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Growth and characterization of bimetallic (Ni,Co) sulfide thin films deposited by spray pyrolysis

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In this work, the bimetallic (Ni,Co) sulfide film of 852.213 nm thickness was successfully deposited using the spray pyrolysis technique at 300 °C. The compound was prepared with a mixture of nickel acetate ($C_4H_6O_4Ni.\ 4H_2O$), cobalt chloride ($CoCl_2.\ 6H_2O$), and thiourea ($CS(NH_2)_2$) as precursors for Ni, Co, and S, respectively. The temperature and sedimentation time were 300 °C and 10 min, respectively; the film was then, characterized without any thermal post-treatment. The structural, morphological, optical and electrical analysis were carried out to investigate the different properties of the material. The X-ray diffraction analysis confirmed the presence of $NiCo_2S_4$ according to the JCPDS Card # 98-004-0019, with an average crystallite size of 34.45 nm. The optical analysis revealed the metallic behavior of the film with an average transmittance of 3.41% in the visible region and a direct optical band gap of 2.15 eV, as well as a high absorption coefficient of $\alpha \approx 10^4 - 10^5\ cm^{-1}$). The elementary composition analysis (EDS) confirmed the presence of Ni, Co and S elements in the film. Morphological analysis revealed a homogeneous, compact, crack-free appearance and a granular surface in all studied areas. On the other hand, the film shows a high electrical conductivity of about 1.42×10^5 S/cm at room temperature. The obtained results show that the bimetallic (Ni, Co) sulfide prepared in this study exhibits a good crystallinity, dense morphology, good stoichiometric ratio and high conductivity. Therefore, it is a potential candidate for application in supercapacitors as electrode material.

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Keywords: Nimetallic (Ni,Co) sulfide, XRD, Spray pyrolysis, Conductivity, MEB & EDS.

1. Introduction

Nanostructured transition metal chalcogenides are considered promising alternatives to precious metal electrocatalysts for energy conversion and storage. The sustainable electro-chemical energy conversion and storage has attracted great interest among researchers, given the degradation of the global environment and the rapid increase in energy consumption [1,2]. Particularly, transition metal sulfides have been widely studied for their remarkable properties and promising applications in photovoltaics, electronics and optoelectronics, such as solar cells, sensors, lithium-ion batteries, fuel cells and thermoelectric devices [3,4]. The sulphur element in this compound acts as a stress-reducing agent in the lattice [5]. On the other hand, the cobalt sulfide (CoS) is investigated as a cathode electrode in lithium-ion batteries with low overpotential, good life, high shock resistance and durability [6]. Further-more, the nickel sulfide (NiS) is

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considered a versatile and multifaceted material, which can be used as cathode/or anode for this type of batteries [7]. NiS is used in numerous applications as a metallic insulator, paramagnetic-antiferromagnetic phase change material, hydrogenation catalyst and solar batteries [8]. The nickel and cobalt ternary sulfide is investigated as a new electrode material for supercapacitors, with improved physical and electrochemical performance. These ternary sulfides are considered as promising class of electrode materials for use in high-performance energy storage devices due to their superior electrochemical activity and capacity [9]. For the first time, Xiao et al. prepared NiCo2S4 nanotube arrays on flexible carbon paper for supercapacitors. The study has reported that exceptional electro-chemical performance was achieved due to the distinctive nanoarchitecture and intrinsically high electrical conductivity of $NiCo_2S_4$ [10]. The growth of metal chalcogenide thin films by chemical precipitation from solutions or by chemical growth processes are currently one of the main methods, with the advantages of cost effectiveness, convenience, ease of extension over a large area and a high degree of direct control [11,12]. The present study focuses on the synthesis and characterization of the structural, optical, morphological and electrical properties of the bimetallic (Ni,Co) sulfide thin film by spray pyrolysis.

