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Characterization of nanostructured photoconducting nickel sulfide thin films grown by novel deposition technique SILAR

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ABSTRACT

The nickel sulfide thin films have number of applications in various devices such as solar selective coatings, IR detectors and as storage electrode in photo-electrochemical storage devices. This paper reports on the preparation of photosensitive nanostructured NiS thin films onto glass substrate by Successive Ionic Layer Adsorption and Reaction (SILAR) method. For deposition of NiS thin films 0.02M nickel sulphate and 0.05M sodium sulphide was used as cationic and anionic source. The structural, electrical and optical properties of the nanostructured NiS films were investigated. The films have rhombohedral lattice structure and the improvement in crystalline quality is observed after post annealing. The photoconductivity of NiS is improved from 2.4×10^{-8} to 1.3×10^{-7} mho-cm⁻¹ after annealing. The optical properties were characterized to estimate the band gap energy. The TEP measurement shows that the deposited films are of p-type. © 2011 Trade Science Inc. - INDIA

KEYWORDS

Thin films;
Nanostructure;
Electrical properties;
Optical properties.

INTRODUCTION

Nanostructured materials have indeed become a very active research field in the areas of solid state physics, solid state chemistry, solid state ionics, material engineering and biotechnology^[1]. The industrial application of nanoscience and nanotechnology needs the development of synthetic materials of tailored made properties that decreases the size of active electronic devices higher speed performance and lower cost^[2]. Nanostructured materials become very popular as their properties changes dramatically when the material dimensions are of the order of nanometers. Thin film can

be defined mathematically by two parallel planes extending infinitely into two directions and restricted in the third direction known as thickness of the film. The thickness of the film can be reduced of the order of few nanometers to prepare nanostructured material.

Metal sulfide thin films have been studied intensively over past 30 years in view of their actual and potential applications in semiconductor industry particularly in optoelectronics^[3]. Recently advanced microelectronics and surface engineering processes are demanding the most controlled deposition processes for future developments. New concepts and design methodologies are needed to synthesize new thin film devices and to inte-

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grate them for various operations. Examples are the control of surface processes, the development of computer memory chips, and the production of two and three-dimensional nanostructures. Several bottom up chemical methods such as Chemical bath deposition (CBD), CVD, Spray pyrolysis, Pulsed laser deposition etc are popular for deposition of nanostructured materials in the form of thin films on some substrates by controlling the thickness of the film. Uplane et al.^[4] have prepared NiS thin films in acidic medium using sodium thiosulphate as sulphur source. The optical band gap was estimated to be 0.8eV with electrical resistivity of the order of 10^4 - 10^5 Ω -cm. Sartale et al.^[5] have deposited NiS thin film onto glass, FTO coated glass and single crystal Si (111) wafer. The XRD studies show that the crystallinity of the NiS thin film depends on the nature of substrate. Pramanik and Biswas^[6] have chemically prepared nickel sulphide thin films onto glass substrate using nickel sulphate and thioacetamide in an alkaline medium. Khiew et al.^[7] have prepared nickel sulfide (NiS) nanoparticles in water-in-oil (w/o) micro emulsion system containing sucrose ester as the surfactants. The synthesized nanoparticles have regular shape in the size range of 3–12 nm. Otero et al and Musetha et al^[8,9] have prepared NiS thin films on glass substrate by aerosol assisted chemical vapour deposition (AACVD) method. Madhusudan and Sehgal^[10] have prepared NiS-PbS and NiS-CdS thin films on commercial aluminum and galvanized iron substrates by spray pyrolysis and have been extensively investigated for their solar-thermal performance over the complete composition range. The highly oriented rhombohedral (γ) phase of NiS was prepared at 10^{-2} Torr by Jinwoo Cheon et al^[11] by vapour deposition method. Pramanik and Bhattacharya^[12] have prepared NiS thin films on various polymer surfaces by using chemical bath deposition method. The deposition of NiS films on etched Si(111) and (012) using pulsed laser ablation was reported by Heayeon Lee et al^[13]. Morphological characteristics of Ni sulfides fabricated by chemical vapor deposition were reported by Gyu-bong Cho et al^[14]. NiS with particulate shape has various application fields such as hydrogenation catalysis and active materials for energy storage^[15-17]. Cheon et al.^[18] have reported deposition of stoichiometric NiS from both a thermal and photochemical CVD routes. Nomura and Hayata^[19]

studied the deposition of NiS_{1.03} by low pressure metal-organic chemical vapour deposition (LPMOCVD).

