Electrosynthesized NiS₂ thin films and their optical and semiconductor studies

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Abstract: Nickel sulfide thin films were prepared using electrodeposition on indium tin oxide-coated glass substrates. Films were characterized using X-ray diffraction for crystallographic analysis. The films were shown to be polycrystalline in nature with good uniformity. From scanning electron micrographs, the surface appeared to be comparatively granular with irregularly shaped grains. From optical analysis, the bandgap range was between 1.22 eV and 1.15 eV with an indirect bandgap nature. Mott-Schottky plot confirmed that the films were found to be n-type, and the semiconductor parameters of the film were derived.

Keywords: X-ray diffraction, scanning electron micrograph, optical studies, Mott-Schottky analysis

Introduction

Photoelectrochemical cells produce a usable electric current, obtaining energy in the form of photons. These cells are found to be grouped together in a series to form the modern solar panel/array. They are generally placed under glass or polymer/plastic for protection from the weather. When they are connected in a series, a lot more electricity is generated, which is a current topic of interest for researchers.¹ The majority of solar cells fabricated to date have been based on silicon, either in a monocrystalline or a large-grained polycrystalline form. The two main reasons for using silicon are, first, that it is an elemental semiconductor with good stability and a well-balanced set of electronic, physical, and chemical properties, which make silicon the preferred material for microelectronics, especially solar energy-based materials; and, second, that silicon use in the electronics industry has increased its commercial value in the photoelectrochemical industry.²

The current material used in solar panels, crystalline silicon, is more expensive and involves a complicated design and alignment.³ Cost reduction becomes a fundamental issue that can be solved by both focusing on the new alternative materials for silicon and simplifying the manufacturing process.⁴ The main concern for electrochemical solar cell technology is to find novel materials that have appropriate properties for electrochemical energy conversion.¹ A study at the Lawrence Berkeley National Laboratory, Berkeley, CA, USA, was performed to determine new materials for solar panels in terms of both performance and affordable cost.⁵

Transition metal chalcogenides have received considerable attention because of their tunable properties. These materials, in thin-film form, are often important candidates for photovoltaic conversion. This is due to a matchable bandgap of 1–3 eV

with solar spectrum, high optical absorption bandgap, and better electrical conductivity. Similarly, they show interesting electric and magnetic properties.⁶ Metal chalcogenide compounds, having a semiconductor nature, are of considerable technical interest in the field of electronics and electro-optical devices.⁷

Any solid or liquid system possesses, at most, a two-dimensional order of periodicity called “thin film.” Properties of thin films often differ significantly from those of bulk, due to surface and interface effects, which may dominate the overall behavior of these films. Thin films can be fabricated by electrodeposition technique – a well-known chemical method.⁷ The preparation of transition metal chalcogenide thin films by electrodeposition method is currently attracting considerable attention, as it is relatively inexpensive, simple, and convenient for large area preparations.⁸ Other preparation techniques, such as sputtering, vacuum evaporation, molecular beam epitaxy, and thermal spray, involve more complicated synthesis procedures, with expensive setup needed to prepare these films. Electrodeposition is an electrochemical liquid phase thin-film and/or powder preparation method where the reactions, either reduction or oxidation, are accomplished using an external current source. The deposition is carried out in an electrochemical cell consisting of a reaction vessel and two or three electrodes.^{9,10} The only drawback of the electrodeposition technique is that ions released through chemical reaction vary after a few depositions if the same solution is used. Nickel selenide thin films have already been shown to be a promising material for solar cell applications in our previous work.¹¹ This present research focuses on the material properties of nickel sulfide, with systematic study of their deposition parameters and suitability for being photoelectrochemical solar cells.

Experimental procedures

Solution preparation

In a typical synthesis of NiS_2 , the original molar ratio between $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ was selected to be 1:3. $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (0.28 g, 0.001 M) was dissolved in deionized water (30 mL). The chelating agent, triethanolamine (12 mL $\approx$ 0.003 M), was added to the solution. NaOH (1.0 g, 0.025 M) was added to keep the pH value at about 10. After mixing for 5 minutes under stirring, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (0.78 g, 0.003 M) was added to the mixture, and the system finally formed a blue, transparent solution. Then, the beaker was placed on a hot plate/stirring machine at a temperature of $40^\circ\text{C} \pm 1^\circ\text{C}$ for 30 minutes. The main purpose of the deposition temperature being maintained at 40°C is to

