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"Studies of Physical Properties of Nanocrystalline Nickel Sulphide Thin Films Grown by Simple Chemical Route"

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ABSTRACT

Nanocrystalline Nickel Sulphide thin films were prepared using chemical bath deposition method on glass substrate. Nickel Sulphate and thiourea were used as starting chemicals. Triethanolamine (TEA) and ammonia was used as the complexing agents. In order to obtain good quality thin films preparative parameters such as concentration, temperature, deposition time, pH of solution have been optimized. Films were characterized using X-ray diffraction for crystallographic analysis. The films were shown to be nanocrystalline in nature with good uniformity. From scanning electron micrographs, the surface appeared to be comparatively granular with irregularly shaped grains. Optical properties of the films were determined from analysis of the measured absorption spectrum. The Nickel Sulphide thin films exhibited direct band gap transition with band gap energy ~2.8 eV. The films were observed to have thickness value range from 300 nm to 500 nm. Electrical properties of Nickel Sulphide film determine using two point probe method. The films are semiconducting, having room temperature resistivity of the order of ~10 Ωcm.

Keywords: Nanocrystalline thin films, Chemical bath deposition, X-Ray diffraction, Scanning electron microscopy, Electrical properties

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INTRODUCTION

The chemical bath deposition (CBD) is simplest method successfully utilized to prepare semiconducting thin films. Chemical bath deposition (CBD) method is also known solution growth. Metal chalcogenide thin films can be prepared by various methods, but chemical processes offer good deposition on suitable substrates by the controlled precipitation of the compounds from the solution. It may allow us to easily control the growth factors such as film thickness, deposition rate and quality of crystallites by varying the solution pH, temperature and bath concentration. Chemical bath deposition (CBD) is a slow process which facilitates better orientation of crystallites with improved grain structure and the preparative parameters are easily controllable. Chemical deposition results in pinhole free and uniform deposition easily obtained. The basic principle involved in the chemical bath deposition method is the controlled precipitation of the desired compounds from a solution of its constituents. This required the ionic product exceed the solubility product [1,2].

Nickel Sulphide belongs to VIII –VI compound semiconductor materials. It has hexagonal crystal structure. The films are black in colour. The optical band gap is 0.35 – 0.8 eV. Electrical resistivity is of the order of $10–10^4$ Ωcm. Nickel Sulphide films have a number of applications in various devices such as solar selective coatings, solar cells, photoconductors, sensors, IR detectors, as an electrode in photoelectrochemical storage device etc. The existence of various compositions of Nickel Sulphide includes: Ni_3S_4, Ni_9S_8, $Ni_{3+x}S_2$, Ni_4S_{3+x}, Ni_6S_5, Ni_7S_6 and NiS_2 makes such studies both interesting and challenging. Due to large number of application many reserachers prepared single crystal as well as polycrystalline NiS in bulk form and in thin film form and studied various characterization[3].

In this paper we discuss on Nickel Sulphide thin films prepared by simple chemical method. The deposition conditions were optimized to get good quality and well adherent films onto glass substrates. The structural, surface morphological, optical and electrical characterizations of Nickel Sulphide films were carried out by means of X-ray diffraction, optical absorption and electrical resistivity measurement.

MATERIALS AND METHODS

1. NiS thin films by CBD method

In CBD methods equipments like hot plate with magnetic stirrer is needed. Electrical conductivity of the substrate is not the necessary requirement. Any insoluble surface to which the solution has a free access will be a suitable substrate for deposition. The low temperature deposition avoids oxidation and corrosion of metallic substrates. Chemical deposition results in pinhole free and uniform deposition easily obtained [3].

2.1 Preparative conditions for NiS by Chemical Bath Deposition

Deposition of NiS thin films using analytical reagent grade (Loba, India) Nickel sulphate and thioacetamide, are generally used as Nickel and sulphide precursors respectively. The films were prepared by taking solutions of 10 ml of (0.8M) Nickel Sulphate in 100ml beaker to which 15 ml of (7.4 M) triethanolamine (TEA) and 10 ml of (0.8 M) thioacetamide added successively. The solution was stirred well so that homogeneous solution is formed. Then 35ml of (14M) ammonia was added and total volume of beaker made up to 100 ml at room temperature. The pH after the mixture thoroughly stirred with glass stirring rod come to ~10. The glass substrates were vertically immersed into the solution and supported on the walls of the beaker. The substrates were taken out from the beaker after 4 hours. The deposited NiS thin film was adhesive, uniform, black color with polycrystalline nature [1-4]. The films on the glass substrates were used to study structural, compositional, surface morphological and optical properties. Film thickness was determined by weighing method using the formula [5],

$$t = \frac{m}{A\,\rho} \qquad \text{-----------} \quad \text{i)}$$

Where, 't' is the thickness of the film, 'm' is the weight gain, 'A' is the area of the coated film and 'ρ' is the density of deposited material [10]. The deposited NiS films having thickness is approximately 500 nm.

