemical bath deposition (CBD) method. The structural, morphological, elemental analysis, functional groups, and optical studies were carried out to examine the effect of bath temperature on the physical properties of NiS thin films. XRD studies revealed that the bath temperature had profound effect on the structure and crystallinity of CBD NiS films. The as-deposited NiS thin films showed amorphous nature at lower bath temperatures (<60°C) whereas the diffraction pattern of NiS thin films deposited at $T_b \geq 70^\circ\text{C}$ showed good crystallinity with hexagonal structure. The average crystalline size of the films was found to be 17 nm. The EDS analysis indicated the approach of stoichiometry with increase of T_b . The optical band gap energy of deposited NiS thin films was decreased from 2.25 eV to 2.03 eV with increase of bath temperature.

Keywords — Bath temperature, Band gap energy, Chemical bath, NiS thin films, Optical, Structural.

I. INTRODUCTION

The energy storage and conversion are the today's major needs of the entire world owing to the increased energy demand and partial accessibility of fossil fuels. In the present scenario, many researchers have focused to develop low cost and green energy storage, and conversion devices such as super capacitor and solar cells [1-3]. Mainly, the transition metal chalcogenides have been attracted much attention during the past decades due to their unique chemical and physical properties as well as their utilization as the catalytic, semiconducting, optical, and magnetic materials [4-8]. In the transition metal chalcogenides, metal sulfides such as the nickel sulphide (NiS), copper sulphide (CuS), zinc sulphide (ZnS), cadmium sulphide (CdS), silver sulphide (AgS) have been extensively studied and used in many applications [9-13]. Among these transition metal sulphides, NiS has been widely utilized in the application of energy storage and conversion devices. In nickel-sulfur system, different phases such as Ni_9S_8 , Ni_7S_6 , Ni_6S_5 , Ni_3S_4 , Ni_3S_2 , NiS_2 and NiS have been reported. Among these phases, NiS exhibits two structures namely hexagonal α -NiS

and rhombohedral β -NiS depending on the preparation conditions [14]. It has been used for many applications such as in solar cells [15], super-capacitors [16] and in lithium ion micro-batteries [17]. NiS is environmentally safe to handle and contains elements that are earth abundant.

NiS was prepared by various techniques such as a hydrothermal method [18], microwave synthesis [19], solvothermal method [20], precipitation method [21], spray pyrolysis method [22], ionic exchange process [23], screen printing method [24], polyol synthesis [25], reflux method [26] and chemical bath deposition method (CBD) [27]. Among these methods, chemical bath deposition has many advantages for the preparation of NiS thin films because it is simple, inexpensive method, suitable for the deposition of large surface area, wastage of material, usage of simple instruments and ease of control over doping of thin films. However, only few reports have been published so far on the deposition of NiS by CBD process with limited information on the film characteristics. Anuar Kassim et al. [28] studied the influence of triethanolamine usage on the properties of CBD grown NiS films. The study indicates

that the number of peaks in the XRD data increased as the concentration of triethanolamine (TEA) was increased up to 0.1M. However, the XRD pattern of NiS films was not provided in that study. The SEM analysis indicates that the grains were much bigger for the films prepared using 0.1 and 0.2M of TEA than that of 0.05M. Paresh Gaikar et al.[27] prepared NiS films on Ti-substrate by chemical bath deposition method without any additive for pseudo capacitor application where the XRD pattern of NiS showed polycrystalline nature. In the CBD, among the various parameters, bath temperature is one of the most important factors that control the release of Ni and sulfur ions in the reaction bath during deposition. To the best of our knowledge, no reports have been published on the effect of bath temperature on the deposition and properties of NiS films deposited by CBD technique. Therefore in the present work, deposition of NiS thin films were carried out by using chemical bath deposition method at different bath temperature, which vary from 50°C to 80°C and the physical properties of the grown films were investigated.