2. Experimental details

2.1. Preparation of bimetallic (Ni,Co) sulfide

The precursor solution consisted of nickel acetate (($C_4H_6O_4Ni.4H_2O$); $7x10^{-2}$ mol/l), cobalt chloride (($Cocl_2.6H_2O$); $7x10^{-2}$ mol/l) and thiourea ($CS(NH_2)_2$; $21x10^{-1}$mol/l) dissolved in 100 ml of bidistilled water. A few drops of acetic acid were then, added to dissolve the solution completely. Prior to deposition, the substrate temperature was set at 300 ± 5 °C and compressed air was used as a carrier gas to generate the aerosol particles. The flow rate was maintained at 0.5 bar. The distance between the nebulizer and the substrate was set at 30 cm. After deposition, the film was slowly cooled to room temperature in ambient air and characterized without post-heat treatment.

2.2. Characterization techniques

Structural analysis was performed with an X-ray diffract meter (XRD; Mini Flex-Rigaku) in the range 25-65 ° with Cu-Kα radiation (λ = 1.5418 Å), using the Brentano-Bragg geometry. The surface morphology was analyzed using a scanning electron microscope (SEM; Qanta 350) equipped with an energy dispersive spectrometer (EDS) for elemental analysis. Transmittance and absorbance were measured using a dual-beam UV-visible spectrophotometer (UV-3101; Shimadzu) in the wavelength range of 300 - 900 nm with a step of 5 nm. An infrared transmission spectrometer (FTIR; Shimadzu, model IR Affinity-1) was used to determine the type of chemical bonding present in the sample in the range of 400 - 4000 cm^{-1}, and film conductivity were measured by the four-point technique.

3. Results and discussion

3.1. X-Ray diffraction

The X-ray diffraction pattern of the prepared bimetallic (Ni,Co) sulfide is shown in Figure 1. The peaks recorded at 2θ = 31.47˚ and 62.01˚ are assigned to the plans (113) and (026) of cubic $NiCo_2S_4$ according to the JCPDS card #98-004-0019. The diffraction pattern with very well resolved peaks corresponds to a highly crystalline compound. In addition, the peak at 2θ = 55.36˚ is ascribed to the plan (044) of Co_3S_4 phase (JCPDS card #98-005-6125). On the other hand, the peaks at 2θ = 29.92˚ and 53.51˚ correspond to (010) and (110) of NiS phase (JCPDS Card: 98-064-6340). These secondary phases are present in the film with low intensity when compared to those of $NiCo_2S_4$, which is the dominant phase. These results show that it is difficult to prepare a pure phase of $NiCo_2S_4$ phase using spray technique, due to the nature of the process of deposition, which is thermal decomposition and oxidation.

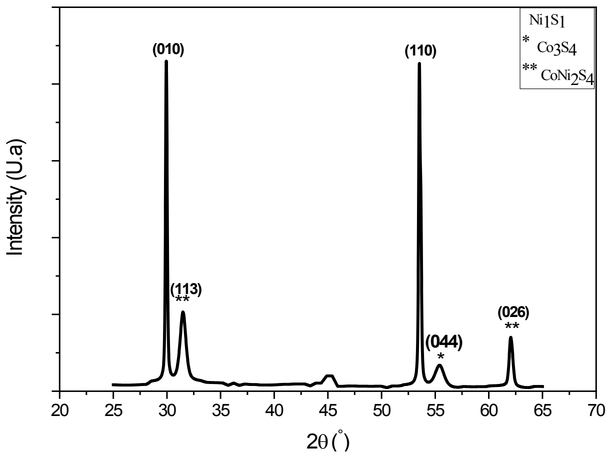


Fig. 1. X-ray pattern of bimetallic (Ni,Co) sulfide thin films.

The inter-plan distance (d_{hkl}) was calculated using Bragg's formula [13].

$$2d_{hkl}sin\theta = n\lambda \tag{1}$$

The texture coefficient (TC_{hkl}) provides information about the probability of growth as a function of the orientation [hkl]. It is given by the formula [14]:

$$TC_{hkl} = \frac{I_{hkl}/I_{0hkl}}{N^{-1}\left[\sum_{i=1}^{n}\frac{I_{hkl}}{I_{0hkl}}\right]} \tag{2}$$

where: I_{0hkl} is the intensity according to the JCPDS card of the plan (hkl) and N is the number of diffraction peaks.

Debye's formula [15] is used to estimate the crystallite size (D) for all diffraction peaks:

$$D = \frac{k \times l}{\beta_{1/2}\cos\theta} \tag{3}$$

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 λ= 1.5406 Å is the wavelength of the X-ray radiation used.