The reaction is,

$NiSo_4 + TEA \rightarrow [Ni\,(TEA)]^{+} + SO_4^{-}$
$CH_3CSNH_2 + nH_2O \rightarrow CH_3CONH_2 + H_2S$
$[Ni\,(TEA)]^{+} + H_2S + NH_3 \rightarrow NiS + TEA + NH_3 + 2H^{+}$

The structural properties of the films are characterized using X-ray diffraction measurements with Bruker D8 Advance X-ray diffractometer in the range of scanning angles 10–100^o (2θ) with radiation Cu Kα1 and 40 kV/40 mA and scanning electron microscopy with Hitachi S-4800 system (15 kV). The UV-Visible absorption spectrum was recorded using spectrophotometer in the spectral range 300 nm to 1100 nm. Optical absorption spectra were measured to determine the band gap. Two point probe method used to measure electric resistivity of the films.

RESULTS AND DISCUSSION

3.1 X-ray Diffraction

The structure characterization of the NiS thin films was carried out using the X-ray diffraction. Fig. 1 shows, XRD patterns of NiS thin films deposited using CBD method at pH ~10 value in as-deposited state. Nanocrystalline nature of NiS films is confirmed from XRD pattern since observed diffraction peaks are weak and are of low intensity. Comparison of *d*-values with JCPDS data for NiS shows that the material is NiS having hexagonal and rhombohedral structure with lattice constants (*a*) = 0.53 nm. NiS film having four diffraction peaks at angles 2θ ~ 37.42°, 46.57°, 60.68° and 81.62° are correspond to (220), (102), (103) and (161) plane respectively and peak positions corresponding to JCPDS 02-1280 and 86-280 [4].

The average crystallite size has been calculated by using Debye–Scherrer's equation as;

$$D_{hkl} = \frac{K\lambda}{\beta cos\theta} \quad \text{-----------} \quad \text{ii)}$$

Where, 'K' is a Scherrer's constant usually ~ 0.94, 'λ' the wave length of X-ray (0.15418 nm), 'β' is the FWHM in radians and 'θ' is the Bragg's angle. We use the reflection at 2θ ≈ 25.51^o. It has been observed that the grain size of as-deposited film is ~ 8 nm. However, the observed broad hump suggests that the synthesized materials are nanocrystalline in nature with very small particle size [6-8, 14].

