

CATHODIC ELECTRODEPOSITION AND CHARACTERIZATION OF Ni₃Se₂ THIN FILMS

K. Anuar*, Z. Zainal, N. Saravanan and A.R. Kartini

Department of Chemistry, Universiti Putra Malaysia, 43400 Serdang,
Selangor, Malaysia

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ABSTRACT

Nickel selenide thin films have been potentiostatically electrodeposited on titanium substrate at room temperature from aqueous solution containing Ni-EDTA and Na₂SeO₃. Various deposition potentials were attempted in order to determine the optimum electrodeposition potential. The films were characterised using x-ray diffraction analysis (XRD) and the photoactivity of the electrosynthesised films were studied using linear sweep voltammetry (LSV). The band-gap energy was determined using UV-visible spectroscopy. The XRD analysis indicated the formation of polycrystalline Ni₃Se₂. The film exhibited *p*-type semiconductor behaviour with good photosensitivity. The bandgap energy (E_g) was about 1.4eV.

1. INTRODUCTION

In order to sustain the present standard of life and development, a reliable and safe supply of electrical energy is vital. The electrical energy currently used mainly comes from fossil fuels and nuclear reactors but there is uncertainty for the future limited resources of fossil fuels and nuclear reactors also adds to the energy problem. Thus, renewable energy sources may play a significant role in sustainable energy supply¹. Solar cells at present furnish the most important long duration power supply for satellites and space vehicles. Solar cells also had successfully employed in small scale terrestrial application². The solar is considered a major candidate for obtaining energy from the sun, since it can convert sunlight directly to electricity with high conversion efficiency and can provide nearly permanent power at low operating cost and is virtually pollution free³. Considerable efforts have been made in recent years in the search for low cost materials for solar energy conversion. Among the materials of great interest are polycrystalline metal chalcogenides⁴⁻¹¹. These compounds are also used as sensor and laser materials, thin films polarizers and thermoelectric cooling materials¹². They possess certain criteria to make them potential candidates in the photoelectrochemical solar cells. The electrodeposition technique has been a promising deposition method to grow thin films. In particular, for absorber films in solar cell, this technique is a perspective competitor because of several advantages such as the possibility for large-scale production, minimum waste of components and easy monitoring

Corresponding author e-mail: anuar@fsas.upm.edu.my

of the deposition process¹³. This technique is generally less expensive than those prepared by the capital-intensive physical methods. Recently, the electrochemical synthesis has been indicated as a promising method for the preparation of semiconductor films. We report here the electrochemical deposition of nickel selenide thin film semiconductor for photoelectrochemical cells on titanium substrates from aqueous solution.

2. EXPERIMENTAL

An EG & G Princeton Applied Research potentiostat driven by a software model 270 Electrochemical Analysis System was used to control the electrodeposition process and to monitor the current and voltage profiles. A conventional three-electrode cell was employed, where the reference electrode is a Ag/AgCl to which all potential were quoted and the counter electrode is platinum (Pt). Titanium (99.99%) was used as the working electrode. The working electrode was polished prior to the deposition process and its surfaces not to be contacted by the electrolyte was sealed using polyethylene terephthalate (PTFE) tape before the insertion into the cell. Ethylenediaminetetraacetate (EDTA) was used to chelate with Ni²⁺ to obtain Ni-EDTA solution. The presence of EDTA in aqueous solution was found to improve the lifetime of the deposition bath as well as the adhesion of the deposited film on the Ti substrate¹⁴. The electrolyte bath comprised of Ni-EDTA and sodium selenite (Na₂SeO₃) solution. Prior to the deposition, a cyclic voltammetry (CV) experiment was carried out between two potential limits (-0.40 to -1.00 V) to probe the effect of the applied potential and to determine the most likely suitable electrodeposition potential for the deposition of nickel selenide. The deposition was attempted at various potentials such as -0.40, -0.50, -0.60, -0.70 V to determine the optimum deposition potential. The experiment was performed at room temperature (27°C) under N₂ blanket without stirring. The pH was maintained at 2.5 using HCl. HCl was added to prevent the formation of hydroxyl species and insoluble compound¹⁴. After the electrodeposition process, the films were washed with distilled water, dried and kept for analysis. The films were characterised by x-ray diffraction (XRD) using a Philips PM 1730 diffractometer for the 2θ range = 2° - 60° with CuK_α radiation. Photoelectrochemical experiments were performed by running linear sweep voltammetry (LSV) between two potentials limits (-0.40 to -1.00 V) in contact with sodium thiosulphate, Na₂S₂O₃·5H₂O (0.02 M) solution. The sequence of constant illumination, chopped illumination and dark period were performed on the PEC cell to study the effect on photoactivity behavior. A halogen lamp (300 W, 120 V) was used for illuminating the electrode. Optical absorption study was carried out using the UV/Vis Shimadzu Lambda 20 spectrophotometer. The film-coated on indium doped tin oxide (ITO) glass was placed across the sample radiation pathway while the uncoated ITO glass was put across the reference path.

