STRUCTURAL, MORPHOLOGICAL, OPTICAL AND ELECTRICAL PROPERTIES OF NICKEL SULPHIDE THIN FILMS

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Chemical bath deposition (CBD) technique was used for the synthesis of the Nickel Sulphide (NiS) thin films. The prepared NiS thin films were found to be polycrystalline and the crystals had hexagonal structure as revealed in the X-ray diffraction (XRD) analysis. The surface morphology of these films was studied by means of scanning electron microscopy (SEM). The optical properties of the NiS thin films were determined using UV-Visible absorption spectrum. The electrical studies were carried out at different frequencies and at different temperatures for the prepared NiS thin films. Further, electronic properties, such as valence electron plasma energy, average energy gap or Penn gap, Fermi energy and electronic polarizability of the NiS thin films were calculated. The AC electrical conductivity measurements revealed that the conduction depended on both the frequency and the temperature. Photoconductivity measurements were carried out to reveal the positive photoconductivity of the NiS thin films.

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1. Introduction

Metal chalcogenide thin films are particularly interesting for the fabrication of large area photodiode arrays, solar selective coatings, solar cells, photoconductors, sensors etc [1]. Nickel Sulphide belongs to VIII –VI compound semiconductor materials. Nickel Sulphide is a transition metal compound and an interesting material, showing metal-insulator transition by doping or as a function of temperature and pressure. Nickel Sulphide compound shows antiferromagnetic semiconductor and paramagnetic properties in low and high temperature phases, respectively. Nickel sulphide thin films have a number of applications in various devices such as solar selective coatings, IR detectors and as a storage electrode in photoelectrochemical storage devices [2, 3]. A variety of methods including electrodeposition, SILAR, pulsed laser ablation, metal-organic chemical vapour deposition, thermal and photochemical chemical vapour deposition can be used for the preparation of nickel sulphide thin films [4-8]. We have selected chemical bath deposition (CBD) method owing to its many advantages like low cost, large area production, simplicity in instrumental operation and low elaboration temperature. This paper presents the synthesis of NiS thin films prepared by using CBD technique. Prepared films were characterized for their structural, surface morphology, optical properties, and electrical studies.

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2. Materials and methods

The substrate cleaning is very important in the deposition of thin films. The substrates were ultrasonically cleaned with deionized water for 10 min and wiped with acetone and stored in a hot oven. The films were prepared by taking solutions of 10 ml of nickel sulphate in 100ml beaker to which 15 ml of triethanolamine and 10 ml of thioacetamide added successively. The solution was stirred well so that homogeneous solution was formed. Then 35ml of ammonia was added and the total volume of beaker made up to 100 ml at room temperature. The pH of the solution was about 10 and very slow stirring was given to the solution during the deposition. A glass substrate was placed vertically inside the vessel with the help of a suitably designed substrate holder. After a time period of 3 hrs, the glass slide was removed from the bath and cleaned with deionized water and dried in the hot oven. Many trials were made by optimizing the deposition parameters to obtain a good quality NiS thin film. The resultant films were homogeneous and well adhered to the substrate with mirror like surface. The deposited good quality NiS thin films were subjected to characterization studies. The XRD pattern of the NiS thin films was recorded by using a powder X-ray diffractometer (Schimadzu model: XRD 6000 using CuKα (λ=0.154 nm) radiation, with a diffraction angle between 20° and 70°. The crystallite size was determined from the broadenings of corresponding X-ray spectrum peaks by using Debye Scherrer's formula. Scanning Electron Microscopy (SEM) studies were carried out on JEOL, JSM- 67001. The optical absorption spectrum of the NiS thin films was taken by using the VARIAN CARY MODEL 5000 spectrophotometer in the wavelength range of 300 – 800 nm. The dielectric properties of the NiS thin films were analyzed using a HIOKI 3532-50 LCR HITESTER over the frequency range 50Hz-5MHz. Photoconductivity measurements were carried out at room temperature by connecting the sample prepared in series with a picoammeter (Keithley 480) and a dc power supply.