II. EXPERIMENTAL

2.1. Preparation of NiS thin films

For the deposition of NiS films using CBD process, nickel sulphate hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) and thioacetamide ($\text{C}_2\text{H}_5\text{NS}$) were used as the precursors for nickel and sulphur ions. 20 ml of 0.8M $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ aqueous solution was taken in a 100 ml beaker. To this solution, 4 ml of triethanolamine (TEA) was added drop wise. TEA acts as a complexing agent during the deposition period. The above mixture was stirred continuously for 15 min and then 4 ml of ammonia (NH_3) was added drop wise. Next, 20 ml of 0.8 M of thioacetamide aqueous solution was added to the above mixture. The pH of the solution was found to be about 9.5 after mixing the chemicals. Cleaning of the substrates prior to film deposition plays a crucial role in controlling the quality and adhesion of the deposited films. Therefore, the substrates were initially immersed in hot chromic acid for 30 min, cleaned using deionize water and then sonicated with doubled distilled water for another 15 min followed by drying in hot air oven. The pre-cleaned soda lime glass substrates were kept vertically in the chemical bath for the deposition of NiS films. The deposition was carried out at different bath temperatures varying in the range of 50-80 °C for a fixed deposition time of 2 h. After deposition of films, the substrates were washed with distilled water, dried and used for characterization and analysis.

2.2. Characterization

The structure analysis of NiS films was carried out by using Rigaku X-ray diffractometer (Miniflex 600) using $\text{Cu } \alpha$ radiation in the 2θ range, 20° - 80°. The morphological

and chemical compositions of the films were analyzed through the Scanning Electron Microscopy (JEOLJSM-IT500) along with the Energy Dispersive X-ray Spectroscopy (AMETEK). The functional groups present in the films were carried out using FTIR spectra (BRUKER) in the wave number range, 400 - 4000 cm^{-1} . The optical properties of NiS thin films were analyzed by using the UV-Vis spectrophotometer (SHIMADZU UV-2600i model) in the wavelength range of 450 – 850 nm.

III. RESULTS AND DISCUSSION

3.1. Structural studies

Fig.1 shows the X-ray diffraction pattern of NiS thin films formed at various bath temperatures used in this study. The films grown at 50°C showed amorphous nature with a broad hump observed near 25°. The films deposited at 60°C showed two small peaks at $2\theta = 30.74^\circ$ and 54.15° that correspond to the (100) and (110) planes of hexagonal NiS. With increase of bath temperature an improvement in the crystallinity of NiS film can be observed. The diffraction pattern of NiS thin films deposited at 70°C and 80°C showed good crystallinity with hexagonal structure of space group P63/mnc. The diffraction pattern of NiS films deposited at bath temperatures $\geq 70^\circ\text{C}$ showed four peaks at $2\theta = 30.10^\circ$, 34.47° , 45.79° and 53.56° , which corresponds to the (100), (101), (102) and (110) planes, respectively. All the diffraction peaks were well matched with the hexagonal structure of NiS as reported in the JCPDS card number: 65-3419. No other impurity phases were observed in the XRD pattern, which suggests the high purity of CBD deposited NiS films. Out of the four crystal planes observed, the plane related to the (100) direction had the highest intensity, which indicated the preferred growth of this orientation. Further, the films deposited at 80°C exhibited sharp and more intense (100) peak with low fringe width at half maximum compared to the films formed at 70 °C, indicating good crystallinity in these films.

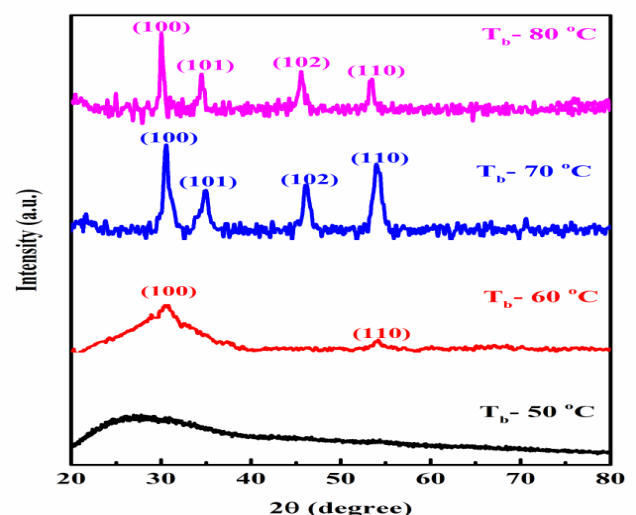


Fig. 1. X-ray diffraction pattern of NiS thin films at various bath temperatures.