The literature survey revealed that no reports were available on preparation of photosensitive NiS thin films by simple chemical method. Hence it is of interest to prepare and study in detail the electrical, optical, morphological and structural properties of these materials, for their possible application in various fields. SILAR method is most simple and relatively less expensive. It is the modified form of chemical bath deposition method. In CBD process the deposition of film occurs when ionic product exceeds solubility product. However, if the reaction rate more, maximum quantity of solution is wasted in forming precipitate. In order to avoid this difficulty SILAR method was developed^[20]. In present communication it is our intention to promote interest in SILAR method for deposition of NiS thin films. The electrical, optical and structural characterizations of nanostructured photosensitive NiS films were carried out.

EXPERIMENTAL DETAILS

The successive ionic layer adsorption and reaction method is mainly based on the adsorption and reaction of the ions from the solution and rinsing between every immersion with deionized water to avoid homogeneous precipitation in the solution. For deposition of NiS thin films, 0.02M nickel sulphate and 0.05M sodium sulphide was taken as cationic and anionic precursor respectively. The substrate was immersed in the cationic precursor, (pH~11) for 30 S, where Ni²⁺ ions were adsorbed on the substrate. After this substrate was rinsed in deionized water for 30 S to remove loosely adsorbed Ni²⁺ ions. The substrate was then immersed in the anionic precursor, sodium sulphide (pH~11) for 30 S, where the S²⁻ ions from the anionic precursor reacts with Ni²⁺ ions on the substrate to produce NiS species. The substrate was then immersed in deionized water for 30 S to remove loosely bounded NiS material. This completes one deposition cycle called SILAR cycle. By repeating such deposition cycles 40 times, nanostructured NiS thin films were prepared.

The film thickness was measured by weight difference method using bulk density of NiS (5.4 g/cm³). The two point dc probe method of dark electrical re-

sistivity was used to study the variation of resistivity with temperature. The structural studies were carried out using Miniflex – Rigaku diffractometer, with Cu-K α radiation of wavelength 1.54Å⁰. JEOL-JSM-6380 analytical scanning electron microscope was used for morphological study. The absorption spectra of as deposited and thermal annealed films were recorded in the range 300 to 1600 nm with the help of a Hitachi spectrophotometer model-330, to find band gap energy. The film of size 0.5 x 1 cm was used to study photoconducting properties. The ohmic contacts were made by silver paste. The dark and photoconductivity of the sample was measured in air at room temperature.

RESULTS AND DISCUSSION

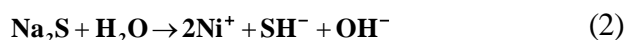
NiS film growth

The formation of NiS thin film involves following steps:

1) From the cationic precursor NiSO₄, Ni²⁺ ions gets adsorbed on the glass substrate.



After rinsing in deionized water for 30 S, substrate was immersed into anionic precursor where S²⁻ ions react with Ni²⁺ to give NiS as,



In SILAR deposition method the different deposition parameters viz concentration, pH, temperature, immersion and rinsing time are very important as they directly affect the growth process. By making several trials, deposition parameters were optimized to get good quality NiS thin films, and are given in TABLE 1. By keeping concentration of Na₂S fixed at 0.05 M, the concentration of Ni precursor was varied from 0.01 to 0.08 M. It was observed that films deposited at lower Ni concentration (< 0.05M) are more adhesive and uniform. However, at higher concentration the film surface is rough and powdery, which may be due to higher growth rate as number of available ions are more at higher concentrations. The optimum anionic and cat-

ionic concentration was found 0.05 and 0.04M and the average growth rate was 2.16 nm cycle⁻¹ (Figure 1).

Using these conditions and by changing number of SILAR cycles the growth mechanism was studied. The

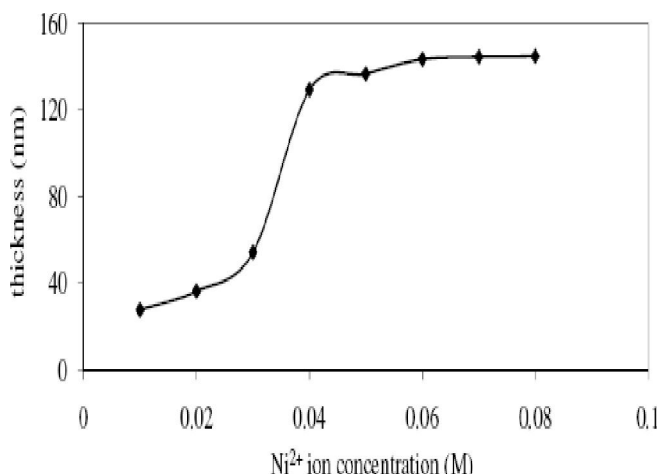


Figure 1 : Variation of NiS film thickness with Ni²⁺ ion concentration for 40 deposition cycles.