avoid any precipitates forming during the electrodeposition process, which may lead to nonstoichiometric films. The electrodeposition of the nickel sulfide thin films was carried out using a Princeton Applied Research Model VersaSTAT 3 potentiostat (Princeton Applied Research, Oak Ridge, TN, USA). The X-ray diffractogram (XRD) of the thin films was obtained on a PANalytical XPERT PROMPD PW 3040/60 diffractometer (PANalytical BV, Lelyweg, the Netherlands) using monochromatic $\text{CuK}\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$) in the range of 2θ angles from 10° to 90° . The scanning electron microscope (SEM) studies were conducted on a JSM 6400 JEOL SEM (JEOL, Tokyo, Japan). The optical absorption spectrum studies were carried out in the wavelength range 200–1,100 nm at room temperature using a Shimadzu 1700 UV-Vis spectrophotometer (Shimadzu Corporation, Kyoto, Japan). An EDUTECH EDU 9100B LCR7 bridge with an inbuilt function generator with a frequency of 1 kHz was used for the measurement of space-charge capacitance to obtain Mott-Schottky plots.

Results and discussion

Cyclic voltammetry studies

The electrodeposition of the nickel sulfide thin films was carried out using a Princeton Applied Research Model VersaSTAT 3 potentiostat. The deposition potential of nickel sulfide thin films was first derived from a cyclic voltammetry technique, followed by synthesis of the chalcogenides by the electrodeposition technique.

Figure 1 shows the cyclic voltammetry of the electrodes in solutions for NiS_2 . The forward scan almost immediately dropped and remained constant until a current drop at -0.5V , suggesting a reduction process. The current change is associated with the reduction of nickel and sulfide ions to form a solid nickel sulfide NiS_2 compound on the substrate.

Figure 1 Cyclic voltammogram of the electrodes in $\text{NiSO}_4 + \text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$.

The deposition of nickel sulfide on the substrate continued until the equilibrium potential was achieved at an interception between forward and reverse scan at approximately -0.9V versus Ag/AgCl . From the results through the cyclic voltammetry measurement of the system, the deposition of NiS_2 thin films on the indium tin oxide-coated glass substrate was carried out at the selected potential -1.0V versus Ag/AgCl . The deposition temperature of the thin films was set and controlled at $40^\circ\text{C} \pm 1^\circ\text{C}$, and the deposition time of the thin films was set at 10 minutes, 15 minutes, 20 minutes, and 25 minutes.

X-ray diffraction studies

The XRD of the thin films was obtained on a PANalytical X'Pert Pro MPD PW3040/60 diffractometer using monochromatic $\text{CuK}\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$) in the range of 2θ angles from 10° to 90° . The XRD analysis revealed that NiS_2 films deposited on indium tin oxide substrates were polycrystalline in nature, due to sharp peaks shown on the XRD patterns (see Figure 2). The structural features fit into a hexagonal structure of NiS_2 films with lattice parameter values $a = 0.489$, $b = 0.596$, and $c = 0.367 \text{ nm}$, which comply with the standard values.¹²

Analysis of XRD patterns reveals that the peaks belonging to NiS_2 are detected for the films prepared at all deposition times investigated in respect of films prepared in the electrolytes. The $(1\ 0\ 1)$ plane present at the 2θ value of 29.8° shows the progressive growth for the higher-thickness films. This confirms that the deposition time directly relates to the growth of crystallographic planes of the films. The crystallite size was calculated from the measurement of full width at

half maximum in different X-ray peaks, and values are in the range of $64\text{--}90 \text{ nm}$ for NiS_2 films. The film thickness of these films was determined by gravimetric weight difference method using a sensitive microbalance, and assuming film density as the bulk density of the compounds. The thickness of the deposited film was in the range of $0.8\text{--}1.2 \text{ }\mu\text{m}$ for the increasing deposition time.

Scanning electron micrographs

Figure 3 shows the analysis of surface morphological studies. The SEM studies were conducted on a JSM 6400 JEOL SEM. A pinhole-free, well-adherent, smooth, and uniform film surface without cracks was obtained.

Microcrystals with white spots in the dark region were formed. Due to the cubic pyrite structure of NiS_2 , microcrystals were obtained from a homogenous solution reaction system. At longer deposition times, the structure of the films starts to break into grains (flakes), although still adhering to the substrate. The grains of the materials keep on growing with time, causing the films to break and forming flake-like structures upon reaching the maximum grain stress point. The cracking in thin films is attributed to drying shrinkage in the case of hydrous films. It has been reported that films with thickness greater than 0.2 mm are prone to cracking.¹⁰

Optical absorption spectrum analysis

Figure 4 shows the optical absorption spectrum analysis of NiS_2 . Metal chalcogenides' crystallographic properties, such as the crystal system, "d" spacing values, and (hkl) planes

Figure 2 X-ray diffraction analysis of NiS_2 thin films.