The average crystallite size was calculated using the Debye-Scherrer equation,

$$D = \frac{0.9 \lambda}{\beta \cos \theta} \text{ nm}$$

Here, λ is the wavelength of X-rays used (Cu $K\alpha$ radiation with $\lambda = 1.542 \text{ \AA}$), θ is the angle of diffraction and β is full width at half maxima. The average crystallite size of NiS films deposited at 70°C and 80°C was found to be 11 nm and 17 nm. As the bath temperature was increased, the kinetic energy of the reacting ions in the aqueous solution was increased that led to the nucleation of more ions in the crystallite with the result of an increase in the crystallite size.

The other structural parameters namely lattice parameters (a and c), micro-stain (ϵ), dislocation density (δ), positional parameters (u), bond length (l) and unit cell volume (V) of NiS thin films deposited at 70°C and 80°C were calculated using the relations given below [29-31]

$$\frac{1}{d^2} = \frac{4(h^2 + hk + k^2)}{3a^2} + \frac{l^2}{c^2}$$

$$\epsilon = \frac{\beta}{4 \tan \theta}$$

Table 1: The structural parameters of NiS thin films prepared at various temperature.

Bath Temperature ($^\circ\text{C}$)	Diffraction peak	FWHM	Grain size (nm)	Dislocation density (10^{15} Lines / m^2)	Micro strain (10^{-3})	Lattice constant (a)	Lattice constant (c)	Positional parameter (u)	Bond length, l (\AA)	Cell volume, V (\AA^3)
70	(100)	0.0106	11	5.43	9.706	3.412	5.336	0.386	2.061	53.79
80	(100)	0.0068	17	2.25	6.300	3.423	5.373	0.385	2.085	54.20

3.2. Morphology analysis

The surface morphology of NiS thin films prepared at different bath temperatures is shown in Fig. 2 (a-d). The NiS thin films deposited at 50°C showed particles with flake like structure. As can be seen from Fig. 2(a), the particles were agglomerated due to amorphous nature. The films deposited at 60°C showed a layered structure and consist of beads shaped particles as shown in Fig. 2(b). The SEM image of NiS films formed at 70°C exhibited completely different morphology compared to films deposited at 50°C and 60°C . The morphology of films, Fig. 2(c), grown at 70°C bath temperature revealed complete and dense coverage of the substrate with grains along with petals shaped particles over it. When the bath temperature was further increased to 80°C , the surface of the deposited film showed agglomerated spherical and small rod shape particles as shown in Fig. 2(d). The change in the morphology with bath temperature was due to temperature effect on the nucleation growth of particles.

$$\delta = \frac{1}{D^2} \text{ Lines}/\text{m}^2$$

$$u = a^2/3c^2 + 0.25$$

$$l = \sqrt{a^2/3 + \left(\frac{1}{2} - u\right)^2 c^2}$$

$$V = 0.866 \text{ xa}^2 \times c$$

where, d_{hkl} is the inter-planar spacing; a and c are the lattice parameters; h , k , and l are the miller indices.

The evaluated crystallite size, micro strain, dislocation density, lattice constants (a & c), positional parameters, bond length and cell volume (a & c) of the prepared thin films were calculated from the XRD spectra and are listed in Table 1. The calculated lattice constants and other structural parameters of CBD NiS were found to be in close agreement with that of the reported NiS values [32].

