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Electrical, Optical, Structural and Morphological Properties of NiS Films

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Abstract

The electrical, optical, structural and morphological properties of NiS films are less studied than other materials such as CdS, CdTe, ZnS, ZnO, CdO etc. Our aim in this work is to deposit NiS films, examine some of their physical properties and investigate their suitability for photovoltaic devices. NiS films were deposited onto glass substrates at a substrate temperature of 300 ± 5 °C using the ultrasonic spray pyrolysis (USP) technique. The variations of temperature-dependent conductivity under the conditions of light and dark were investigated and it was seen that illumination reduces conductivity. The activation energy for the doped region and the energy-gap for the intrinsic region were found as 6.79 meV and 0.90 eV, respectively. The resistivity was measured via two-probe method as 6.89×10^6 ohm·cm in the voltage range 1−10 V. The crystal structures were investigated by x-ray diffraction (XRD) and it was determined that the crystalline nature was not well-developed and was close to amorphous structure. The surface morphology was examined by scanning electron microscopy (SEM), with the observations that the film surfaces were not completely homogeneous. The elemental analyses were also studied by energy dispersive x-ray spectroscopy (EDS).

Key Words: USP technique, NiS films, Electrical and Optical Properties, Crystal Structures, Surface morphologies.

1. Introduction

NiS is a transition metal compound and an interesting material, showing metal-insulator transition by doping or as a function of temperature and pressure. NiS compound shows antiferromagnetic semiconductor and paramagnetic properties in low and high temperature phases, respectively. The metal-nonmetal phase transitions in NiS have long been studied, but the transition mechanisms have not yet been absolutely understood [1, 2]. The optical spectra of NiS have been observed in IR and it was determined that at low temperature (below ~260 K) they are p-type and narrow band gap semiconductors with an energy gap of 0.15 eV [1]. NiS films have been used as catalysts and coatings in photovoltaic cells [3]. Catalysts have broad application in the oil industry, for the separation of sulphur and nitrogen that often coexists with hydro-compounds from insulators [4]. NiS is used as a holder in hydro-process catalysts. In pure nickel sulphide production, NiS and Ni_3S_2 form as co-phases [5]. Today, glass coatings are frequently put on the surfaces of glass panels used in modern buildings. In most cases, these glass panels are thermally hardened for security and durability. If there are NiS phases in the glass, these hardened glasses may more easily crack under stretch, as caused by the phase transition of the NiS from hexagonal structure to rhombohedral [6]. Thus work on NiS is increasing day by day due to its involvement in the cracking process of glass panels [7]. NiS heat analyses have been used with plasma-mass spectroscopy to determine the platinum group elements in geological materials. This determination process is rather fast and sensitive [8, 9, 10]. There are a few works on the growth, and especially, electrical properties of NiS films in the literature. Our purpose in this work is to obtain NiS films using USP technique and to investigate their electrical, optical, structural and surface properties. We will investigate whether these films can be used in IR detectors.

2. Experimental Details

NiS films were deposited onto glass substrates 10 × 10 mm^2 at 300 ± 5 °C substrate temperature using USP technique. 0.05 M $NiCl_2$ (>95% pure) and 0.05 M $CS(NH_2)_2$ (98% pure) were used as spraying solutions. The substrate temperature was measured using an iron-constantan thermocouple. During the spraying process the substrates were heated by an electrical heater. The solution flow rate was measured with a flowmeter and it was held constant at 5 cc·min^{-1}. Compressed purified air was used as the carrier gas (1.5 bars). The thickness of the films were measured as 3.83 μm using an Elcometer 345 Digital Coating Thickness Gauge. The electrical contacts were made through gold electrodes of thickness about 650 nm on the surface of the films using vacuum evaporation technique.

To extract information about the current transport mechanisms, the current as a function of temperature and current-voltage (I-V) relationship were investigated. Current as a function of temperature was studied over temperatures T = 130−420 K in dark, and 85−405 K under the illumination of a red LED (at 10^{17} phot/cm^2). The current was measured with a Keithley 619 Electrometer and a Hewlett Packard 34401A multimeter. The I-V relationship was measured using a HP 4140B pA meter and DC voltage source. The I-V relationship was measured in dark over the voltage range 0.01−100 V. In addition, using the two-probe technique, the I-V characteristics of the NiS film was examined in the voltage range 1−10 V under dark, to calculate films' resistivity.