3. Results and discussion

3.1 Structural characterization

The XRD pattern of the NiS thin films was recorded by using a powder X-ray diffractometer with a diffraction angle between 20º and 70º. The crystallite size was determined from the broadening of corresponding X-ray Peaks. The XRD pattern of the NiS thin films is shown in Fig.1. The excellent peaks (300), (021), (200), (220), and (131) were obtained in the powder X-ray diffraction studies. The observed peaks corresponding to the formation of hexagonal phase of NiS were indexed according to hexagonal structure. The average nano-crystalline size (D) was calculated using the Scherrer formula,

$$D = \frac{0.9\lambda}{\beta \cos\theta} \tag{1}$$

where λ is the X-ray wavelength (CuKα radiation and equals to 0.154 nm), θ is the Bragg diffraction angle, and β is the FWHM of the XRD peak appearing at the diffraction angle θ. The average crystalline size that was calculated from X-ray line broadening peak and Scherrer equation was found to be about 22 nm.

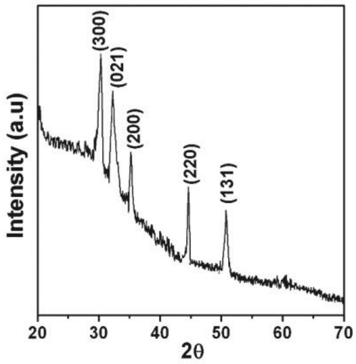

Fig.1.XRD spectrum of NiS thin films

3.2 Surface morphology

Scanning Electron Microscopy (SEM) can provide a highly magnified image of the surface and the composition information of surface regions of the materials. The resolution of scanning electron microscope can approach a few nano meters and the very high magnifications. Fig.2 shows the SEM images of the NiS thin films and it was observed from the micrographs that NiS film was homogeneous, fine grained and well covered to the substrate with the overgrowth of some particles.

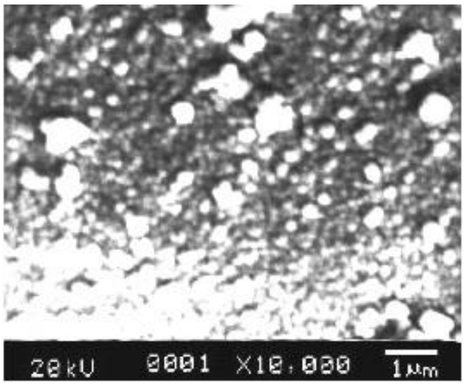

Fig.2 SEM Image of the NiS thin films

3.3 UV Analysis

Optical absorption measurement was carried out on NiS thin film. Fig.3 shows the variation of the optical absorbance with the wavelength of the NiS thin film. The optical absorption coefficient was calculated in the wavelength range of 300 to 800 nm. The optical band gap was calculated using Tauc plot as shown in Fig.4. The band gap of NiS was found to be 0.4 eV. The optical absorption coefficient (α) was calculated from transmittance using the following relation

$$\alpha = \frac{1}{d}\log\left(\frac{1}{T}\right) \tag{2}$$

where T is the transmittance and d is the thickness of the films. As a direct band gap material, the films under study have an absorption coefficient (α) obeying the following relation for high photon energies (hν)

$$\alpha = \frac{A(h\nu - E_g)^{1/2}}{h\nu} \tag{3}$$

where E_g is the optical band gap of the films and A is a constant. A plot of variation of $(\alpha h\nu)^2$ versus hν is shown in Fig.4. E_g was evaluated using the extrapolation of the linear part. Using Tauc's plot, the energy gap (E_g) was calculated to be 0.4 eV.

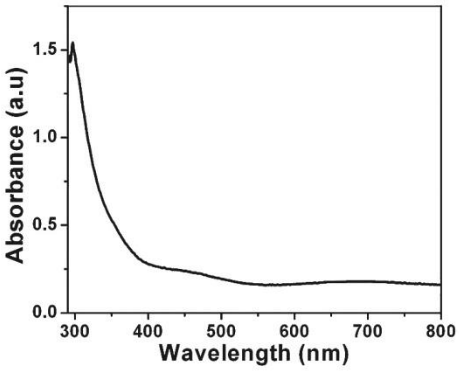

Fig.3 Optical absorption spectrum of NiS thin film

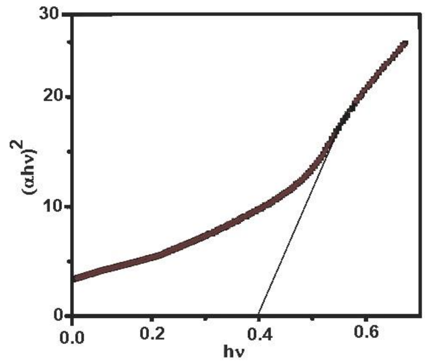

Fig.4 Plot of $(\alpha h\nu)^2$ versus hν of NiS thin film

3.3.1 Determination of Optical Constants

Two of the most important optical properties: the refractive index and the extinction coefficient which are generally called optical constants. The amount of light that transmits through thin film material depends on the amount of the reflection and absorption that takes place along the light path. The optical constants such as the refractive index (n), the real dielectric constant (ε_r) and the imaginary part of dielectric constant (ε_i) were calculated. The extinction coefficient (K) could be obtained from the following equation,