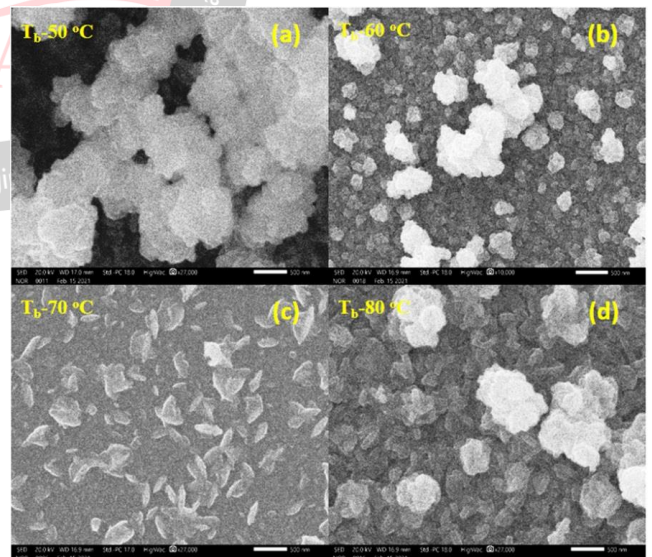


Fig. 2. Scanning electron microscope images of NiS films deposited at various bath temperatures.

3.3. Composition studies

The EDS spectra of NiS thin films deposited at different bath temperatures are shown in Fig.3 (a-d). It revealed that films deposited at 50°C and 60°C showed Ni and S along with O. The detection of oxygen in these layers might be

due to the surface adsorption of oxygen or oxygen from Ni(OH)_2 formed along with NiS as such low temperatures may not be sufficient for complete reaction to occur in the solution. However, films prepared at bath temperatures in the range of 70-80°C showed only Ni and S, which indicates complete conversion of the bath mixture into NiS with increase of temperature. The composition of elements estimated for NiS films formed at different bath temperatures from the EDS spectra is given in Table 2.

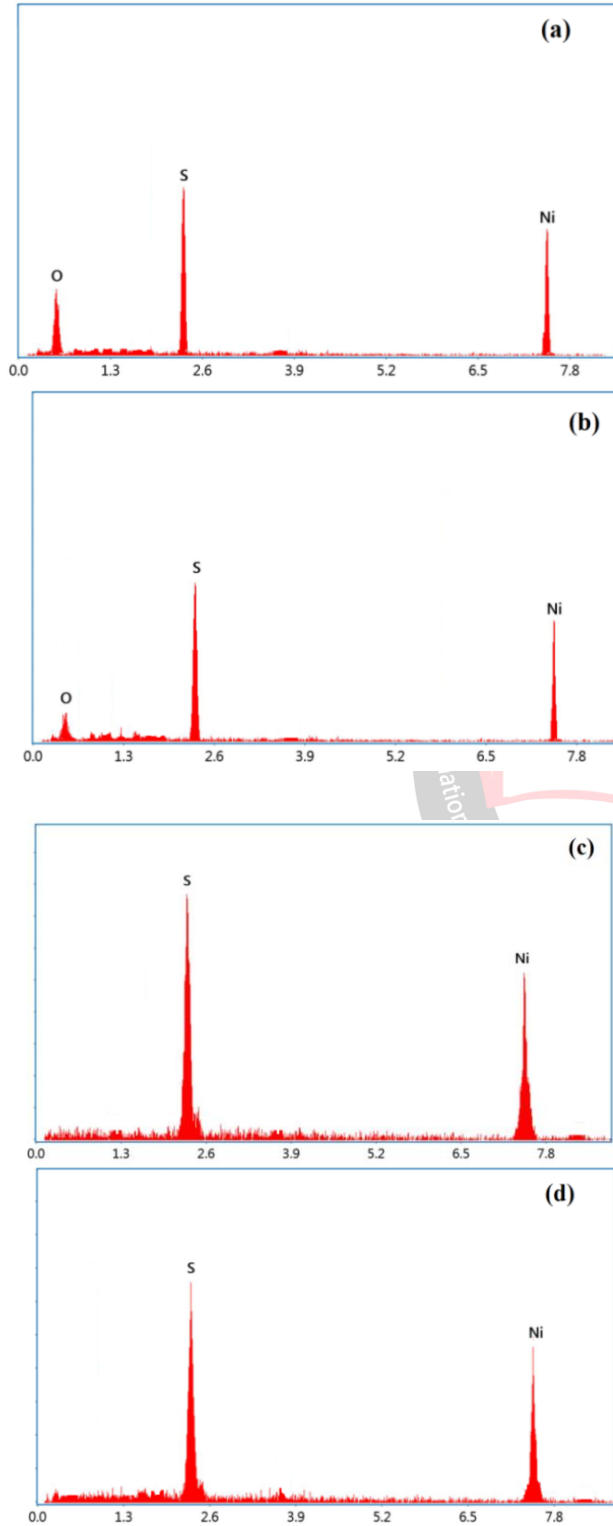


Fig. 3. EDS spectra of NiS films formed at T_b = (a) 50°C, (b) 60°C (c) 70°C and (d) 80°C.