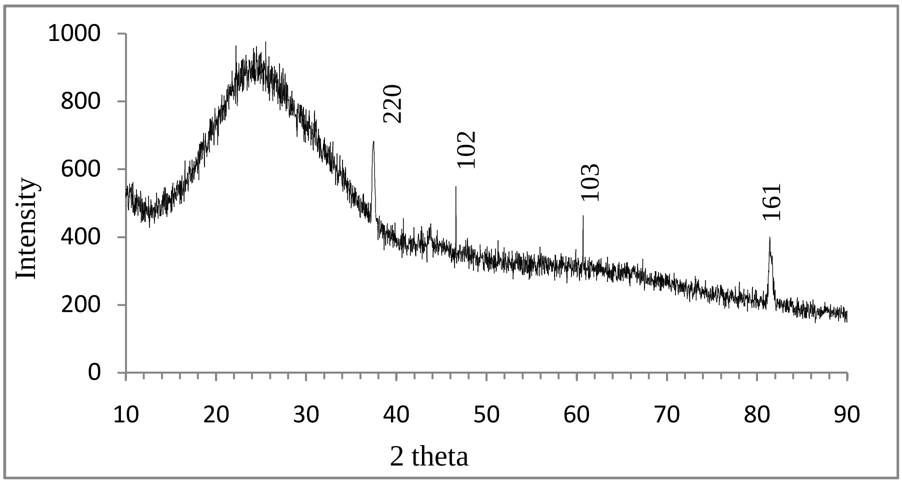

Fig. 1 XRD pattern of NiS thin films deposited onto glass

3.2 Scanning electron microscopy

We are studied the surface morphology of as-deposited NiS thin film by taking scanning electron microscopy as shown in Fig. 2. It is observed from the micrographs that NiS film is homogeneous, fine grained and well covered to the substrate with overgrowth of some particles.The overall surface structure is seen to have grains of spherical shape. These films revealed that grains were very small in size with no well defined grain boundaries. Fig.2 shows that, film surface have some holes indicating porosity is present. Formation of such type of surface morphology is desired for NiS films, for application in electrochemical capacitive performance. The average grain size of the NiS film is found that ~100 nm. It was found that the morphology of NiS structure changes as per deposition method and the preparation parameters like number of cycle, bath temperature, concentration of solution, pH, deposition time, etc. It is observed that the average grain size determined by SEM is comparatively larger than measured by XRD. This larger value of grain sizes may be due to the agglomeration of grain [6,9,10].

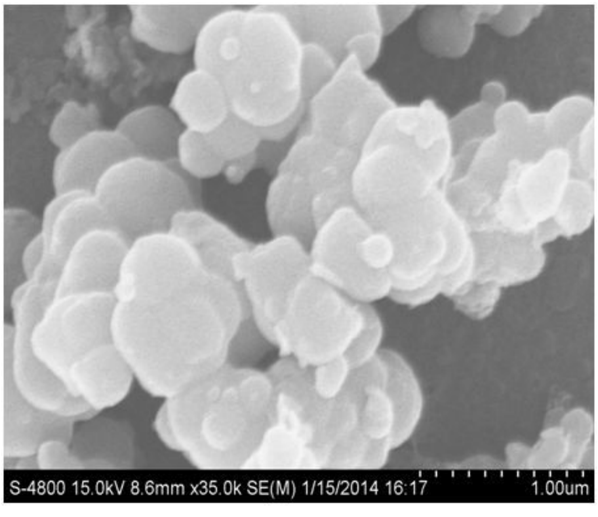

Fig. 2 SEM of NiS film deposited onto glass substrate

3.3 Optical properties

The absorption spectrum of NiS recorded in the UV-Vis region is shown in Fig. 3(a). Optical absorption of NiS thin films was studied in the wavelength range 300–1100 nm. It shows that the Nickel Sulphide have high absorption in the ultra-violet region at about 349.5 nm than in any other region of the spectrum.

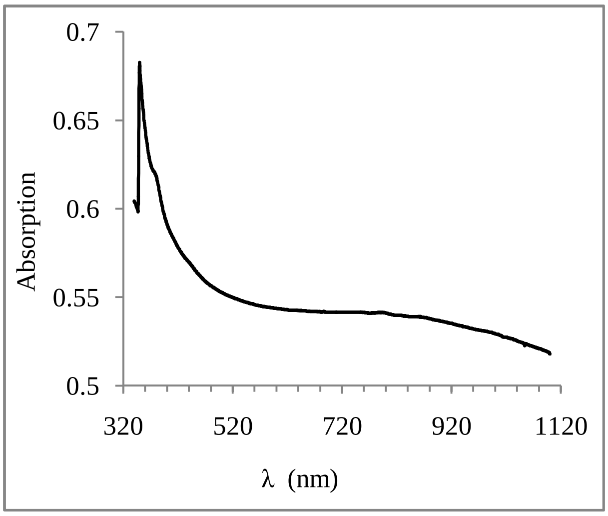

Fig. 3(a) Plot of Absorption against λ for NiS thin films

The band gap was estimated using the Tauc's relationship [12] between absorption coefficient α and the photon energy '$h\nu$'.

$$\alpha h\nu = A(h\nu - E_g)^n \quad \text{-----------} \quad \text{iii)}$$

Where, 'ν' is the frequency, 'h' is the Planck's constant Eg is the band gap energy, 'A' and 'n' are constants. For allowed direct transitions, $n = \frac{1}{2}$ and for allowed indirect transitions, n = 2. The plot of $(\alpha h\nu)^2$ vs $h\nu$ is shown in Fig. 3(b) for NiS films having thickness, ~500 nm. The variation of $(\alpha h\nu)^2$ with $h\nu$ for NiS films is a straight line indicating that the involved transition is direct one. Band gap energy 'Eg' was determined by extrapolating the straight line portion to the '$h\nu$' axis. The optical band gap energy was found to be 2.8 eV for the as-deposited NiS film. This makes the material to be suitable for devices for good absorption of UV radiation that is, it can be used as a UV filters [11-13].

