STUDY OF THE STRUCTURAL, OPTICAL, ELECTRICAL AND MORPHOLOGICAL PROPERTIES OF NICKEL SULFIDE THIN FILMS USED IN SUPERCAPACITORS

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Article Info	Abstract
<p>Received: 09.11.2020 Accepted: 27.01.2021</p> <p>Keywords: NiS; spray-pyrolysis; thin films; optical gap; conductivity</p>	<p>Nickel sulfide (NiS) thin film has been deposited on glass substrates by spray-pyrolysis at 325 ± 5 °C. The precursor aqueous solution was synthesized using hexahydrated nickel nitrates and thiourea. The structural, morphological, optical and electrical properties were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), UV-visible spectroscopy and four probes electrical measurements. The XRD analysis confirmed the hexagonal structure of NiS thin film, which was found to crystallize along [010] direction with an average crystallites size of 10.5 nm. The lattice parameters are $a = b = 3.420$ Å and $c = 5.300$ Å in the space group $P6_3/mmc$. The optical properties of the films were investigated through the transmittance and the reflectance measurements. The results revealed that the material exhibits a direct optical band gap of 1.03 eV. The elementary composition analysis confirmed the presence of Ni and S with a stoichiometry ratio (Ni/S) of 1.05. The morphology analysis revealed a homogenous crack-free, compact appearance and a granular surface in all scanned areas. The average roughness of the surface was 6.48 nm. On the other hand, the film exhibits a high electrical conductivity ca. 1.10×10^5 S/cm at room temperature. The above results show that the prepared NiS in this study has a good crystallization, dense morphology, good stoichiometric ratio and high conductivity; therefore, it stands as a potential candidate for application in supercapacitors as an electrode material.</p>

1. Introduction

Recently, transition metal sulfides (TMS) has become one of the subjects of great interest to researchers due to the high electrical conductivity [1], good electrochemical

stability [2], respect for the environment and low cost of production [3]. Some (TMS) such as NiS, CoS, SnS, CuS and ZnS have been widely exploited as new electrode materials for supercapacitors due to their distinctive properties compared to the oxides and hydroxides of these minerals [4]. In the TMS family, Nickel sulfide (NiS) belongs to the semiconducting compounds VIII-VI. Furthermore, the NiS depicts a metallic transition induced by doping and an antiferromagnetic behavior at high temperatures [5].

NiS exists in two phases: hexagonal structure (α -NiS) and rhombohedral structure (β -NiS). In literature thin films of NiS have been deposited by different methods such as spray-pyrolysis [6], chemical bath deposition (CBD) [5], hydrothermal [7], successive ionic layer adsorption and reaction (SILAR) [8], thermal evaporation [9], electro-deposition [10] and sol-gel [11]. The present study deals with the synthesis and the characterization of the structural, optical, morphological and electrical properties of the α - NiS phase deposited by spray-pyrolysis at 325 °C.

2. Experimental details

2.1. Preparation of nickel sulfide (NiS)

NiS was deposited on a well-cleaned glass substrate using spray-pyrolysis technique. The precursor solution consisted of nickel nitrates hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; 10^{-1} mol/l) and thiourea ($\text{CS}(\text{NH}_2)_2$; 2×10^{-1} mol/l), dissolved in 100 ml of ionized water. A few drops of acetic acid were added for complete dissolution. The temperature of the substrate was fixed at 325 ± 5 °C, prior to deposition and compressed air was used as a vector gas to produce aerosol particles. The flow rate was kept at 0.5 bar. The distance between the nebulizer and the substrate was set at 25 cm. In order to achieve uniform deposits, the spray gun of the nebulizer is connected to a manually operated stepper motor to control the position of the spray in the plane (X, Y). After deposition, the film was slowly cooled to room temperature under ambient air. The characterization was conducted on the film without any thermal treatment. The films thickness was estimated using the weight method using the following formula [12]:

$$e = \frac{m}{\rho \times S} \quad (1)$$

where: e is film thickness of the film, m is mass deposited on the substrate, S is the area of the film and ρ is the density of NiS (5.50 g/cm^3 [13]). It was found to be $\sim 936 \text{ nm}$.

