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Metallic behavior of NiS thin film under the structural, optical, electrical and ab initio investigation frameworks

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HIGHLIGHTS

- NiS thin films are synthesized by Spray pyrolysis.
- NiS is a low band gap compound.
- These films have interesting electrical properties showing a metallic behavior.
- Computational study confirms the electrical measurements.

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ABSTRACT

Nickel sulfide (NiS) thin films were deposited on the glass substrates by spray pyrolysis at 250 °C 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. The optical properties, investigated through transmittance and reflectance measurements reveal that the direct band gap energy (Eg) is around 0.55 eV. The electrical study shows a metallic behavior of the current II-VI binary compound.

This behavior regarding NiS II-VI binary sulfide was confirmed by numerical studies based on the density functional theory (DFT) were adopted. The ground state quantities, such as lattice parameter, bulk modulus and its pressure derivative as well as the elastic constants were obtained. The values are consistent with the stability of hexagonal structure. The band structure and the states densities of such material were studied. The results show that there is an agreement between experimental and simulation.

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1. Introduction

Nickel sulfide NiS material belongs to Metal sulfides which have emerged as a new group of promising active compounds for supercapacitors. Recently, the electrodeposited method leading to the synthesis of porous NiS thin films on Ni substrates has been tested as anode for lithium-ion intercalation and showed large capacities and good cycling stability [1]. Later, Xiaoyan Yan et al. [2] have reported the synthesis of porous NiS nanoflake arrays by ion exchange reaction from NiO and their high performance supercapacitor properties.

On the other hand, (NiS) thin films were tested in photovoltaic domain [3]. These films were synthesized as counter electrode (CE) in quantum dot sensitized solar cells (QDSSCs) for polysulfide redox reactions. It has been shown that these films, grown on fluorine-doped tin oxide substrate result in the formation of highly efficient CE for liquid-junction QDSSCs. Under AM1 illumination the QDSSC based NiS CE significantly exhibited conversion efficiency of 2.97%. Likewise, these films grown by electrodeposition process on PVP polymer were tested as frequency switching device that

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generates a frequency of 50 Hz under sun illumination [4]. Moreover, this material was tested in sensitivity applications as a catalyst for photodegradation of furfural by clinoptilolite zeolite incorporated NiS under UV irradiation [5] Nickel sulfide thin films were obtained chemically by many deposition methods [6–9]. The nickel sulfide has interesting magnetic and electrical properties. For temperatures below TN = 265K, NiS behaves as a semiconductor material, whereas for temperatures above TN it has a metallic behavior [10]. The same authors found that the NiS has a paramagnetic → antiferromagnetic transition at the same temperature TN (Neel temperature). During this transition, the structure of NiS does not change but the values of the lattice parameters undergo discontinuities indicating that the transition is first order. There is no change of structure during the transition of the semiconductor antiferromagnetic phase to the paramagnetic metal phase. However a discontinuity in the lattice parameters Komoto and Sparks [10] suggest that the transition is particularly due to the magnetic interaction. Nevertheless, Mott [11] suggests that the presence of a band gap is due to the Hubbard effect before TN. SC → metal transition destroys the magnetic order and antiferromagnetic→ paramagnetic transition at the same time. Recent measures of electrical properties of nickel sulfide are apparently contradictory: Sartale and Lokhande [7] reported that the conductivity of nickel sulfide thin films prepared by « SILAR » method increases with the temperature suggesting a semiconductor character of such material and even suggest activation energy of the order of 0.15 eV. This is not surprising given the fact that the films are very thin (below 100 nm) and it has been proven that some very thin metal films may be semiconductor [12]. Nitesh Kumar et al. [13] claimed that the nickel content is at the origin of the semiconductor or metallic behavior of nickel sulfide thin films; for low temperatures, NiS and Ni3S2 are semiconductors, while NiS2 has a metallic behavior. On the other hand, it is worth noting that NiS material in nano-forms may be of a great interest in possible sensitivity devices. Indeed, Ubale and Bargal [14] reported that nickel sulfide thin films with nanostructured future grown by SILAR process on glass substrates crystallized in the rhombohedral structure phase. They found that these films exhibited p type character. Moreover, noticeable enhancements in both the crystalline quality and the photoconductivity behavior of such films after an appropriate post annealing have been obtained. Also, the same authors [15] synthesized alloys based on the mixture of NiS and CdS for photovoltaic applications. It is found that the band gap as well as the activation energies of annealed $(NiS)_x(CdS)_{(1-x)}$ film decrease with an improvement in photosensitive property.