Figure 3 Scanning electron micrographs of NiS_2 thin films at different deposition times: (A) 10 minutes, (B) 15 minutes, (C) 20 minutes, and (D) 25 minutes.

were analyzed. The optical absorption spectrum studies were carried out in the wavelength range 200 nm to 1,100 nm at room temperature using a Shimadzu 1700 UV-Vis spectrophotometer. The optical value of NiS_2 ranges from 1.22 eV to 1.15 eV. Similar values were also obtained for NiSe_2 thin films, which confirms that nickel chalcogenides are suitable as good conducting materials.¹¹ The value of the optical bandgap is smaller as the deposition time increases. The variation of bandgap energy (E_g) with the deposition time shows a nonlinear decrease. It is observed that with the increase of deposition time of the films, the E_g decreased from 1.22 eV to 1.15 eV, in a good E_g range, with the reported value for similar chalcogenides.¹⁰

Thermoelectromotive force measurements

The thermoelectromotive force (thermo-emf) generated due to application of temperature difference across the

Figure 4 Optical absorption spectrum analysis of NiS_2 thin films.

semiconductor gives information about the type of carriers in it. The variation of thermo-emf with temperature was studied for the NiS_2 thin films. The polarity of the thermo-emf developed confirms the n-type nature of NiS_2 . The thermo-emf developed increases with increases in temperature difference applied across the films, which may be attributed to the increased concentration and mobility of the charge carriers.

Mott-Schottky analysis

Mott-Schottky plots have been drawn (in dark conditions) to evaluate the semiconductor parameters as shown in Figure 5. An EDUTECH EDU 9100B LCR7 bridge with an inbuilt function generator with a frequency of 1 kHz was used for the measurement of space-charge capacitance to obtain Mott-Schottky plots drawn using the capacitance data at a frequency of 1 kHz (in the dark) for the system $n-\text{NiS}_2|\text{K}_2\text{SO}_4, \text{KI}, \text{I}_2, \text{H}_2\text{SO}_4|\text{graphite}$. The value of flatband potential (V_{fb}) was obtained using the equation:

$$1/C_{sc}^2 = (V - V_{fb} - k_B T/e)^2 / \epsilon \epsilon_0 e N_D \quad (1)$$

where ϵ is the dielectric constant of free space (8.854×10^{-12} F/m), ϵ is the dielectric constant of NiS_2 (6.52), e is the electronic charge (1.603×10^{-19} C), and N_D is the doping density, which is calculated from the slope of the graph. T is the temperature of the operation (300 K), k_B is the Boltzmann's constant (1.38×10^{-23} J/K), and C_{sc} is the space charge capacitance.

The positive slope of the Mott-Schottky plot reconfirms the n-type conductivity of NiS_2 films, as shown in Figure 5. The intercept of the linear plot ($1/2 C_{sc} = 0$) was taken as the electrode potential of the semiconductor at which the bond

Figure 5 Mott-Schottky plot of NiS_2 thin films.

bending is zero. This potential is the flatband potential and is equal to -0.48 VSCE. The depletion layer width (W) was calculated from the equation:

$$W = \{(2\epsilon\epsilon_0 V_b / e N_D)\}^{1/2} \quad (2)$$

where V_b is the built-in voltage or the band bending. For a photoelectrochemical solar cell, the larger the value of band bending, the greater the conversion efficiency. Therefore, the increased photoconversion efficiency with the increase of film thickness is attributed by both a decrease of bandgap and an increase in band bending observed by both optical and Mott-Schottky analysis.

Conclusion

NiS₂ films can be prepared using the electrodeposition technique from an aqueous bath. All films obtained were well adherent to the substrates with an “ion-by-ion” growth mechanism. The XRD studies revealed that the films are polycrystalline in nature. It can be found that the optical bandgap energy of all types of films decreases as the deposition time of the film increases. The reasons for this change can be one of the following: (1) large size of the dislocation, (2) quantum size effect, and (3) changing barrier height because of variation in grain size in the polycrystalline film. The decrease in energy bandgap after longer periods of deposition time is also attributed to improvement in the crystallinity, as supported by the XRD studies. SEM studies show that the films are continuous and uniform without pinholes. From the optical studies, the energy gap range is calculated as 1.22 eV– 1.15 eV and possesses an indirect nature. From the Mott-Schottky plot, the semiconductor parameters are determined, and the type of the film was found to be n-type, which makes this material capable of being used as a photoelectrochemical/solar cell.

Acknowledgment

The work presented in this manuscript was supported by the Ministry of Higher Education, Putrajaya, Malaysia, sponsored by KeTTHA/FRGS grant (Project No FRGS/2011/FKP/TK02/1 F00120). The authors would also like to thank Universiti Teknikal Malaysia Melaka, Hang Tuah Jaya, Malaysia, for its support.

Disclosure

The authors report no conflicts of interest in this work.

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