$$K = \frac{\lambda \alpha}{4\pi} \tag{4}$$

The extinction coefficient (K) was found to be 0.0025at λ =800 nm. The transmittance (T) is given by

$$T = \frac{(1-R)^2 \exp(-\alpha t)}{1 - R^2 \exp(-2\alpha t)} \tag{5}$$

Reflectance (R) in terms of absorption coefficient could be obtained from the above equation. Hence,

$$R = \frac{1 \pm \sqrt{1 - \exp(-\alpha t + \exp(\alpha t)}}{1 + \exp(-\alpha t)} \tag{6}$$

Refractive index (n) could be determined from reflectance data using the following equation,

$$n = -\frac{(R+1) \pm \sqrt{3R^2 + 10R - 3}}{2(R-1)} \tag{7}$$

The refractive index (n) was found to be 1.82 at λ =800 nm. The high refractive index makes NiS film suitable for use in optoelectronic devices. From the optical constants, electric susceptibility (χ_c) could be calculated using the following relation

$$\varepsilon_r = \varepsilon_0 + 4\pi\chi_C = n^2 - k^2 \tag{8}$$

Hence,

$$\chi_C = \frac{n^2 - k^2 - \varepsilon_0}{4\pi} \tag{9}$$

where ε_0 is the permittivity of free space. The value of electric susceptibility (χ_c) was 2.31 at λ=800 nm. Since electrical susceptibility is greater than 1, the material can be easily polarized when the incident light is more intense. The real and imaginary parts of the dielectric constant (ε_r) and (ε_i) respectively could be calculated from the following relations

$$\varepsilon_r = n^2 - k^2 \tag{10}$$

$$\varepsilon_i = 2nk \tag{11}$$

The values of real dielectric constant (ε_r) and imaginary dielectric constant (ε_i) at λ =800 nm were estimated to be 3.254 and 0.00245 respectively. The lower value of dielectric constant and the positive value of the material help produce induced polarization due to intense incident light radiation.

3.4 Dielectric Studies

The dielectric properties of the NiS thin films were studied for different frequencies and different temperatures. The dielectric constant and the dielectric loss were calculated at different frequencies and different temperatures. This is shown in Figs.5 and 6. It was observed (Fig.5) that the dielectric constant decreased greatly and sharply with increasing frequency and then attained almost a constant value in the high frequency region. The higher value of dielectric constant at lower temperature was due to the space charge polarization. Defect related conduction process could be related to the dielectric values at higher temperatures and lower frequencies. Fig.6 shows the dielectric loss as a function of frequency. The amount of charge carriers increases by thermal activation and the place of loss peak shifts to top frequency with increasing temperature being indicated by the rise in the maximum out value of dielectric loss with temperature. Dipolar or orientation polarization arises from molecules having a permanent electric dipole moment that can change its orientation when an electric field is applied. Space charge polarization arises from molecules having a permanent electric dipole moment that can change its orientation when an electric field is applied [9]. The large value of the dielectric constant is due to the fact that NiS thin films act as a nanodipole under electric fields. The small-sized particles necessitate a large number of particles per unit volume, resulting in an increase of the dipole moment per unit volume, and a high dielectric constant [10]. The dielectric loss studied as a function of frequency at different temperatures is shown in Fig.6. Dielectric loss also shows a trend similar to the one shown by the dielectric constant. The decrease in the dielectric loss with the increase in frequency for all the temperatures suggests that the dielectric loss is greatly dependent on the frequency of the applied field. The high values of dielectric loss at low frequencies could be related to the charge lattice defect of the space charge polarization [11].