TABLE 1 : Optimized deposition parameters for the deposition of NiS thin films.

Preparative parameter	Cationic precursor	Anionic precursor
	NiSO ₄	Na ₂ S H ₂ O
Concentration(M)	0.04	0.05
pH	11	11
Immersion cycles	40	40
Immersion time (S)	30	30
Rinsing time(S)	30	30
Deposition temperature (K)	301	301

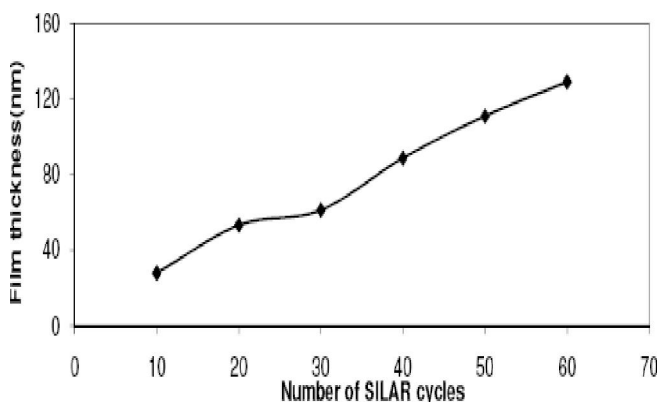


Figure 2 : Variation of NiS film thickness with number of deposition cycles.

optimized SILAR deposition cycles are considered 40, as above it on the film surface loose powder is found. The variation of NiS film thickness with number of

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SILAR growth cycles is shown in Figure 2. The film growth rate was found ~ 2.79 nm cycle⁻¹ up to 20 cycles and then reduces to ~ 2.16 nm cycle⁻¹ at 60th cycle; it is due to reduction of ion concentration in the precursor solution.

Structural studies

The XRD pattern of as deposited and annealed NiS thin film is shown in Figure 3. The comparison between observed and standard 'd' values with ASTM data shows good agreement between observed and standard 'd' values^[21] which reveal that deposited material is NiS with rhombohedral crystal structure (TABLE 2). The as deposited film shows five peaks (101), (021), (220), (401) and (021) and after annealing their intensity increases remarkably with additional two peaks (300) and (211). It was observed that after annealing there is remarkable improvement in crystallite size of NiS. The crystallite size was calculated by using full width at half maximum (FWHM) and Sherrer's formula. The grain size for as deposited and air annealed NiS thin films at 573 K for 30 minute was found to be

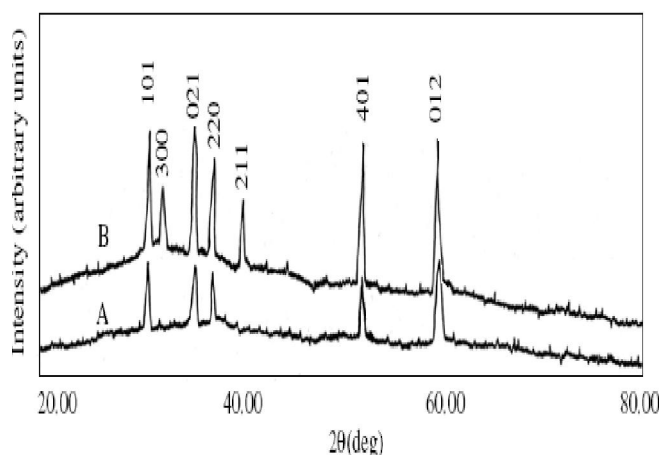


Figure 3 : XRD patterns of NiS films: (A) as deposited and (B) annealed at 573 K temperature.

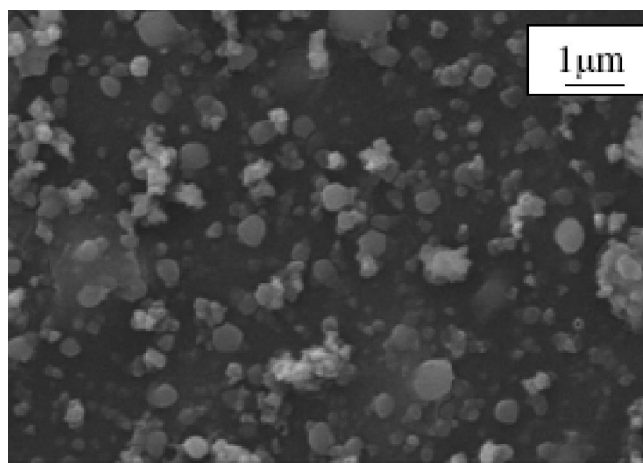
TABLE 2 : Comparison of the observed 'd' values of NiS thin film with standard diffraction data (JCPDS Card No.12-0041).

