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Characterization of nickel sulphide thin films prepared by modified chemical method

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Semiconducting nickel sulphide (NiS) thin films were deposited onto glass substrates using a new modified chemical bath method (MCBD). The MCBD is the solutions grow technique in which substrates are immersed in cations and anions alternatively and film growth takes place on the substrates. The preparative conditions such as concentration, *p*H, temperature, immersion time, immersion cycles, etc are optimized to get nanocrystalline NiS films. The characterization of the films was carried out by using X-ray diffraction, scanning electron microscopy, optical absorption and electrical resistivity. The XRD analysis of the as-grown NiS films showed hexagonal structure. The average grain size is found to be 14 nm. Electrical resistivity measurements showed semiconducting nature with at room temperature resistivity which is found to be of the order of 10 Ωcm for as-deposited NiS films. Scanning electron micrographs (SEM) reveal a very dense surface structure with the presence of irregular shaped grain particles of size ~200 nm. The optical absorption studies show that the absorption coefficient of the NiS thin film is high and a direct band gap of ~2.4 eV has been observed.

Keywords: Nickel sulphide, Thin film, Chemical bath deposition, XRD, SEM, Optical properties, Electrical properties

1 Introduction

In chemical bath deposition (CBD) method, deposition of metal chalcogenide semiconducting thin films occurs due to substrate maintained in contact with dilute chemical bath containing metal and chalcogen ions. The film formation on substrate takes place when ionic product exceeds solubility product. However, this results into precipitate formation in the bulk of solution, which cannot be removed. This results in unnecessary formation of precipitation and loss of material. In order to avoid such unnecessary precipitation, a CBD is modified and known as modified chemical bath deposition. The MCBD is also known as successive ionic layer adsorption and reaction (SILAR) method. The MCBD technique remains one of the simplest, efficient, cost effective methods and convenient for large area deposition of films. The MCBD method was first reported in 1985 by Ristov *et al*. and the name SILAR was introduce to this method by Nicolau (1985) for the deposition of metal chalcogenides thin films. In modified chemical bath deposition cycle, the substrate is immersed into cationic and anionic precursor solutions (adsorption and reaction) and rinsed with highly purified water in between to avoid homogeneous precipitation. In MCBD method, the deposition rate and the thickness of the film can be easily controlled over a wide range by changing the deposition cycles. At low deposition temperature, diffusion of ions in thin film is low; hence MCBD method is suitable for growing multi-layer metal chalcogenide thin films[1-4].

In the present work, the successful deposition of good-quality nickel sulphide thin films using the modified chemical bath deposition (MCBD) method has been reported. The nickel sulphide thin films were prepared from aqueous solution of nickel sulphate ($NiSO_4$) and sodium sulphide (Na_2S) as sources of Ni^{2+} and S^{2-} ions, respectively. The structural, morphological, optical and electrical characterizations of nickel sulphide films were carried out by means of X-ray diffraction, scanning electron microscopy, optical absorption and electrical resistivity.

2 Experimental Details

2.1 Deposition Procedure

For the deposition of NiS thin films, cationic precursor was 0.1 M nickel sulphate. The *p*H was adjusted to ~9 by adding liquid ammonia. The source for anionic precursor was 0. 5M sodium sulphide solution with *p*H ~12. The solutions were taken into separate beakers of 50 ml capacity each. For rinsing purpose, distilled water was used. The deposition was carried out at room temperature (27°C) using

unstirred conditions. In MCBD method concentration, *p*H and temperature of precursor solutions and the time duration for adsorption, reaction and rinsing are important parameters. By making several trial experiments, NiS thin film deposition conditions were optimized. When the substrate is immersed in cationic precursor solution (nickel sulphate) for 65 s, nickel ions get adsorbed on the substrate surface. The substrate is rinsed in double distilled water for 45 s to remove the loosely bound or excess nickel ions. Then, the substrate is immersed in anionic precursor solution (sodium sulphide) for 65 s. The sulphide ions react with pre-adsorbed nickel ions to form a layer of NiS over substrate. Rinsing the substrate again in the distilled water for 45 s separated out the unadsorbed sulphide ions. This completes one MCBD cycle. After repeating such 55 cycles, black colour NiS thin film of thickness ~0.3 μm was obtained[1,3]. Film thickness was determined by weighing method using the formula[5]:

$$t = \frac{m}{A\rho} \qquad \ldots(1)$$

where t is the thickness of the film, m the weight gain, A the area of the coated film and ρ is the density of NiS.

