# SUCCESSIVE IONIC LAYER ADSORPTION AND REACTION (SILAR) METHOD

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**Abstract:** *Nickel sulfide (NiS) thin films were deposited on the glass substrates by Silar Method at room temperature using an aqueous solution which contains nickel chloride hexahydrate and thiourea as precursors. X-ray diffraction analysis confirms that the hexagonal structure is being part of $P6_3/mmc$ space group of the deposited films with (100) preferred orientation and lattice parameters a = 3.441 Å and c = 5.320 Å. Scanning electron micrographs (SEM) reveal a homogeneously deposited very dense surface structure with the presence of irregular shaped grain particles. The optical absorption studies show that the absorption coefficient of the NiS thin film is high and a direct band gap of ~1.03 eV has been observed. The thickness of the film is found to be 350 nm.*

***Keywords:*** ***Thinfilms, NiS, XRD, bandgap, silar.***

## 1. INTRODUCTION

Recent usage of Solar cells, Sensors and photoconductors and infrared detectors etc., they are prepared by binary compounds belong to VIII-VI compound semiconductor materials [1]. Therefore we have planned to prepare semiconductor materials; by literature survey [2-10], Thin films forms the better approach. Thin films are of particular interest for fabrication of large area arrays, solar selective coatings, solar cells, photoconductors, sensors, photo thermal solar coatings etc [1, 2]. Thin films can be fabricated in various ways.

A variety of methods, including electro deposition [11], SILAR [12], pulsed laser ablation [13], metal-organic chemical vapour deposition [14], thermal and photochemical chemical vapour deposition [15] can be used for the preparation of nickel sulphide thin films. In this study we have prepared NiS thinfilms by SILAR technique. SILAR method is ideal for making crystalline thin films [16]. Deposition process can be done by immersing the substrate into the separately placed cations and anions solution, follows by a rinsing after each reaction, which is the cheapest method; no need of target or it does require vacuum at any stage of the deposition process [17]. Effortless behavior of SILAR method attracts the attention to prepare thin films by this method. Doping of films is simple, there are no restrictions in the substrate dimension and the thickness of the films can be controlled by changing the deposition cycle number [18].

In this article, we have reported that NiS thin films, prepared by glass substrates under SILAR method. As deposited NiS thin films shows amorphous structure. It exhibits an optical behavior in the indirect allowed transition region.

## 2. Experimental Techniques

### 2.1Silar method

#### 2.1.1 Solution Preparation

Nickel Nitrate solution is shown in Fig.1 (a), 0.1M Nickel nitrate(18.02g) is taken in the beaker of 50ml capacity, the liquid ammonia is added to the beaker until the pH of the solution is adjusted to ~ 8.This solution is called as cationic precursor. For rinsing purpose the distilled water is used to remove excess nickel ions as in Fig.1 (b). Sodium sulphide solution is shown in Fig.1(c), 0.5M Sodium Sulphide (39.02) is taken in the beaker of 50 ml capacity, the distilled water is added until the ph of the solution is adjusted to ~10 and is stirred to get the dissolved solution. For rinsing the distilled water is used as shown in Fig. 1(d) to remove sulphide and the unreacted Ions.

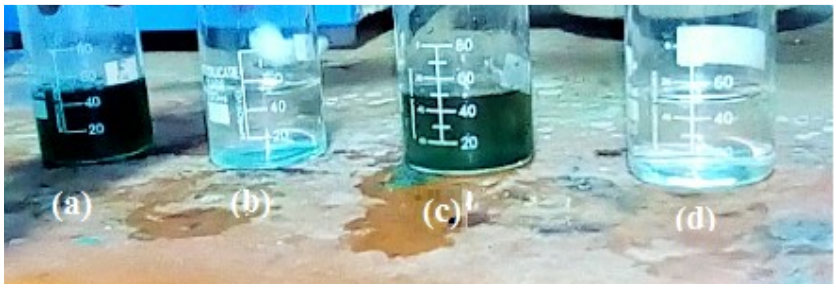


Fig.1 **Preparation of NiS thinfilms by Silar technique**

**2.1.2 Deposition Procedure**

The deposition was carried out at room temperature (27ºC) using unstirred conditions. In SILAR method concentration, pH and temperature of precursor solution and the time duration for adsorption, reaction and rinsing are important parameters. By making several trial experiments Nis thin film deposition conditions are optimized.

When the substrate is immersed in cationic precursor solution (nickel nitrate) for 60 seconds, nickel ions get adsorbed on the substrate surface. The substrate is rinsed in flowing distilled water for 40 seconds to remove the loosely bound or excess nickel ions. Then the substrate is immersed in anionic precursor solution (sodium sulphide) for 60 seconds. The sulphide ions react with preabsorbed nickel ions to form a layer of Nis over substrate. Rinsing the substrate again in the distilled water for 40seconds separated out the unreacted or unadsorbed sulphide ions or powdery NiS material. This completes one SILAR deposition cycle. After completion of one cycle the glass substrate is annealed. After repeating such 25 cycles, NiS film was obtained.