Sample	Observed d (Å ⁰)		Standard Value	
	As deposited	Annealed film	d (Å ⁰)	hkl
NiS film	2.9433	2.9405	2.946	101
	-	2.7775	2.777	300
	2.5252	2.5335	2.513	021
	2.4023	2.4024	2.406	220
	-	2.2413	2.228	211
	1.7387	1.7446	1.7372	401
	1.5443	1.5452	1.5470	012

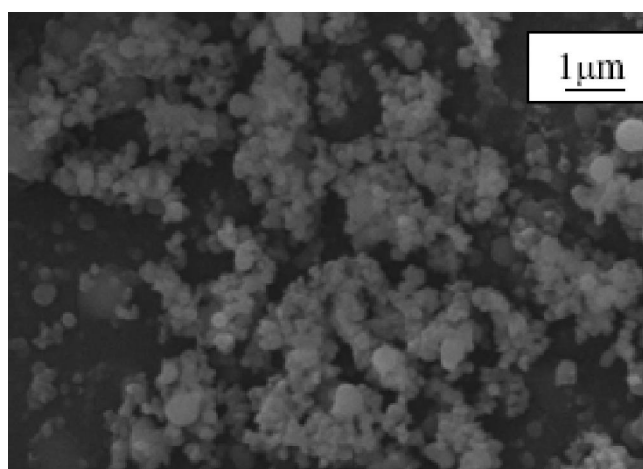
13 and 21 nm respectively

Scanning electron microscopy is the convenient method for studying the microstructure of thin films. The microstructure of as deposited and annealed NiS thin film is shown in Figure 4. It was observed from micrograph that NiS film is homogeneous and well covered with overgrowth of some particles. The majority particles were circular in shape and grown on background of homogenous uniform material. The annealed film shows cabbage type particles with rough surface, due to agglomeration of grains. A clear difference in morphology before and after annealing is observed.

Energy Dispersive X-ray analysis



(A)



(B)

Figure 4 : SEM images of NiS thin film: (A) as deposited and (B) annealed at 573K.

The quantitative analysis of as deposited NiS was

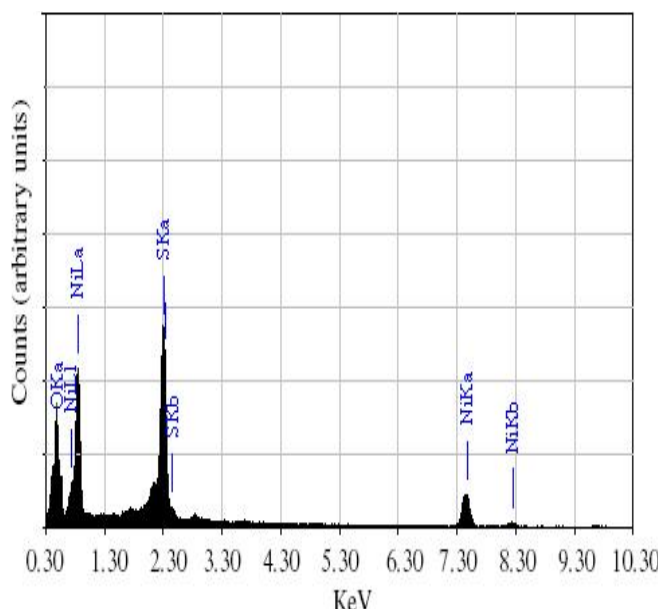


Figure 5 : EDAX spectrum of as deposited NiS thin film.

carried out by energy dispersive X-ray analysis. The elemental analysis was carried out for Ni and S, the average ratio of atomic percentage of Ni:S was 52:48 showing that the films contain NiS with deficiency of sulphur. Figure 5 shows EDAX spectrum of NiS thin film. The inclusion of oxygen is unavoidable which is common feature in chemically deposited metal chalcogenide films^[22-24].

I-V characteristics

The silver paste was used to make ohmic contacts for NiS thin films. The nature of contact was checked by two probe method. The I-V characteristic of NiS/Ag contact is shown in Figure 6. The I-V characteristics for as deposited and annealed NiS thin films are found to be linear, which shows that silver produces ohmic contacts with NiS. The annealed film show is more current than as deposited film which may be due to improvement in crystallite structure.