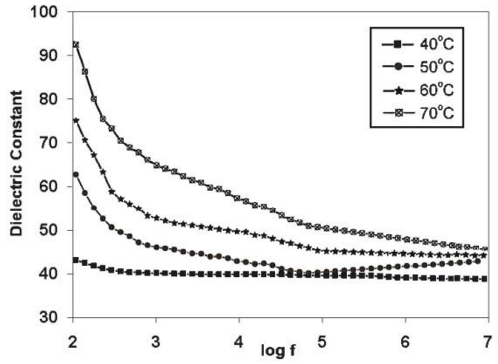

Fig.5 Dielectric constant of NiS thin film

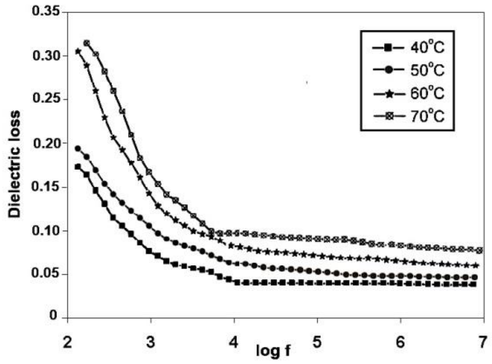

Fig.6 Dielectric loss of NiS thin film

The high frequency dielectric constant was required as input, to evaluate electronic properties like valence electron plasma energy, average energy gap or Penn gap, Fermi energy and electronic polarizability of the NiS thin films. Theoretical calculations showed that the high frequency dielectric constant is explicitly dependent on the valence electron Plasma energy, an average energy gap referred to as the Penn gap and Fermi energy. The Penn gap was determined by fitting the dielectric constant with the Plasmon energy. The following relation was used to calculate the valence electron plasma energy, $\hbar\omega_p$

$$\hbar\omega_P = 28.8\left(\frac{Z\rho}{M}\right)^{1/2} \tag{12}$$

According to the Penn model, the average energy gap for the NiS thin films is given by

$$E_P = \frac{\hbar\omega_P}{(\varepsilon_\infty - 1)^{1/2}} \tag{13}$$

where $\hbar\omega_P$ is the valence electron plasmon energy and the Fermi energy is given by

$$E_F = 0.2948\,(\hbar\omega_P)^{4/3} \tag{14}$$

Then, the electronic polarizability (α) using the relation,

$$\alpha = \left[\frac{(\hbar\omega_P)^2 S_0}{(\hbar\omega_P)^2 S_0 + 3E_P^2}\right] \times \frac{M}{\rho} \times 0.396 \times 10^{-24} cm^3 \tag{15}$$

where S_0 is a constant given by

$$S_0 = 1 - \left[\frac{E_P}{4E_F}\right] + \frac{1}{3}\left[\frac{E_P}{4E_F}\right]^2 \tag{16}$$

The Clausius-Mossotti relation,

$$\alpha = \frac{3}{4}\frac{M}{\pi N_a \rho}\left[\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2}\right] \tag{17}$$

The following empirical relationship is also used to calculate (α),

$$\alpha = \left[1 - \frac{\sqrt{E_g}}{4.06}\right] \times \frac{M}{\rho} \times 0.396 \times 10^{-24} cm^3 \tag{18}$$

where E_g is the bandgap value determined through the UV visible spectrum. The high frequency dielectric constant of the materials is a very important parameter for calculating the physical or electronic properties of materials. All the above parameters as estimated are shown in Table 1.

Table 1 Electronic parameters of the NiS thin films

Parameter	**Value**
Plasma energy (hω_p)	20.72 eV
Penn gap (E_p)	0.85 eV
Fermi Energy (E_F)	16.60 eV
Electronic polarizability (using the Penn analysis)	5.24 x 10^{-24} cm^3
Electronic polarizability (using the Clausius-Mossotti relation)	5.32 x 10^{-24} cm^3
Electronic polarizability (using bandgap)	5.16 x 10^{-24} cm^3

3.4.1 AC conductivity (σ_{ac}) studies

The ac conductivity (σ_{ac}) was calculated for the NiS thin films from the following formula

$$\sigma_{ac} = \varepsilon_0 \varepsilon_r \omega \tan\delta \tag{19}$$

where ε_o is the vacuum dielectric constant (8.85 × 10^{-12} farad/m), ε_r is the relative dielectric constant and ω is the angular frequency $\omega = 2\pi\nu$ of the applied field. Fig.7 shows the variation of ac conductivity with various frequencies and temperatures. It is seen that the value of ac conductivity increases with increase in frequency [12]. The activation energy of the NiS thin films was found to be 0.17 eV which represents the average energy of the carriers with respect to Fermi energy, if the carriers can only move at the bottom or top of the well-defined band.