The residual stress (ε_{hkl}) and the dislocation density (δ_{hkl}) in the layer were evaluated using the following formulae [16]:

$$\varepsilon_{hkl} = \frac{\beta_{\frac{1}{2}}}{4\tan\theta} \tag{4}$$

$$\delta_{hkl} = \frac{1}{D_{hkl}^{2}} \tag{5}$$

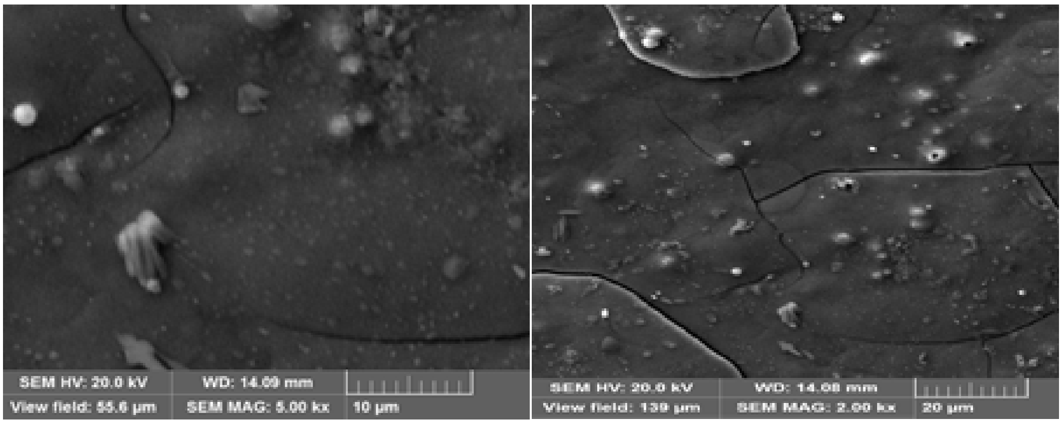
In addition, the average crystallites size ⟨D⟩, micro-stress ⟨ε⟩ and dislocation density ⟨δ⟩ can be determined using the following formulas [17]:

$$\begin{cases} \langle D \rangle = \dfrac{\sum TC_{hkl} \times D_{hkl}}{n} & (6) \\[2ex] \langle \varepsilon \rangle = \dfrac{\sum TC_{hkl} \times \varepsilon_{hkl}}{n} & (7) \\[2ex] \langle \delta \rangle = \dfrac{\sum TC_{hkl} \times \delta_{hkl}}{\sum TC_{hkl}} & (8) \end{cases}$$

The average values of the crystallite size, micro-density and dislocation density are 34.45 nm, 4.745×10^{-3} and 3.122×10^{15} (lines/nm²), respectively. The values obtained correspond to a high-quality thin film.

3.2. SEM and EDS analysis

The morphology of the bimetallic sulfide prepared was examined by a scanning electron microscope (SEM). Figure 2 (a) and (b) show the surface morphology recorded with different scales: 10 µm and 20 µm, respectively. It is observed that the surface of the film is smooth, uniform, firmly bonded to the substrate, porous and granular. Therefore, a greater surface area to volume ratio and therefore a greater specific surface area is achieved.



(a) *(b)*

Fig. 2. SEM image of bimetallic (Ni, Co) sulfide thin film at (a)10 µm and (b) 20 µm.

The elementary analysis (EDS) micrographs of the film (Fig. 3) confirmed the presence of Ni, Co and S elements. In addition, the analysis showed the presence of other elements such as oxygen (O) and silicon (Si), which originate from the SiO_2 glass substrate. The presence of carbon C is possibly due to the thiourea ($SC(NH_2)_2$) used in the synthesis.