Table 2: Measured elemental composition of NiS films using EDS.

Sl No	Bath temperature, T_b (°C)	Atomic %			Ni/S
		O	S	Ni	
1	50	9.79	48.05	42.16	0.88
2	60	5.6	48.12	46.28	0.96
3	70	-	50.1	49.9	0.99
4	80	-	49.89	50.11	1.00

3.4. FTIR analysis

Fig. 4 represents the FTIR spectra of NiS films prepared at various bath temperatures. The spectra showed two major peaks at 456 cm^{-1} and 517 cm^{-1} related to Ni-S stretching vibrations. These peaks are in close agreement with the characteristics vibration modes of Ni-S, confirming the formation of NiS on the substrates [33, 25]. In general, the peaks observed close to 3600 cm^{-1} corresponds to the hydroxyl (OH) stretching vibration of the absorbed water molecules [34]. However, in the FTIR spectra of NiS layers deposited at 70°C and 80°C showed very small peaks in the wave number range of $3200\text{--}3600\text{ cm}^{-1}$, which indicates the high quality of NiS films with very less water content in the layers.

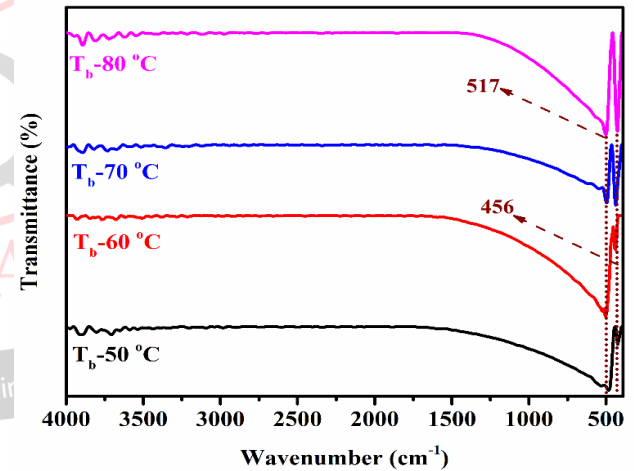


Fig. 4. FTIR spectra of NiS films deposited at various bath temperatures.

3.5. Optical properties

The absorbance spectra of NiS films deposited at different bath temperatures are shown in Fig.5. It can be observed from the figure that the optical absorbance is decreased sharply with increase of wavelength near the fundamental absorption region, indicating the direct nature of the energy band gap in these films. Also, there is an increase of absorption in the films with increase of bath temperature, which might be due to the increase of crystallite size in the films.

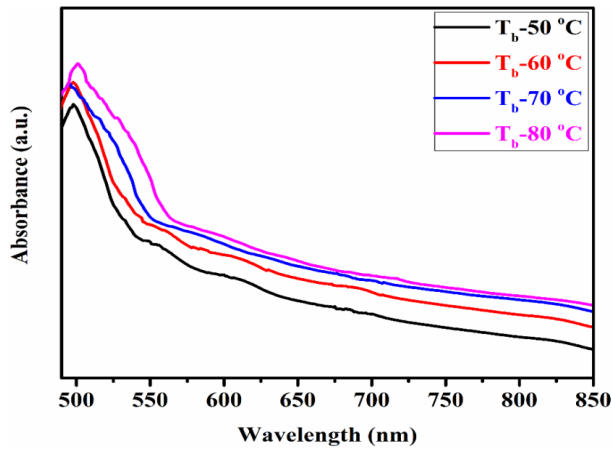


Fig. 5. Absorbance spectra of NiS thin films deposited at different bath temperatures.