Electrical resistivity

The dark electrical resistivity measurement was carried out in the temperature range 300 to 400K. The measurement showed that the resistivity of as deposited and annealed thin film was of the order of $10^4 \Omega\text{-cm}$ at 393K. It was observed that resistivity decreases with increase in temperature indicating semiconducting

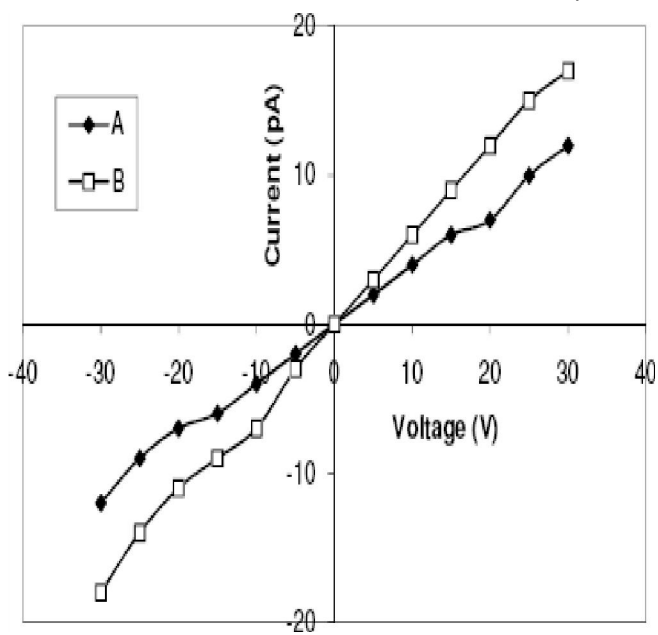


Figure 6 : I-V characteristic of NiS thin film: (A) as deposited and (B) annealed at 573K.

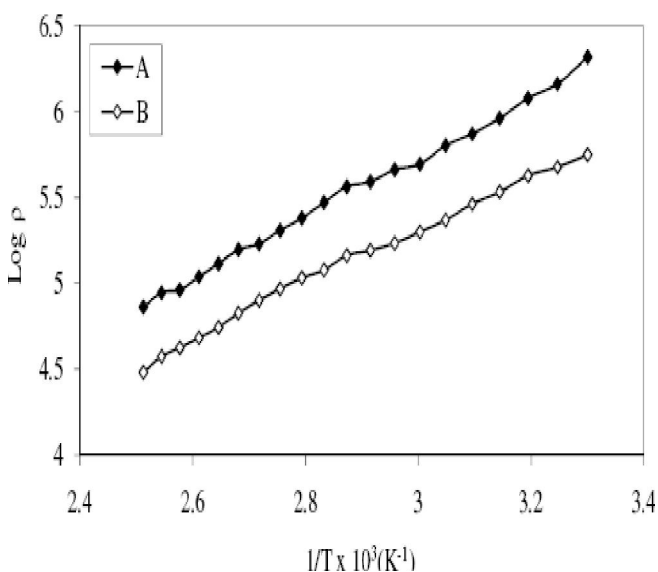


Figure 7 : Variation of $\text{Log } \rho$ with $1000/T$ for NiS film: (A) as deposited, (B) annealed at 573K

nature of film. The resistivity decreases slightly after annealing, it may be due to improvement in crystalline quality of film. The variation of $\text{Log } \rho$ with $1000/T$ for as deposited and annealed NiS thin film is as shown in Figure 7. The activation energy is calculated from the slope and was found to be 0.15 eV for as deposited NiS film and 0.13 eV for annealed film.

Photoconductivity

The dark and photoconductivity of as deposited and annealed NiS thin film was measured at room tem-

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perature (300K) under identical condition. The I-V curves of dark conductivity and photoconductivity for as deposited and annealed NiS films are shown in Figure 8. It was found that both conductivities were increased after annealing. It may be due to diffusion of sulphur atoms towards surface of crystal.

The effect of intensity on photocurrent is studied

TABLE 3 : Dark conductivity and photoconductivity at 300 K for as deposited and annealed NiS thin film.

NiS	Dark conductivity (σ_d) (mho-cm ⁻¹)	Photo conductivity (σ_p) (mho-cm ⁻¹)
As deposited thin film	1.6×10^{-8}	2.4×10^{-8}
Annealed thin film	8.8×10^{-8}	1.3×10^{-7}