2. 2. Characterization

The structural analysis was carried out using an X-ray diffractometer (DRX; Mini Flex-Rigaku) with a Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$) in the range of $20 - 60^\circ$, using the Brentano-Bragg geometry. The morphology of the surface was analyzed using a scanning electron microscope (SEM; Qanta 350) equipped with an energy dispersive spectrometer (EDS) for elementary analysis. The surface roughness was investigated using an atomic force microscope (AFM type VEECO digital instrument). A dual-beam UV-visible spectrophotometer (UV-3101; Shimadzu), was used to measure the transmittance and reflectance in the wavelength range of $300 - 1100 \text{ nm}$ with a resolution of 5 nm . The electrical measurements were recorded using the four-probe method.

3. Results and Discussions

3.1 X-Ray Diffraction

Fig. 1 shows the XRD pattern of NiS prepared by the spray-pyrolysis technique. It is observed that the obtained film is polycrystalline and crystalize in a hexagonal structure (Space group No. 194: $P6_3/mmc$) strongly oriented along (010) direction. The intensity of the reflection on this plane is greater than that of the other diffraction peaks corresponding to (011), (012) and (110) plans. The XRD pattern was indexed according to the JCPDS card #98-064-6340. The Wyckoff positions of Ni and S ions are given in table 1.

Table 1: Wyckoff positions of Ni and S ions in the hexagonal structure.

Ion	Ox	Wyck	Site	x/a	y/b	z/c
Ni1	2	2a	-3m.	0	0	0
S1	-2	2c	-6m2	1/3	2/3	1/4

On the other hand, the broad band observed on the XRD pattern is due partially to the amorphous phase; thus, confirming the formation of polycrystalline layer. The data obtained in this study are also in a good agreement with the previous reports in the literature on NiS films prepared by spray-pyrolysis and other techniques [6, 14, 15].

Fig. 1. X-ray pattern of NiS thin film.

The unit cell parameters a , b and c , were determined using the following formula [16]:

$$\frac{1}{d_{hkl}^2} = \frac{3}{4} \left(\frac{h^2 + k^2 + hk}{a^2} \right) + \frac{l^2}{c^2} \quad (2)$$

The unit cell volume was evaluated using the following formula:

$$V = a^2 \times c \times \sin(60^\circ) \quad (3)$$

Table 2 summarizes the structural parameters compared to those of the corresponding JCPDS card. The results are in good agreement with the standard card (JCPDS card No. 98-064-6340). The slight mismatch suggests the presence of structural disorder in the film.

Table 2: Lattice parameters (a , b and c) and the unit cell Volume (V) compared to the data of JCPDS card.

Our data			JCPDS card			$V (\text{\AA}^3)$
$a=b (\text{\AA})$	$c (\text{\AA})$	c/a	$a=b (\text{\AA})$	$c (\text{\AA})$	c/a	
3.412	5.277	1.546	3.420	5.300	1.550	53.202

The ratio (c/a) of 1.546 is slightly smaller than the standard value (1.550) of the hexagonal structure. This may be due to vacancies in the lattice that cause local changes and

contraction of the lattice. The inter-plans distance (d_{hkl}) was calculated using Bragg formula [17] .

$$2d_{hkl} \sin \theta = n\lambda \quad (4)$$

On the other hand, the texture coefficient (TC_{hkl}), which is calculated in terms of the intensity of each orientation (I_{hkl}), gives information on the probability of the growth according to an orientation (hkl). This coefficient is given by the following relation [18]:

$$TC_{hkl} = \frac{I_{hkl}/I_{0hkl}}{N^{-1} \left[\sum_{i=1}^n \frac{I_{hkl}}{I_{0hkl}} \right]} \quad (5)$$

where: I_{0hkl} is the intensity according to the JCPDS card of the plan (hkl) and N is the number of diffraction peaks. The obtained values of TC_{hkl} are gathered in Table 3. It is observed that the value of the largest texture coefficient corresponds to the peak (010), which indicates that it is the preferred orientation. Hence, the peak (010) has the highest intensity when compared to the other peaks.

The crystallites size (D) was estimated for all diffraction peaks using Debye formula [19]:

$$D = \frac{k \times \lambda}{\beta_{1/2} \cos \theta} \quad (6)$$

where: k is a constant ($k = 0.90$), $\beta_{1/2}$ is the full width at half the maximum of the diffraction peak, θ is the Bragg angle for each plan (hkl) and $\lambda = 1.5406 \text{ \AA}$ is the wavelength of the X-ray radiation used.