## 3. Results and Discussion

**3.1 Thickness of the film**

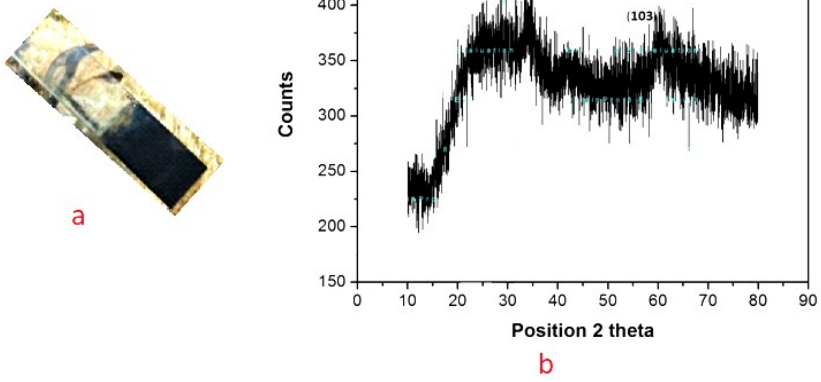


Fig. 2 (a) **NiS thin films by SILAR method**
(b) **XRD pattern of NiS thin films**

Fig. 2(a) shows the as prepared NiS thinfilms. Fig. 2(b) shows the XRD pattern of the NiS thinfilms is annealed at room temperature obtained by silar method. It shows that room temperature obtained by silar method. It shows that the NiS thin films is in hexagonal structure [19] with the following (1 0 1) (1 0 3) peaks. The cell parameters are a=3.439(α); b=3.439(β); c=5.352. Table: 1 shows the observed Powder XRD data of NiS thinfilms.The calculated lattice parameters are compared with standard value obtained from the JCPDS data (card number: 65-5762). Thickness of the thin film is found to be 350 nm.

Table: 1 **NiS thinfilms Powder XRD data**

| Position [°2Th.] | Height [cts] | FWHM Left [°2Th.] | d-spacing [Å] | Rel. Int. [%] |
|---|---|---|---|---|
| 11.0692 | 4.32 | 1.6059 | 7.99337 | 15.07 |
| 34.2024 | 28.69 | 1.6059 | 2.62170 | 100.00 |
| 60.1431 | 18.63 | 1.6059 | 1.53855 | 64.95 |

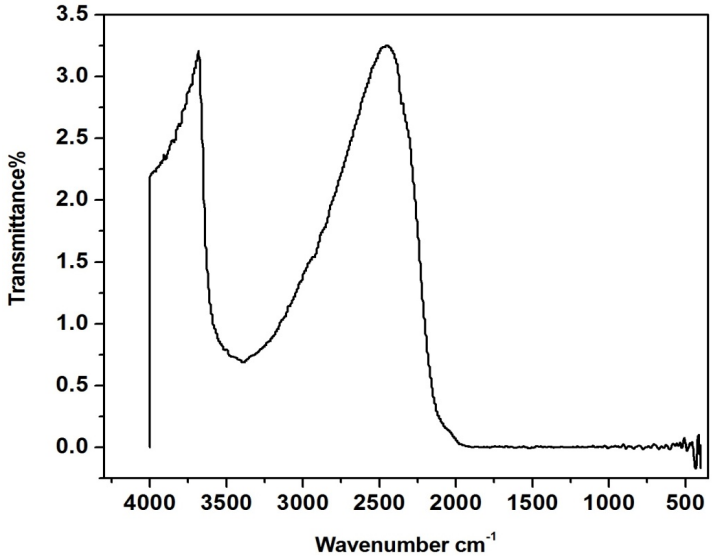


Fig.3 **FTIR of NiS**

The FTIR spectrum of the as-synthesized NiS is shown in Fig. 3 Two weak peaks at **3480cm**$^{-1}$ and **1985** cm$^{-1}$, respectively, are due to C–H stretching modes. The above peaks are in well agreement with the reported values [20]. This confirms the formation of NiS thinfilms.

### 3.3 Optical absorption studies

The optical properties of NiS thinfilms obtained at ambient temperature using UV–vis transmittance and reflectance spectroscopy (Fig. 4). The optical spectra of NiS films were studied at room temperature (27ºC). The average optical transmittance and reflectance are about 0.62% and 1.10% respectively. Moreover, the absence of the interference fringes in the long wavelength region is mainly due to the roughness of the film.