NiS film volume was characterized by XRD via a Rigaku x-ray diffractometer, using 1.5405 Å CuK_α radiation. The surface morphologies of the films were investigated using a Jeol JSM-5600 LV SEM and a CamScan scanning electron microscope. The microanalyses were made by the Noran Voyager EDS 3050.

3. Results and Discussion

Current as a function of temperature in NiS films were measured in dark and light in the temperature ranges 130−420 K and 85−405 K, respectively, from which conductivity as a function of temperature $\sigma \sim$T was calculated and is plotted in Figure 1. It was determined from these plots that there is no noticeable increase in conductivity values up to about 370 K in dark and 350 K in light, after which there is a sharp increase. When the conductivity values of the films in dark and light are compared, it was seen that the dark conductivity is larger than the conductivity in light. So, we can say that illumination has a negative effect on the conductivity of NiS films. When the effects of heat and light are applied simultaneously, the effect of heat is more dominant on the ionization of donor atoms and donor-like traps, with light producing an undesired effect. Photoconductivity ($\Delta\sigma = \sigma_{\text{light}}$- σ_{dark}) and photosensitivity ($\Delta\sigma$ / σ_{dark}) [11] values of NiS films were also calculated to access information about its sensitivity to light. The ratio $\Delta\sigma/\sigma_d$ can exhibit three possibilities:

$\Delta\sigma/\sigma_d < 0$ for $\sigma_{\text{light}} < \sigma_{\text{dark}}$(negative sensitivity to light)

$\Delta\sigma/\sigma_d = 0$ for $\sigma_{\text{light}}\sigma_{\text{dark}}$(insensitivity to light)

$\Delta\sigma/\sigma_d > 0$ for $\sigma_{\text{light}} > \sigma_{\text{dark}}$(sensitivity to light)

Table 1 gives us the conductivity in dark and light, photoconductivity $\Delta\sigma$ and photosensitivity $\Delta\sigma/\sigma_{\text{dark}}$ values for various temperatures. It is clear from this table that NiS films are negatively effected by light.

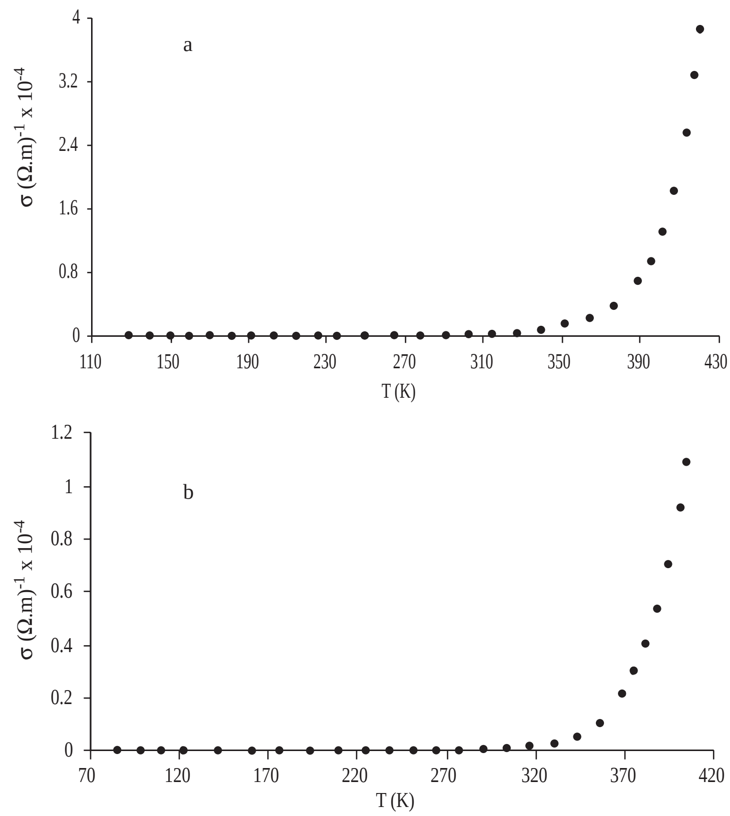


Figure 1. σ(T) plots of NiS films **(a)** in dark and **(b)** in light.

Table 1. Temperature-dependent conductivity values of NiS films.