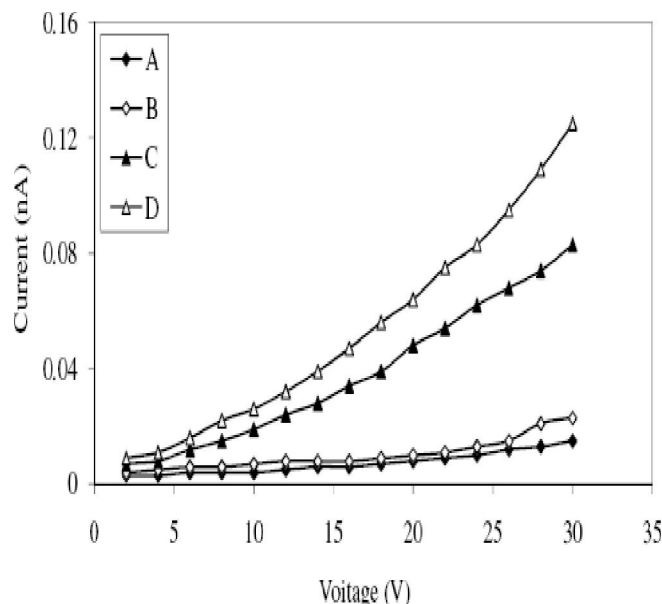


Figure 8 : Variation of current (nA) with voltage (V) for NiS thin films: (A) dark conductivity and (B) photoconductivity of as deposited film; (C) Dark conductivity and (D) photoconductivity of annealed film, at 300K temperature.

with the help of dc two probe method at room temperature. The variation of current with light intensity is shown in Figure 9. It was found that photoconductivity increases after annealing it may be due to sulphur deficiency in NiS composition. The dark and photoconductivity for as deposited and annealed NiS thin film measured at 30V is given in TABLE 3. The conductivity of as deposited NiS film changes by 0.8×10^{-8} (mho-cm⁻¹), however the annealed film shows change in conductivity by amount 4.2×10^{-8} (mho-cm⁻¹). It means that annealed films are more photosensitive.

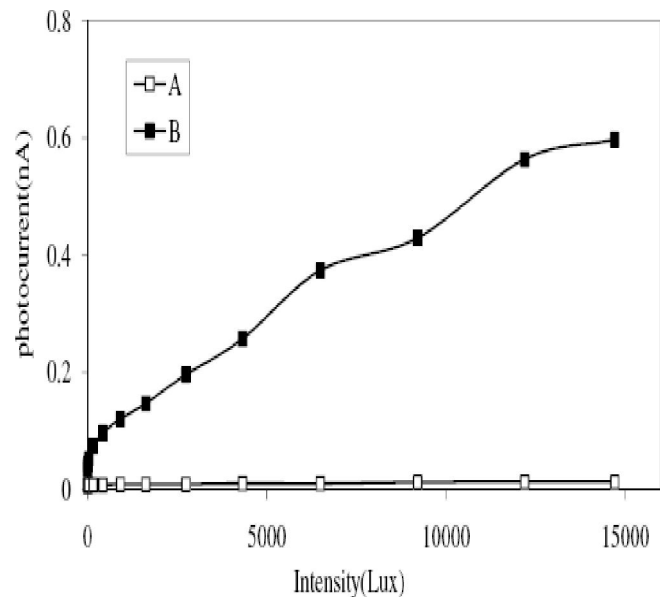


Figure 9 : Variation of current (nA) with light intensity (Lux) for NiS thin film: (A) As deposited film and (B) film annealed at 573K.

Optical properties

In present investigation optical absorption of NiS thin films were studied in the wavelength range 300-1600 nm (Figure 10) The spectra revealed that the NiS films have low absorbance in the visible region of the spectrum. However, absorbance was lowest for sample A compared with B, C and D. The low absorbance of sample A can be attributed to the lowest thickness. Further, the absorption edge was seen to be shifted slightly towards higher wavelength (red shift) as the annealing temperature was increased. This shift indicates decrease in band gap, which can be attributed to increase in grain size with annealing temperature.

The variation of $(\alpha h\nu)^2$ with $h\nu$ for NiS thin films is shown in Figure 11. The bandgap energy is determined by extrapolating the straight line to the energy axis and is found to be decrease from 0.92 to 0.79eV after annealing. The bandgap energy determined by plotting the straight line to the energy axis is found to be 0.92, 0.9, 0.86 and 0.79 eV for as deposited and annealed at 373, 573 and 773K temperature NiS film respectively.