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° (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 300-1100 nm. Optical absorption spectra were measured to determine the band gap. Two point probe method used to measure electric resistivity of the films.

3 Results and Discussion

3.1 Nickel Sulphide Film Growth

NiS thin films were grown onto glass substrates under optimized conditions. Figure 1 shows the plot of NiS film thickness against number of MCBD growth cycles. Film thickness was determined by weighing method and it was found to be about ~0.3 μm for 55 cycles. It is observed that, after 55 cycles thickness of thin film slightly decreases. The growth rate was found to be about ~80 Å per cycle. Sartale and Lokhande have reported the film thickness increases linearly up to 150 cycles, after which thickness goes on decreasing due to the formation of outer porous layer of NiS. Formation of inner compact and outer porous layer (duplex structure) has been observed for many chemically deposited thin films[1,3,5].

3.2 Structural Studies

The structure characterization of the NiS thin films was carried out using the X-ray diffraction. Figure 2 shows XRD patterns of NiS thin films deposited using MCBD method in as-deposited state. Nanocrystalline nature of deposited NiS films is confirmed from XRD pattern as observed, diffraction peaks are weak and of low intensity. Comparison of d values with JCPDS data for NiS shows that the material is NiS having rhombohedral structure with lattice constants (a) = 0.44 nm. NiS films having three diffraction peaks at angles 2θ ~ 32.04°, 37.21°, 81.50° correspond to (300), (220) and (161) plane,respectively and peak positions[6] corresponding to JCPDS 86-2281.

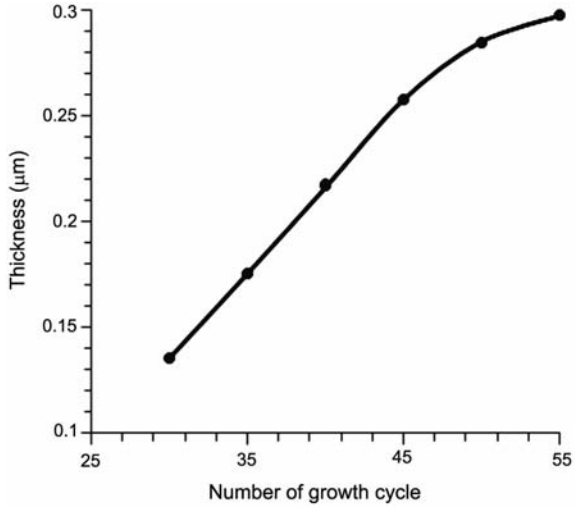

Fig. 1 — Number of MCBD growth cycle

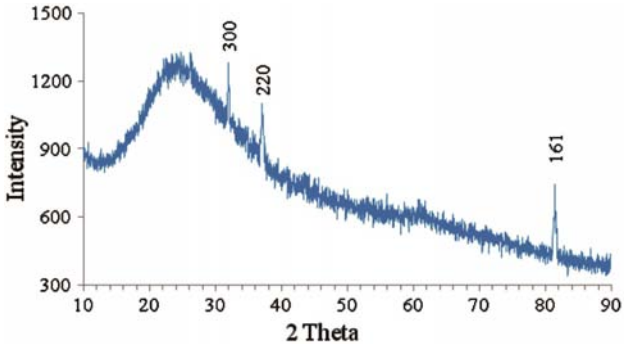

Fig. 2 — XRD pattern of NiS thin films deposited onto glass

The average crystallite size has been calculated by using Debye-Scherrer's equation as:

$$D_{hkl} = \frac{K\lambda}{\beta \cos\theta} \qquad \ldots(2)$$

where K is Scherrer's constant usually ~0.94, λ the wavelength of X-ray (0.15418 nm), β' the FWHM in radians and θ is the Bragg's angle. The reflection at $2\theta \approx 26.301°$ is used. It has been observed that the grain size of deposited film is 14 nm when film is as-deposited. However, the observed broad hump suggests that the synthesized materials are nanocrystalline in nature with very small particle size[7-9,14].