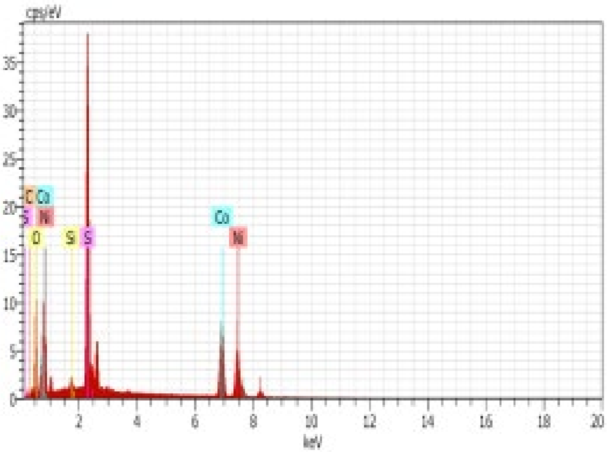


Fig. 3. EDS spectrum of bimetallic (Ni,Co) sulfide thin films.

3.3. FTIR analysis

Figure 4 shows the infrared transmission spectra of bimetallic (Ni,Co) sulfide. The peak at 559,36 cm^{-1} is attributed to Ni-S stretching vibration [18-21]. The bands near at 655,80 and 790,81 cm^{-1} are attributed to C-S bonding vibrations [19, 20, 22] and the band at 983,70 cm^{-1} is due to C=O stretching vibration of adsorbed CO_2 from ambient atmosphere [23]. The bands observed at 1126,43 and 1427,32 cm^{-1} were attributed to C-H bonding vibrations [18,23,24]. The absorption bands at 1631,78 and 3425,58 cm^{-1} corresponded to O-H bonding vibrations, indicating the presence of absorbed H_2O [25]. Therefore, the spectra depicted all the characteristic band of $NiCo_2S_4$ sulfide.

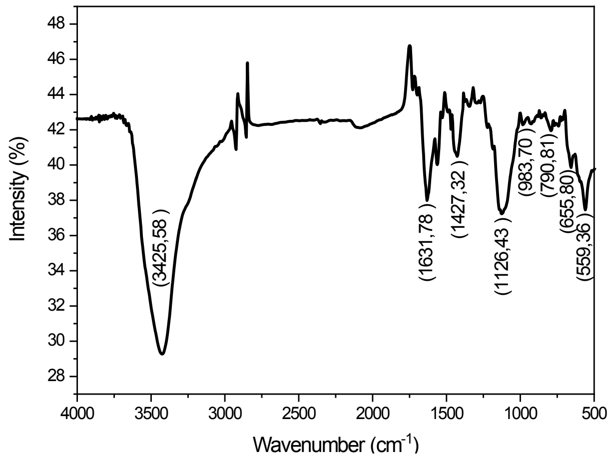


Fig. 4. FTIR images of bimetallic (Ni,Co) sulfide thin film.

3.3. Optical properties

Fig. 5 shows the transmission spectra of bimetallic (Ni, Co) sulfide recorded at room temperature. It can be seen that the optical transmittance decreases in the ultraviolet range. How-ever, above 400 nm there is an improvement in the transparency of the film, which can be attributed to a reduced scattering effect and lower propagation losses. The average optical transmittance is 3.41 %. Furthermore, the absence of interference fringes in the long wave-length range is mainly due to the roughness of the film.

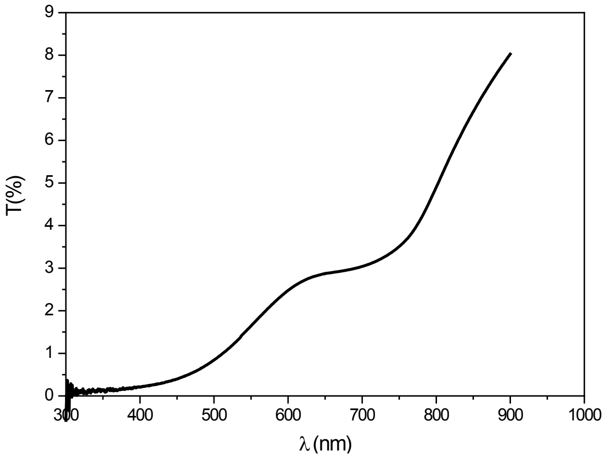


Fig. 5. UV-visible transmittance spectra of bimetallic (Ni,Co) sulfide thin film.