The optical energy band gap of films was estimated through Tauc plots, which are shown in Fig. 6. The evaluated band gap energy of NiS layers deposited at 50°C, 60°C, 70°C and 80°C were found to be 2.25 eV, 2.15 eV, 2.06 eV and 2.03 eV respectively. The higher band gap values of 2.25 eV and 2.15 eV determined for films deposited at 50°C and 60°C might be due to the presence of little amount of oxygen in the films in the form of NiO and Ni(OH)₂ phases as evident from EDS and FTIR analysis [35], although such phases were not noticed in the XRD. When the bath temperature was increased to 80°C, the adsorbed water molecules were removed from the films, which led to a decrease of band gap to 2.03 eV [36]. These values of band gap energy of NiS films are in good agreement with that of bulk NiS [37] and reported values in thin films [38].

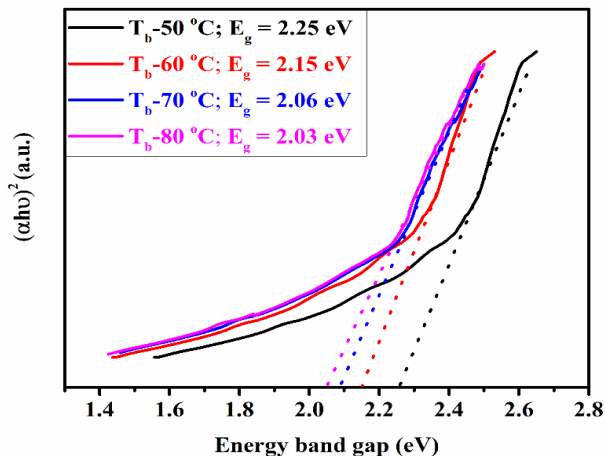


Fig. 6. Tauc's plots of NiS layers formed at different bath temperatures.

Fig. 7 shows the spectral variation of refractive index, n and extinction coefficient, k of NiS films deposited at various bath temperatures as a function of wavelength. From Fig. 7(a), it is observed that the value of refractive index ' n ' decreased with increase of wavelength and shifted towards the longer wavelengths as bath temperature increased to 80°C. This might be due to decrease in packing density with increase of bath temperatures from 50°C to 80°C [39]. From Fig. 7(b), it is observed that the extinction

coefficient falls sharply at the initial stage ($\lambda \sim 520-580$ nm) and thereafter its change is marginal above these wavelengths. The sharp decrease might be due to decrease in the optical scattering and absorbance. The initial decrease of ' k ' values with wavelength indicates the light absorption at specific wavelengths as reported in the literature [40, 41].

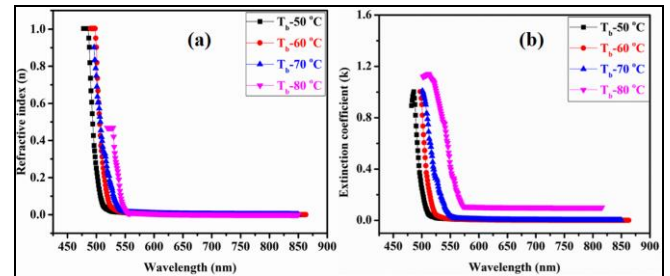


Fig. 7. Change of (a) refractive index and (b) extinction coefficient with wavelength in NiS films.

IV. CONCLUSIONS

The NiS thin films were successfully deposited by the chemical bath deposition method at different bath temperatures that vary in the range of 50°C-80°C. The XRD studies revealed amorphous nature in NiS layers for $T_b < 70^\circ\text{C}$ and only single phase with an intense (100) plane along with hexagonal crystal structure for $T_b \geq 70^\circ\text{C}$. The SEM analysis showed bath temperature dependent growth of NiS particles with a change in the surface morphology. The EDS analysis indicated near stoichiometric composition for the layers deposited at $T_b = 80^\circ\text{C}$. The FTIR studies showed the characteristic vibrational modes of Ni-S. The optical band gap of the films was decreased from 2.25 eV to 2.03 eV with increase of bath temperature from 50°C to 80°C. The single phase, near stoichiometric and highly absorbing NiS films formed at $T_b = 80^\circ\text{C}$ might be useful in the energy conversion and energy storage applications.

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