Temperature (K)	σ_{dark} $(\Omega\cdot\text{m})^{-1}$	σ_{light} $(\Omega\cdot\text{m})^{-1}$	$\Delta\sigma$ $(\Omega\cdot\text{m})^{-1}$	$\Delta\sigma/\sigma_{\text{dark}}$ Values
406	1.81×10^{-4}	1.09×10^{-4}	-0.72×10^{-4}	-0.40
402	1.31×10^{-4}	0.96×10^{-4}	-0.35×10^{-4}	-0.27
395	9.37×10^{-5}	7.00×10^{-5}	-2.37×10^{-5}	-0.25
358	1.66×10^{-5}	1.05×10^{-5}	-0.61×10^{-5}	-0.37
345	9.81×10^{-6}	5.13×10^{-6}	-4.68×10^{-6}	-0.48
316	1.95×10^{-6}	1.30×10^{-6}	-0.65×10^{-6}	-0.33
297	7.44×10^{-7}	4.67×10^{-7}	-2.77×10^{-7}	-0.37
278	2.49×10^{-7}	1.67×10^{-7}	-0.82×10^{-7}	-0.33
257	6.91×10^{-8}	6.07×10^{-8}	-0.84×10^{-8}	-0.12
193	2.42×10^{-8}	1.53×10^{-8}	-0.89×10^{-8}	-0.37
131	1.72×10^{-8}	1.58×10^{-8}	-0.14×10^{-8}	-0.08

A plot of lnσ vs. 10^3/T for graph of NiS films in dark over the temperature range 130−420 K is shown in Figure 2. Note the presence of two distinct regions which separate at about 235 K; above 235 K is the intrinsic region, and below 235 K is the doped region. This is consistent with NiS being a narrow band-gap material. The conductivity slowly increased with increasing temperature in the doped region, and sharply in the intrinsic region. The slopes of these two regions were calculated and the activation energy in the doped region and energy-gap of NiS films in the intrinsic region were found as 6.79 meV and 0.90 eV, respectively. The energy gap value of NiS does not comply with those values reported in the literature. When the XRD pattern in Figure 4. is examined, it can be seen that NiS films exhibit Ni_7S_6 and Ni_3S_4 phases. We think that the source of the disagreement in energy gap is the variation of phases formed in the deposited films.

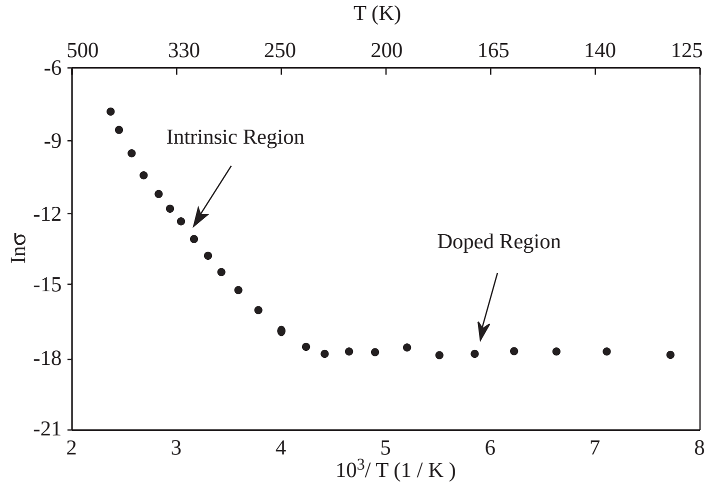


Figure 2. Graph of logarithmic conductivity vs. inverse temperature ($\ln\sigma(1/T)$) of NiS films in dark.

The I-V characteristic of NiS films is shown in Figure 3. It was determined from this plot that current changes linearly with increasing voltage in the 0.01−100 V voltage range where ohmic conduction is dominant. The resistivity of NiS films was found to be 6.89×10^6 Ω·cm in the voltage range 1−10 V as measured via the two-probe technique. Using the hot-probe method, the electrical conductivity was found to be n-type, in contradiction to the p-type reported in the literature [1]. However, it is known that materials like ZnSe and SnS show both n-type and p-type conductivities. Our results show that NiS exhibits the same dual nature.

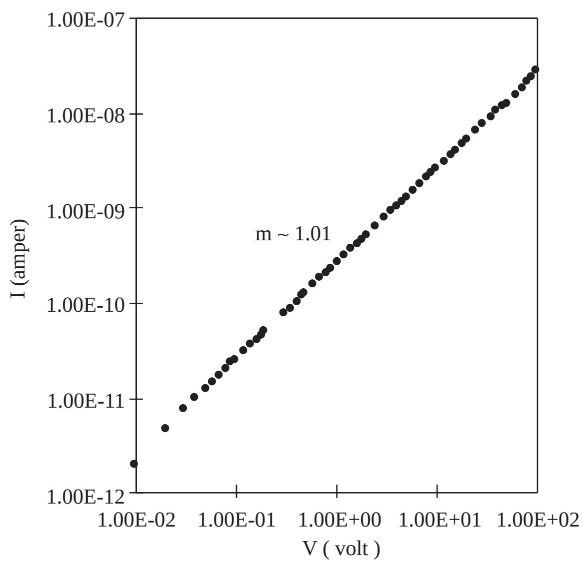


Figure 3. The I-V characteristic of NiS films under dark.