Thermo emf

The polarity of thermoemf was found to be positive towards the cold end indicating that, NiS is p-type semiconductor. The dependence of thermoemf on temperature for as deposited NiS and annealed NiS thin film

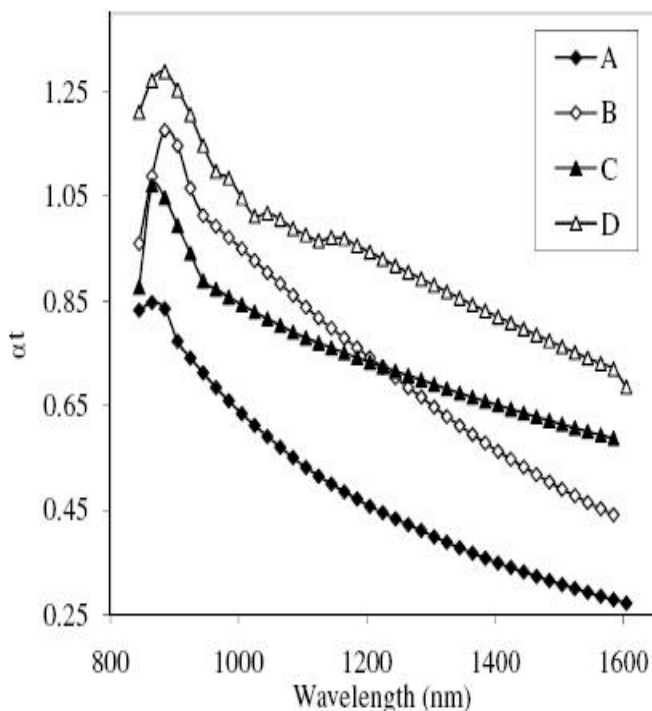


Figure 10 : Variation of (αt) with wavelength for NiS thin films : (A)as deposited, (B)annealed at 373K, (C)annealed at 573K and (D)annealed at 773K.

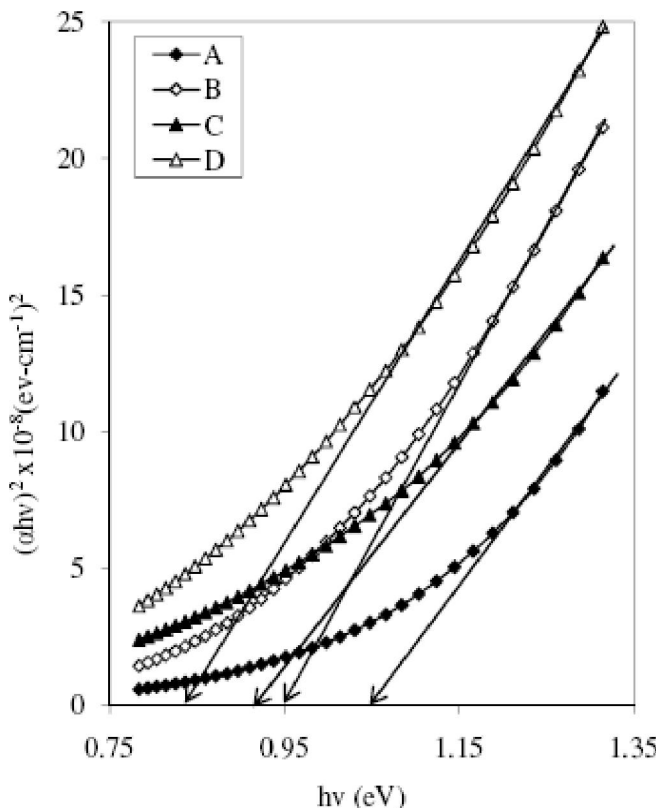


Figure 11 : Variation of $(ahv)^2$ with hv for NiS thin films : (A)as deposited, (B)annealed at 373K, (C)annealed at 573K and (D)annealed at 773K.

was shown in Figure 12. The plot shows that as temperature difference ΔT increases, thermoemf also increases. This is attributed to increase in carrier concentration and mobility of charge carriers with rise in temperature. The curve for as deposited NiS and annealed NiS crosses each other at 317.6 K. The thermoemf curve for annealed film is more linear in nature as compared to curve for as deposited film. It happens as the film morphology of as deposited film gets changed during the measurement of readings of thermoemf due to heating, however the annealed film has stable morphology.

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CONCLUSION

The simple SILAR method was used to deposit large area nanostructured photosensitive NiS thin films on glass substrate. XRD studies showed that the NiS films have rhombohedral crystal structure. The bandgap energy determined is found to be decrease from 0.92 to 0.79eV after annealing. The room temperature re-