The residual stress (ϵ_{hkl}) and the dislocation density (δ_{hkl}) in the film were evaluated using the following formulas [20] :

$$\left\{ \begin{array}{l} \delta = \frac{1}{D^2} \\ \epsilon = \frac{\beta_{1/2}}{4 \tan \theta} \end{array} \right. \quad (7)$$

$$\quad (8)$$

Table 3: Texture coefficient (TC_{hkl}), crystallites size (D_{hkl}), residual stress (ϵ_{hkl}) and dislocation density (δ_{hkl}).

(hkl)	d_{hkl} (nm)	D_{hkl} (nm)	$\epsilon_{hkl} \times 10^{-3}$	$\delta_{hkl} \times 10^{15}$ (lines/nm ²)	TC_{hkl}
010	0.296	28.015	0.509	1,274	0.893
011	0.258	9.446	13.207	11.206	0.404
012	0.198	14.680	6.508	4.639	0.605
110	0.171	15.146	5.448	4.358	0.297

In addition, the average crystallites size $\langle D \rangle$, micro-stress $\langle \epsilon \rangle$ and the dislocation density $\langle \delta \rangle$ can be determined using the texture coefficient according to the formulas [6]:

$$\langle D \rangle = \frac{\sum TC_{hkl} \times D_{hkl}}{n} \quad (9)$$

$$\langle \epsilon \rangle = \frac{\sum TC_{hkl} \times \epsilon_{hkl}}{n} \quad (10)$$

$$\langle \delta \rangle = \frac{\sum TC_{hkl} \times \delta_{hkl}}{\sum TC_{hkl}} \quad (11)$$

The average values of the crystallites size, micro-stress and the dislocation density are 10.5 nm, 3.865×10^{-3} and 4.442×10^{15} (lines/nm²), respectively. The obtained values are compatible with a high quality thin film. It is a well-established fact that the dislocations in the film acquire more energy and exhibit higher mobility during crystallization. These activated dislocations segregate towards the grains boundaries and are neutralized as the crystallization of the film proceeds.

3.2. Optical properties

Fig. 2 shows the transmission and reflectance spectra of NiS recorded at room temperature. It observed that both transmittance and reflectance decrease in the ultra-violet range. However, an enhancement of the transparence of the film is observed above 400 nm owing to a reduced scattering effect and propagation losses. 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. 2. UV-visible reflectance and transmittance spectra of NiS thin film.

Furthermore, it is observed that the film reflectance is higher than its transmittance. This phenomenon can be related to the oscillation of the free carriers plasma, depicting the metallic behavior of the film [6]. The absorption coefficient (α) was calculated from the transmittance and the reflectance spectra, using the following formula [21]:

$$\alpha = \frac{1}{e} \ln \left(\frac{(1 - R)^2}{T} \right) \quad (12)$$

where: d is the thickness, R is the reflectance and T is the transmittance. Fig. 3 shows the variation of the absorption coefficient (α) as a function of wavelength (λ). The average absorption coefficient is $4.12 \times 10^4 \text{ cm}^{-1}$, which is of the same order of magnitude observed in semiconducting reflecting thin films and it is close to those reported in the literature for semiconducting thin films [22].

The optical band gap of the material was determined using Tauc formula [23]:

$$\alpha h\nu = B(h\nu - E_g)^p \quad (13)$$

where: 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 $(\alpha h\nu)^2$ versus energy ($h\nu$).

Fig. 3. Evolution of the absorption coefficient (α) of NiS thin film.

Fig. 4. Plots of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) of NiS thin film.

The linear extrapolation of the curve yields the intersection point with the abscissa axis, which corresponds to the energy of the optical transition. The optical band gap of the film was found to be 1.03 eV, in a good agreement with the values reported in the literature [22]. In addition, the value of the optical gap agrees 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. Therefore, an additional energy is required for the

electronic transition due to the band filling of the band edges in addition to the shift due to the particle size [24].

3.3. Electrical studies

The electrical conductivity of NiS was determined by the four-points probe method, it is based on the measured sheet resistance of the films as expressed by the following formula [25]:

$$\begin{cases} R_{sh} = \frac{\pi}{\ln 2} \times \frac{V}{I} \\ \sigma = \frac{1}{\rho} = \frac{1}{e \times R_{sh}} \end{cases} \quad (14)$$

$$(15)$$

where: ρ is the electrical resistivity, e is the film thickness, I is the applied current = 1 nA and V is the measurement voltage. Table 4 summarizes the results of the electrical measurements.