The XRD pattern and the values related to the peaks on this pattern are given in Figure 4. and Table 2, respectively. It was determined that the preferential orientation of the films is (222), with the most intense peak at $2\theta = 29.10°$. The other peaks seen on the XRD scan have low intensities and wide half-peak widths. Also, the crystallinity level of the NiS films is not good and close to amorphous structure. Half-peak widths and grain diameters for the preferential orientations of NiS films were calculated using the expression

$$B = \frac{0.9\lambda}{tCos\theta},$$

where B is the half peak width of the peak with maximum intensity, t is the grain diameter, θ is the Bragg angle and λ is the wavelength of light used for illumination [12, 13, 14]. The following parameters were calculated for NiS films: lattice parameters $a = 11.113$ Å, $b = 9.372$ Å and $c = 13.483$ Å; unit cell volume as 1396.327 Å^3; half-peak width $B = 6.507 \times 10^{-3}$ radian; and grain size $t = 220$ Å.

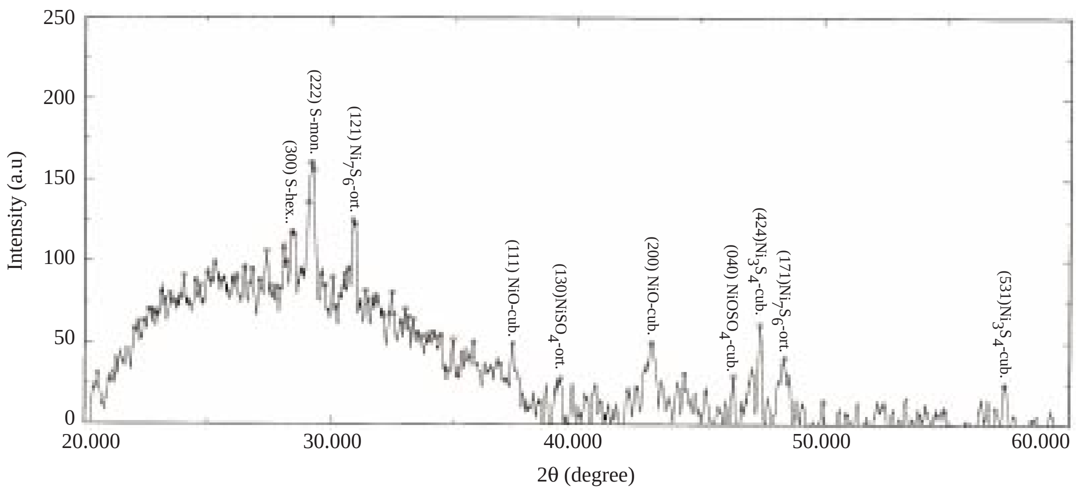


Figure 4. The XRD pattern of NiS films.

Table 2. The values related to the peaks on XRD pattern of NiS films.