3.3 Scanning Electron Microscopy

The surface morphological studies of the NiS films have been carried out from scanning electron micrographs (SEM). Figure 3 shows the SEM image of NiS films prepared by MCBD method. The film is very dense and composed of many irregular round-shaped grains in the as-deposited state. The average grain size is in the range 100-200 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, *p*H, deposition time, etc. Figure 2 shows that film surface has holes indicating porosity is present. 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. Formation of such type of surface morphology is desired for NiS films for application in electrochemical capacitive performance[7,10,11].

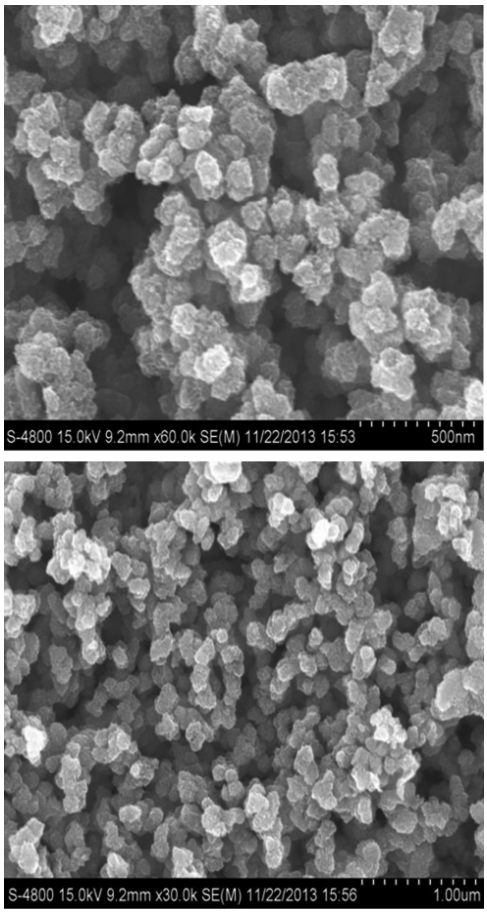

Fig. 3 — SEM of NiS film deposited onto glass substrate

3.4 Electrical Resistivity Studies

The two point-probe *dc* method was employed to understand the variation of electrical resistivity with temperature in as deposited NiS films. The electrical resistivity of NiS films was studied in air and it is found to be of the order of 10 Ωcm. The variation of log of resistivity (log ρ) with reciprocal of temperature ($10^3/T$) is shown in Fig. 4. It was seen that resistivity decreases with temperature indicating semiconducting nature of films[7]. The thermal activation energy was calculated using the relation:

$$\rho = \rho_0 \exp\left(\frac{E_g}{KT}\right) \qquad \ldots(3)$$

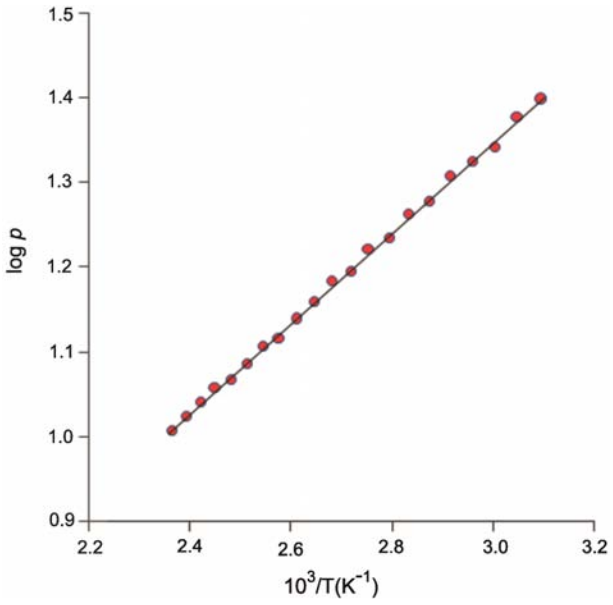

Fig. 4 — Variation of log ρ with $10^3/T$ of NiS thin film deposited onto glass substrate