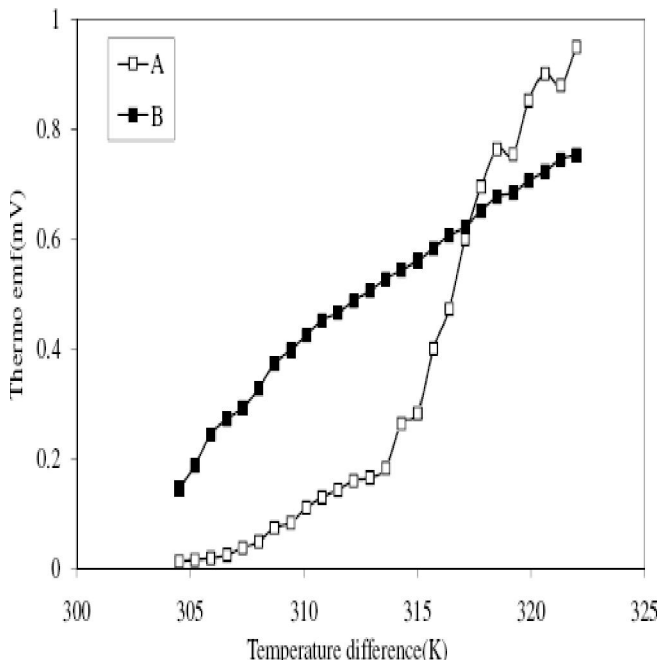


Figure 12 : Variation of thermo emf (mV) with temperature difference (K) for NiS thin film: (A) As deposited and (B) annealed at 573K.

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sistivity is of the order of $10^4 \Omega\text{-cm}$ at 393K. The NiS thin films grown by the SILAR method exhibit p-type electrical conductivity. The IV characteristic and thermoemf curve of annealed film shows more linearity than as deposited film which is the characteristic of stable morphology. It was found that annealed films are more photosensitive.

REFERENCES

- [1] J.Schoonman; Solid State Ionics, **135**, 5 (2000).
- [2] L.I.Maissel, R.Gilana; In Hand Book of Thin Film Tech.Mc.Grow Hill, New York (1970).
- [3] A.U.Warad, M.D.Uplane, S.H.Pawar; Mater.Chem.Phy., **13**, 91 (1985).
- [4] M.M.Uplane, P.S.Patil, M.D.Uplane, C.D.Lokhande; Bull.Electrochem., **11**, 569 (1995).
- [5] S.D.Sartale, C.D.Lokhande; Mater.Chem.Phy., **72**, 101 (2001).
- [6] P.Pramanik, S.Biswas; J.Solid State Chem., **65**, 145 (1986).
- [7] P.S.Khiew, N.M.Huang, S.Radiman; Soot.Ahmad.Mater.Chem.Phy., (2003).
- [8] R.Otero, J.L.Martín, de Vidales, C.Heras; J.Phys.Conden.Matter., **10**, 6919 (1998).
- [9] Phumudzo Musetha, Neerish Revaprasadu, Azad Mohamed Malik, Paul O'Brien; Mater.Res.Soci., **31**, 12 (1998).
- [10] M.Madhusudan, H.K.Sehgal; Energy Conver.Manag., **21**, 199 (1981).
- [11] Jinwoo Cheon, David S.Talaga, Jeffrey I.Zink; Chem.Mater., **9**(5), 1208 (1997).
- [12] P.Pramanik, S.Bhattacharya; J.Mater.Sci.Lett., **6**(9), 1105 (1987).
- [13] Heayeon Lee, Masaki Kanai, Tomoji Kawai, Shichio Kawai; Jpn.J.Appl.Phys., **32**, 2100 (1993).
- [14] Gyu-Bong Cho, Kang-Woo Bae, Tae-Hyun Nam, Jun-Hee Lee; J.Alloys.Comp., **477**, 24 (2009).
- [15] Y.Yermakov, A.N.Startsev, V.A.Burmistrov; Appl.Catal., **11**, 1 (1984).
- [16] K.I.Tanaka, T.Okuhara; Catal.Rev.Sci.Eng., **15**, 249 (1977).
- [17] R.Jasinski, B.Burrows; J.Electrochem.Soc., **116**, 422 (1969).
- [18] J.Cheon, D.S.Talaga, J.Zink; Chem.Mater., **9**, 1208 (1997).
- [19] R.Nomura, H.Hayata; Trans.Mater.Res.Soc., **26**(4), 1283 (2001).
- [20] A.U.Ubale, A.S.Daryapurkar, R.B.Mankar, R.R.Raut, C.H.Bhosale; Mater.Chem.Phy., **110**/1, 180 (2008).
- [21] JCPDS card no. 12-0041.
- [22] C.D.Lokhande, B.R.Sankapal, R.S.Mane, H.M.Pathan, M.Muller, M.Giersig, V.Ganesan; Appl.Surf.Sci., **193**, 1 (2002).
- [23] C.D.Lokhande, P.S.Patil, A.Ennaoui, H.Tributsch; Appl.Surf.Sci., **123**, 294 (1998).
- [24] C.D.Lokhande, P.S.Patil, H.Tributsch, A.Ennaoui; Solar Energy Matter.Solar Cells, **55**, 379 (1998).