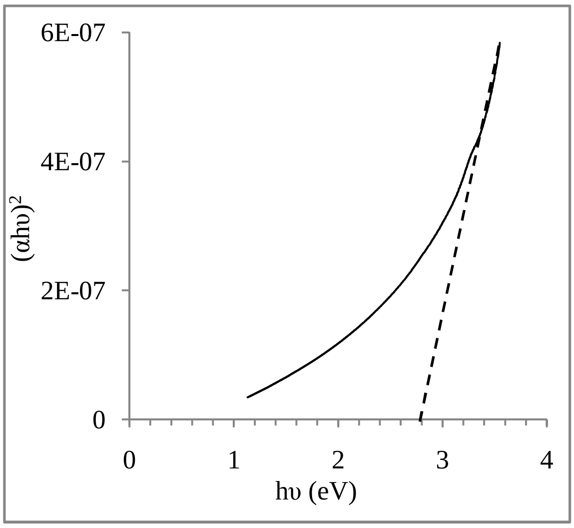

Fig. 3(b) Plot of $(\alpha h\nu)^2$ against $h\nu$ for NiS thin films deposited onto glass substrate

3.4 Electrical resistivity studies

The electrical resistivity at room temperature of NiS thin film was found to be of the order of ~10 Ωcm. The variation of logarithm of resistivity (log ρ) with the inverse of temperature (1000/T) is shown in Fig. 4. The decrease in electrical resistivity with increase of temperature suggested the semiconducting behaviour of as-deposited films [6].

The thermal activation energy (Ea) was calculated using the following relation:

$$\rho = \rho_0 \, exp\left(\frac{E_a}{KT}\right) \qquad \text{------------- iv)}$$

Where, 'ρ' is the resistivity at temperature T, 'ρ_0' constant, K Boltzmann constant and T is the absolute temperature. At room temperatures activation energy (E_a) is ~ 0.41 eV which is good agreement with the results reported in earlier investigations made by S.D. Sartale et.al. [12].

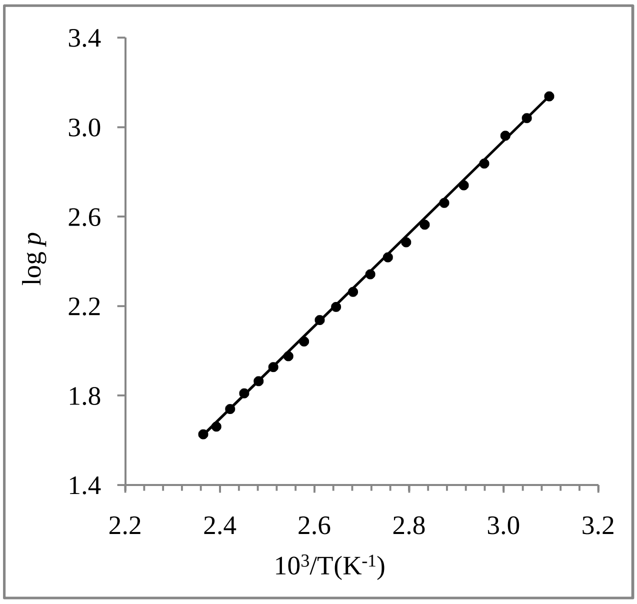

Fig. 4 Variation of log ρ with 10^3/T of NiS thin film deposited onto glass substrate

CONCLUSION

The CBD method was successfully used to deposit NiS thin films from Nickel Sulphate and thioacetamide as cationic precursor and anionic precursor. Under optimized conditions, films having thickness ~500 nm. X-ray diffraction patterns of film shows that the peaks are correspond to hexagonal structures and it has been observed that the grain size of deposited film is ~8 nm. SEM of film as deposited film showed irregular distribution of particles with the grain sizes ~100 nm. Optical band-gap of NiS thin film is found that 2.8 eV for as-deposited state. The room temperature electrical resistivity is extremely high and is found to be order of 10 Ωcm and the activation energy is 0.41 eV. Formation of such type of NiS thin films used for application in electrochemical capacitive performance.

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