The purpose of this study is to provide some additional information to the existing data on the physical properties of NiS and compare it with state-of-the-art first-principles calculations.

2. Experiment

2.1. Film preparation

NiS thin films were successfully prepared on 1 × 2 cm^2 glass substrates by spraying an aqueous solution, containing pent hydrate nickel chloride ($NiCl_2$,$5H_2O$,10^{-2} M) and thiourea ($SC(NH_2)_2$, 2×10^{-2} M) as precursors. The Nickel and sulphur concentrations were taken as constants with a concentration ratio of [S]/[Ni] = 3. The substrate temperature was of the order of 250 °C. The solution and gas flow rates were kept at 2 cm^3 min^{-1} and 4 L min^{-1} respectively, corresponding to a mini-spray pyrolysis. Nitrogen was used as the carrier gas to avoid chemisorption of oxygen.

2.2. Characterization techniques

X-ray diffraction spectra were obtained by means of a Philips (PW1429) system, using two CuK_α monochromatic radiations (λ_1 = 1.54050 Å, λ_2 = 1.54438 Å). The optical measurements were carried out in the wavelength range 300–2500 nm, using unpolarized light by means of a spectrophotometer (Perkin Elmer Lambda 950). An integrating sphere coupled to the spectrophotometer was used for these measurements. The conductivity measurements were made by the four points contact method. Finally, the Hall measurements were performed at a magnetic field above 100 mT.

3. Results and discussion

3.1. X-ray diffraction analysis

Fig. 1 shows be seen that NiS sample, prepared at 250 °C, is mainly crystallized in hexagonal phase and characterised by (100), (101), (102) and (110) lines according to JCPDS 89-7141 card. XRD shows also a preferred orientation of the crystallites along (100) direction.

The reticular distance d_{hkl} values of NiS thin films (Table 1) were also calculated using Bragg equation:

$$2d_{hkl}\sin\theta = n\lambda \quad (1)$$

Lattices parameters *a* and *c*, for the hexagonal compact phase, were calculated using the following expression [8]:

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

The calculated values of a and c were found to be 3.441 Å and 5.320 Å, respectively. These calculated values are in agreement with JCPDS standard data (a = 3.439 Å, c = 5.321 Å).

Moreover, the texture coefficient (TC), which indicates the maximum preferred orientation of the films along the diffraction plane, means that the increase in the preferred orientation is associated with the increase of the number of grains along that plane. $TC_{(h\ k\ l)}$ values were calculated from X-ray data using the

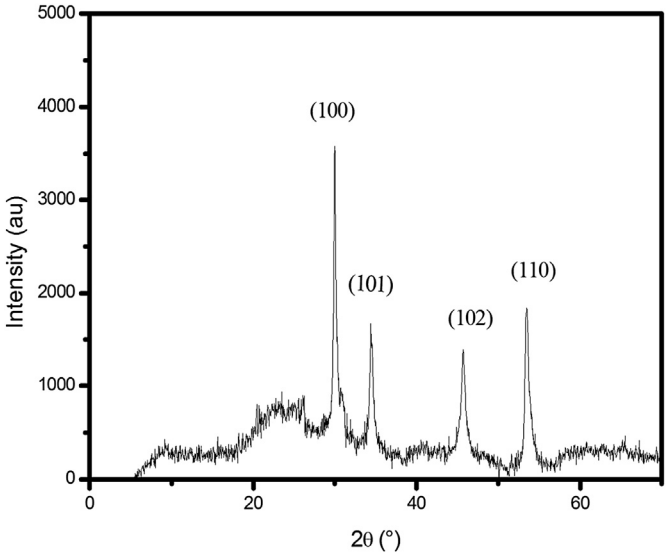

Fig. 1. XRD diagrams of NiS thin films.

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