In this type of compound, the low optical transmittance of the film is due to a high reflectance. This phenomenon can be related to the plasma oscillation of the free charge carriers, which shows the metallic behaviour of the film [17]. The absorption coefficient (α) was calculated from the transmission spectrum according to the following formula [26]:

$$\alpha = \frac{1}{e} ln\left(\frac{1}{T}\right) \tag{9}$$

where: e is thickness, R is reflectance and T is transmittance. The average absorption coefficient is 6.99×10^4 cm^{-1}, which is of the same order of magnitude as for semiconductor reflective thin films and is close to the values reported in the literature [27].

The optical band gap of the material was determined using Tauc formula [28]:

$$(\alpha h\nu)^2 = A(h\nu - E_g) \tag{10}$$

where: B is a constant, p is an integer that takes the value 1/2 or 2 for direct or indirect transitions, respectively. Fig. 6 shows the plot of $(\alpha h\nu)^2$ versus energy (hν).

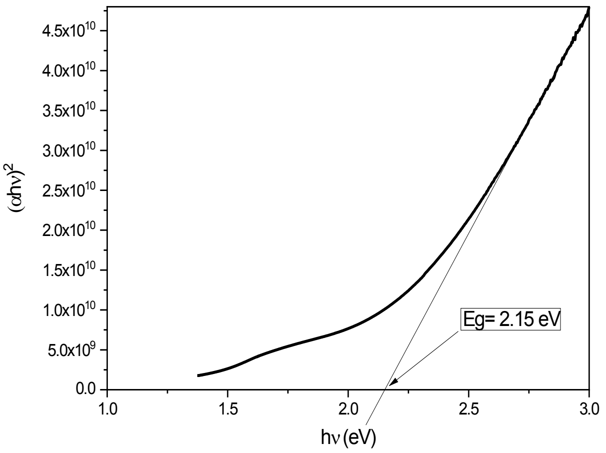


Fig. 6. Plots of $(\alpha h\nu)^2$ versus photon energy (hν) of bimetallic (Ni, Co) sulfide thin film.

The linear extrapolation of the curve gives an intersection with the abscissa axis, which corresponds to the optical transition energy. The optical gap of the film was determined to be 2.15 eV and agrees well with the values given in the literature [27].

3.4. Electrical properties

The electrical conductivity of the bimetallic (Ni. Co) sulfide was determined by four-point probe method based on the measured sheet resistance of the films and expressed by the following formula [29]:

$$\begin{cases} R_{sh} = \frac{\pi}{ln2} \times \frac{V}{I} & (11) \\ \sigma = \frac{1}{\rho} = \frac{1}{e \times R_{sh}} & (12) \end{cases}$$

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 1 shows the results of the electrical measurements.

Table. 1. Electrical parameters of bimetallic (Ni,Co) sulfide.

Thin film	bimetallic (Ni,Co) sulfide
Film thickness e (nm)	852.213
Sheet resistance R_{sh} (Ω/sq)	8.28×10^{-2}
Electrical resistivity ρ $(\Omega.cm)^{-1}$	7.06×10^{-6}
Electrical conductivity σ (S/cm)	$1.42\times10^{+5}$

It is observed that the film has a very high electrical conductivity of 1.42×10^{5} (S/cm). This confirms the metallic behavior of the prepared bimetallic (Ni. Co) sulfide. In addition, these results are close to the data reported in the literature [30, 31]. Hence, the bimetallic (Ni. Co) sulfide prepared in this study is very attractive as an electrode material for use in supercapacitors.

4. Conclusion

In the present study, we have successfully deposited the bimetallic (Ni,Co) sulfide at 300 °C using the spray pyrolysis technique. The film was then characterized without any post thermal treatment. The film was characterized by UV-Visible, FTIR, XRD and SEM and EDS analysis. The XRD results showed that the material exhibited a good crystallinity. The esti-mated average particle size was 34.4 nm. Morphological analysis showed that the surface was smooth, dense and granular. Elemental analysis confirmed the presence of Ni, Co and S elements in the sample. The optical analysis showed that the film has an average transmit-tance of 3.41 % in the visible region and a direct optical bandgap of 2.15 eV. On the other hand, the film shows a very high electrical conductivity of 1.42×10^{5} S/cm at room temperature. From the above results, it can be concluded that the compound prepared in the present study can be used as an electrode material for high-performance energy storage devices and in supercapacitors.

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