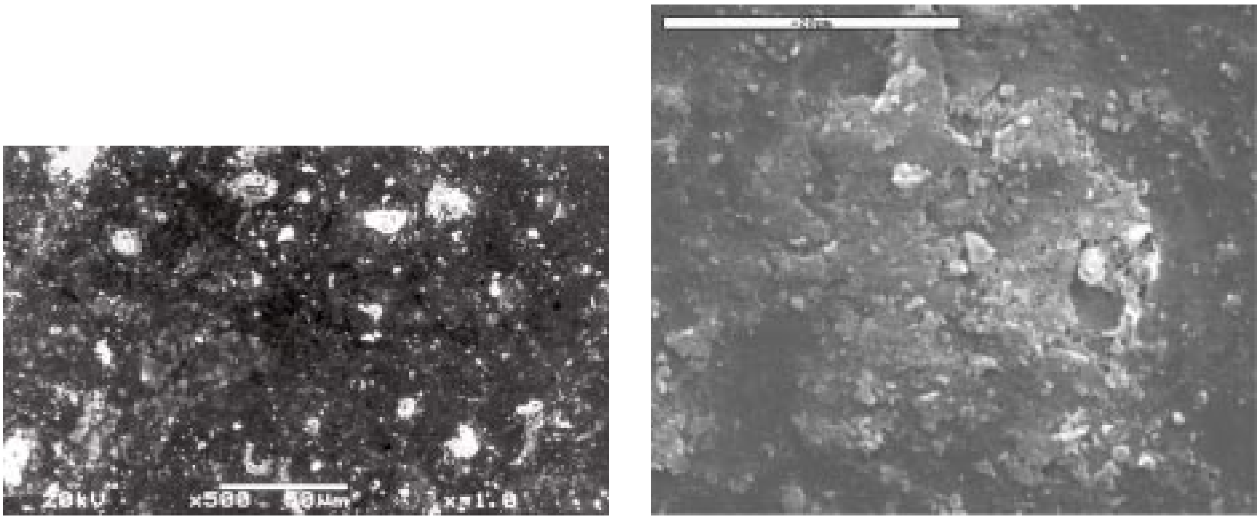
2θ	d (Å)	(hkl)	Crystal Structure	I / I_o Ratio
28.40	3.1401	(300)	Hexagonal S	73
29.10	3.0661	(222)	Monoclinic S	100
30.70	2.9099	(121)	Orthorombic Ni_7S_6	59
37.38	2.4038	(111)	Cubic NiO	31
39.32	2.2895	(130)	Orthorombic $NiSO_4$	18
42.98	2.1026	(200)	Cubic NiO	31
46.34	1.9577	(040)	Orthorombic $NiSO_4$	19
47.42	1.9156	(422)	Cubic Ni_3S_4	38
48.40	1.8791	(171)	Orthorombic Ni_7S_6	25
57.34	1.6055	(531)	Cubic Ni_3S_4	15

Figures 5a and 5b show typical SEM micrographs of the NiS films. Note in Figure 5a there are bright regions randomly distributed in different sizes on the film surface. Figure 5b shows a micrograph taken from this bright region. It can be more clearly seen that the surface of the film is not homogeneous. We think that the USP technique used to produce the films or the chemical reaction on glass substrates during the growth process of the film, caused this undesired formation.

The EDS microanalysis results are given in Table 3. These results show that Ni and S elements in the starting spray solution exist in solid films. But, when we look at the elemental weights, Ni element is more dominant in the solid films. This situation shows that the films are not formed in NiS phase, consistent with XRD results.

Table 3. The EDS microanalyses results of NiS films.

Element	ZAF	Atom %	Elemental Weight %	Weight % Error
Ni-K	1.014	84.60	90.96	±9.96
S-K	1.479	15.40	9.04	±2.36
Total	-	100.00	100.00	-



(a) (b)

Figure 5. SEM micrographs of NiS films (a) × 500 (b) × 3000.

4. Conclusions

In this work, NiS films were produced by USP technique at a substrate temperature of 300 ± 5 °C and some of their physical properties were investigated. The results of temperature-dependent conductivity in the overall temperature range, under dark and light conditions, were presented and it was seen that NiS films are not photoconductive materials. It was inferred from the results that the effect of heat plays a dominant role in the ionization of donor atoms and donor-like traps when heat and light effects are applied simultaneously. Also, it was found that NiS films have an activation energy on the order of meV in dark and an energy gap of 0.90 eV. The conductivity mechanisms of the films were examined as a function of the applied voltage and they were found to have ohmic conduction mechanisms. The resistivity of NiS films under dark were high, an undesired result for dedectors and optoelectronic devices. We think that less resistive films may possibly be obtained by annealing in H_2, N_2 or metal atmospheres. The XRD patterns showed that the films are polycrystals. The crystalline nature of the films were not well-developed. SEM micrographs of NiS films were also examined. It was seen that there are islands with different sizes and colors randomly distributed on the surfaces. We think that small grain size caused the surface roughening to increase. It is also responsible for the spoiled crystalline nature. Because, the smaller the grain size, the more the grain number and grain boundaries. These form the surface defects that effects the structural and morphological properties of the films. EDS microanalyses showed that Ni and S elements are present in solid films, as hoped. As a result, NiS films can be used in IR dedectors because of their suitable band gaps. In future works, we will investigate the effect of different parameters such as substrate temperature, flow rate, and molarity to produce high quality films for IR applications.

Acknowledgments

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