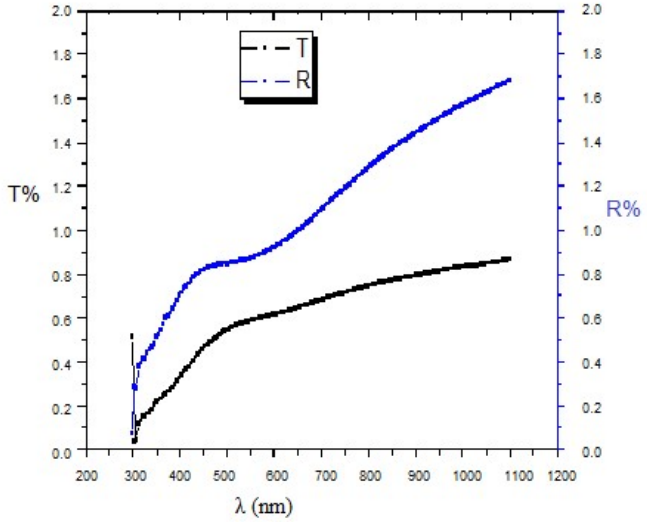


Fig. 4 **UV-visible reflectance and transmittance spectra of NiS thin film.**

NiS thin films reflectance is superior to its transmittance. This can be correlated to the oscillation of the free carrier's plasma, shows metallic behavior of the film [5]. The absorption coefficient (α) was calculated from the transmittance and the reflectance spectra, using the following formula [21]

$$\alpha = \frac{1}{d} ln \frac{(1-R)^2}{T} \qquad \text{--------- (1)}$$

In equation (1), d is the thickness, R is the reflectance and T is the transmittance. Fig. 5 shows the variation of the absorption coefficient (α) as a function of wavelength (λ). The optical band gap of the material was determined using Tauc formula [22]

$$\alpha h\nu = B(h\nu - E_g)^p \text{ ---------- (2)}$$

In equation (2), B is a constant; p is an integer that takes the value 1/2 or 2 for direct or indirect transitions, respectively. Fig. 4 shows the plot of $(\alpha h\nu)^2$ Vs energy (hν).

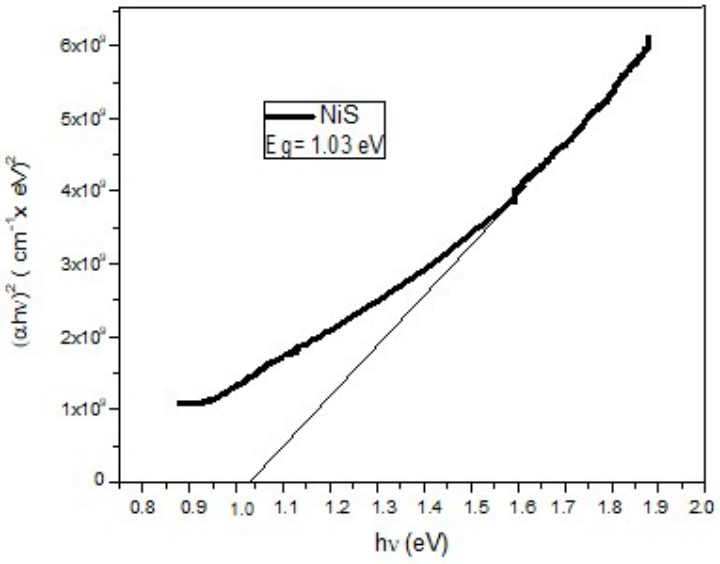


Fig. 5 **Plots of $(\alpha h\nu)^2$ versus photon energy (hν) of NiS thin film.**

Fig. 5 shows the linear extrapolation of the curve gives the optical band gap of the film, it was found to be 1.03 eV, is well agreed with the reported values [23]. Furthermore, the value of the optical gap concurs with the structural analysis, which is blue shifted when compared to that of the bulk material, nearby 0.8 eV. This blue shift of ~230 meV of the band edges can be understood if we consider the quantum confinement pooled alongside with the Moss-Burstein effect. It shows an additional energy is necessary for the electronic shift owing to the band filling of the band edges in accumulation to the shift because of the particle size [24].

**3.4 SEM**

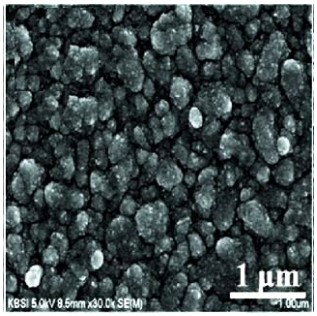


Fig. 6 **NiS thin films SEM Image**

Scanning electron microscopy (SEM) can provide a highly magnified image of the surface and composition information of surface regions of the materials. The resolution of SEM can approach a few nano meters and the very high magnifications.
Fig. 6 shows the SEM image of NiS thinfilms with the magnification of 800000X is presented. And it was observed from the micrographs that NiS film was homogeneously deposited without micro cracks [25].

## 4. Conclusion

Semiconducting NiS thin films are deposited onto glass substrate using SILAR method. Silar method is a process in which the deposition rate and thickness of the film can be easily controlled over a wide range by changing the deposition cycles. The crystal structures of the NiS thin films were investigated by X-ray diffractometer and their main diffraction peaks are well agreed with other studies. The films were found to have polycrystalline, homogeneous structure and covered the substrates well. Some of the thin film with equal distribution of grains, mostly falling in nanometer regime, was clearly seen. The thickness of NiS film is found to be 350 nm measured using stylus profilometer. The elementary groups are identified using FTIR analysis. Optical bandgap of the NiS thinfilms studied using UV visible spectrum is found to be 1.03eV. UV spectrum gives transmittance in the visible region.

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