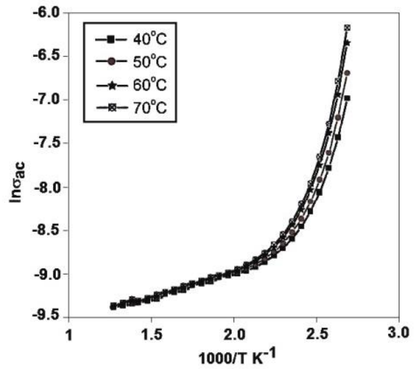

Fig.7. Variation of ac conductivity with frequency at various temperatures.

3.5. Photoconductivity Studies

The DC input to the sample was increased from 0 to 600 volts in steps and the corresponding dark current was noted from the electrometer. For determining the photocurrent, the NiS sample was illuminated with an incandescent light bulb (40 W) and the corresponding photocurrents were measured. The variation of photocurrent (Ip) and dark current (I_d) with applied field are shown in Fig.8. Both photo and dark currents of lead sulphide increase linearly with applied voltage. It is observed from the plot that the dark current is less than the photocurrent, suggesting that NiS exhibits positive Photoconductivity which can be attributed to the generation of mobile charge carriers caused by absorption of photons. This is because of an increase in the number of charge carriers or their life time in the presence of radiation [13].

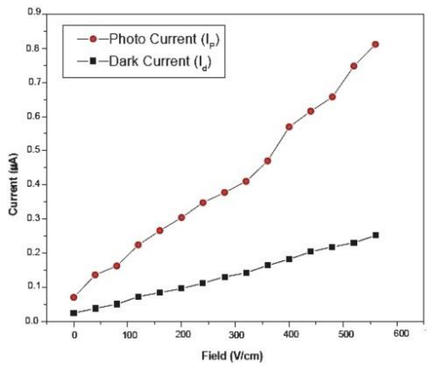

Fig.8.Photoconductivity study of NiS Thin films

4. Conclusion

The Nickel Sulphide (NiS) thin films were prepared by using CBD technique. The XRD studies showed well crystallized and hexagonal structure of NiS thin films. The morphology of the NiS thin films was characterized by using SEM. The optical band gap was found to be 0.4 eV. The dielectric properties of the NiS thin films were calculated for different frequencies and temperatures. In addition, the plasma energy of the valence electron, Penn gap or average energy gap, the Fermi energy, and electronic polarizability of the NiS thin films were also determined. The AC electrical conductivity was found to increase with an increase in the temperature and the frequency. The results revealed that the AC electrical conductivity varied almost linearly with the applied frequency in the high range and increased with different temperatures. The activation energy was found to be 0.17 eV. Photoconductivity measurements were carried out to reveal the positive photoconductivity of the NiS thin films.

References

[1] R.S. Mane, C.D. Lokhande, Mater. Chem. Phys. **65**,1 (2000)
[2] T.H. Johnson, Proc. Int. Opt. Eng. **433**,60 (1984)
[3] S. Leitz, G. Hodes, R. Tenne, J. Manassen, Nature **326**,863 (1987)
[4] K.Anuar, Z.Zulkarnain, N.Saravanan, A.Zuriyatina, R.Sharin, Materials Science (Medziagotyra), **10**, 157 (2004).
[5] S.D.Sartale, C.D.Lokhande, Chemistry and Physics, **72**,101 (2001)
[6] H.Y.Lee, M.Kanai, T.Kawai, S.Kawai, Japan Journal of Applied Physics,**32**, 2100 (1993)
[7] R.Nomura, H.Hayata, Transactions of the Materials Research Society of Japan, **26**, 1283 (2001)
[8] J.W.Cheon, D.S.Talaga, J.I.Zink, Chemistry of Materials, **9**, 1208 (1997)
[9] S. Suresh, C. Arunseshan, Appl Nanosci, **4**, 179 (2014)
[10] Sagadevan Suresh, Appl Nanosci, **4**, 325 (2014)
[11] S.Sagadevan, A.Shanmuga sundaram , Chalcogenide Letters, , **11**, 159 (2014)
[12] S.Thirumavalavan, Mani K and S.Suresh, Journal of Ovonic Research, **11**, 123 (2015)
[13]S.Thirumavalavan, K.Mani and Suresh Sagadevan, Chalcogenide Letters, **12**, 237 (2015)