Table 4: The electrical parameters of NiS.

Thin film	Film thickness e (nm)	Sheet resistance R_{sh} (Ω/sq)	Electrical resistivity ρ ($\Omega.\text{cm}$) ⁻¹	Electrical conductivity σ (S/cm)
NiS	936.253	9.74×10^{-2}	9.11×10^{-6}	1.10×10^5

It is observed that the film exhibits a very high electrical conductivity of 1.10×10^5 (S/cm). Thus, confirming the metallic behavior of the prepared NiS, which support the above claim about the Moss-Burstein effect. Also, these results are close to the reported data in the literature [26, 27]. It is evident that the NiS prepared in this study is highly attractive as an electrode material for application in supercapacitors.

3.4. SEM and EDS analysis

Fig. 5 shows the SEM and EDS micrographs of NiS thin films. The SEM micrograph show that the surface of the film is rough, porous and granular with a random distribution. This morphology yields a greater surface/volume ratio and thus, the specific surface of the film is higher when compared to that of a smooth film. In addition, it is observed that the film was homogeneously deposited without micro-cracks.

Fig. 5. (a) SEM image and (b) EDS analysis of NiS thin film

The EDS micrograph of the films (Fig. 5 b), confirm the presence of Ni and S elements with an atomic ratio of 1.05. Furthermore, the analysis revealed the presence of other elements such as oxygen (O) and silicon (Si) which originate from the SiO₂ glass substrate. While, the presence of carbon C is probably due to thiourea (SC(NH₂)₂) involved in the synthesis. It is pertinent to note that the atomic percentage of nickel to sulfur is almost equal to 1, suggesting the formation of a sulfur-poor surface; this is due to the property of sulfur to be volatile at high temperatures.

3. 5. AFM analysis

The surface roughness is an important physical parameter in some properties, especially optical scattering. Fig. 6 (a and b) shows 2D and 3D micrographs of the NiS surface, recorded in a scanning area of 1 ×1 μm². The surface depicts a granular and dense morphology. The analysis of the surface profile yields the average roughness (R_a) and root mean square roughness (R_{RMS}), the geometric mean of the heights of all points on the surface scanned by the microscope. These parameters are defined as follows [18]:

$$\left\{ \begin{array}{l} R_a = \frac{1}{l} \int_0^l |z - z_i| dx \\ R_{RMS} = \sqrt{\frac{1}{l} \int_0^l |z - z_i|^2 dx} \end{array} \right. \quad (16)$$

$$\left\{ \begin{array}{l} R_a = \frac{1}{l} \int_0^l |z - z_i| dx \\ R_{RMS} = \sqrt{\frac{1}{l} \int_0^l |z - z_i|^2 dx} \end{array} \right. \quad (17)$$

where: l is the length of the sample, Z_i is the height reference and Z is the profile value. The values of R_{RMS} and R_a were found to be 8.07 and 6.48 nm, respectively. It can be observed that both R_a and R_{RMS} are very small when compared to the thickness of the film *i.e.* (R_a, R_{RMS}) $\ll e$. Thus, the surface is very smooth and suitable for use in microelectronic and optoelectronic devices [28].

Fig. 6. (a) 2D and (b) 3D-AFM images of NiS thin film.

4. Conclusion

In the present study, we have successfully deposited at 325 °C the α -phase of nickel sulfide (NiS) using spray-pyrolysis technique. Then, the film was characterized without any post-thermal treatment. The morphology analysis showed that the surface is smooth, dense and granular. the elementary analysis confirmed the presence of Ni and S with an atomic ratio of 1.05. The XRD analysis confirmed the polycrystalline character of the film with a hexagonal structure oriented along (010) direction. The average crystallites size was found to be 10.5 nm. The optical analysis demonstrated the metallic behavior of the film with an average reflectance of 1.10% in the visible range and a direct optical band gap of 1.03 eV. Furthermore, the film exhibits a very high electrical conductivity of 1.10×10^5 S/cm at room temperature. The above results indicate that the NiS phase prepared in this study is a good candidate as an electrode material for application in supercapacitors.

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