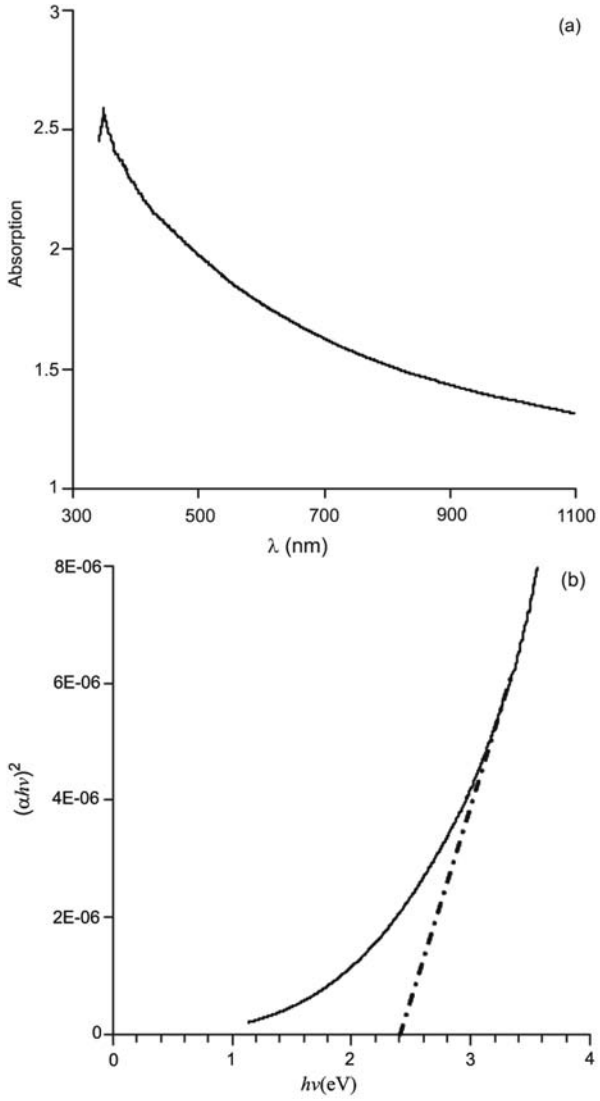

Fig. 5 — Plot of (a) absorption against λ for NiS thin films and (b) $(\alpha hv)^2$ against hv for NiS thin films deposited onto glass substrate

where ρ is resistivity at temperature T, ρ_0 is constant, K the Boltzmann constant and E_a the activation energy required for conduction. The activation energy was found to be of the order of 0.12 eV for film having thickness ~300 nm. Several researchers have reported the activation energy for NiS thin films prepared by different methods, which is found to be in good agreement with this result[3,6].

3.5 Optical Properties Studies

The absorption spectrum of NiS recorded in the UV-Vis region is shown in Fig. 5(a). Optical absorption of NiS thin films was studied in the wavelength range 300-1100 nm. It shows that the nickel sulphide has high absorption in the ultra-violet region at 349 nm than in any other region of the spectrum.

The band gap was estimated using the Tauc's relationship[3] between absorption coefficient (α) and the photon energy (hv).

$$\alpha hv = A(hv - E_g)^n \quad \ldots(4)$$

where v is the frequency, h the Planck's constant, E_g the band gap energy, A and n are constants, respectively. For allowed direct transitions, n = ½ and for allowed indirect transitions, n = 2. The plot of $(\alpha hv)^2$ versus hv is shown in Fig. 5(b) for NiS films having thickness, ~300 nm. The variation of $(\alpha hv)^2$ with hv for NiS films is a straight line indicating that the involved transition is direct one. Band gap energy E_g was determined by extrapolating the straight line portion to hv axis. The optical band gap energy was found to be 2.4 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[12,13].

4 Conclusions

The MCBD method was successfully used to deposit NiS thin films from nickel sulphate ($NiSO_4$) and sodium sulphide (Na_2S) as cationic precursor and anionic precursor, respectively. Under optimized conditions, films are having thickness ~300 nm. X-ray diffraction patterns of film show that the peaks correspond to hexagonal structures and it has been observed that the grain size of as-deposited film is ~14 nm. SEM of as-deposited film showed irregular distribution of particles with the grain size ~100 nm. Optical band-gap of NiS thin film is found to be 2.4 eV for as-deposited state. The room temperature electrical resistivity is extremely high and is found to be of the order of 10 Ω cm and the activation energy is 12 eV. Formation of such type of NiS thin films can be used for application in electrochemical capacitive performance.

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