3. RESULTS AND DISCUSSION

The CV of the electrodeposition bath containing acidified Ni-EDTA (40 ml, 0.02M) and Na₂SeO₃ (40 ml, 0.02M) is shown in Figure 1. The forward scan showed a very low value up to -0.40 V, whereby the small wave at -0.40 V was onset followed by a strong cathodic current starting at -0.50 V. This is in response with a reduction process associated with Ni(II) reduction on the

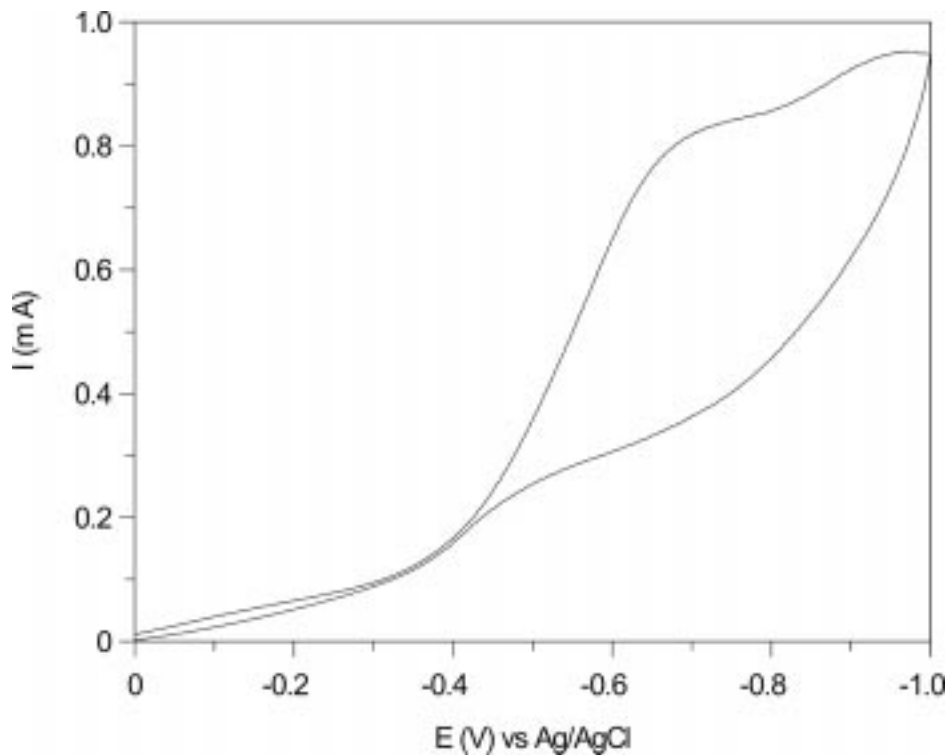


Figure 1 : Cyclic voltammogram of solution mixture of Ni-EDTA and Na_2SeO_3

Ti substrate. Sharper cathodic peak attributable to hydrogen evolution is evident as the sweep reaches -0.95 V and above. During the reverse scan, the current reduces as the sweep past -0.70 V. The reduction process appears to be irreversible as no anodic peak appears. Hence, the CV graph conclusively suggests that a deposition on the working electrode can be expected when the potentials above -0.40 V are applied and the deposit is stable from the dissolution. After the complete CV run, a grey, uniform and smooth film was clearly observed on the working electrode.

The following experiments were carried at different deposition potentials, -0.40, -0.50, -0.60 and -0.70 V. Figure 2 shows the XRD pattern of the samples prepared at these potentials. The intensity of the peaks increased as the potential was increased to a more negative value from -0.40 to -0.60 V. However, the film prepared at -0.70 V showed a decrease in the intensity. Four peaks could be observed for the film prepared at -0.60 V at $2\theta = 28.7, 44.6, 53.2$ and 58.9° corresponding to interplanar distances of 3.1, 2.0, 1.7, 1.5 Å (Table 1). These values are in good agreement with the JCPDS values of 3.0, 2.1, 1.7 and 1.5 Å (File No. 19-0841). The films were subjected to the photoactivity test, which could determine the suitable potential needed to prepare a film with good photoresponse. This is also an important test as the films are expected to be a semiconductors, thus should be sensitive to light, by showing a photocurrent in the region corresponding to their minority carriers current flow. Only the film prepared at -0.50 V showed

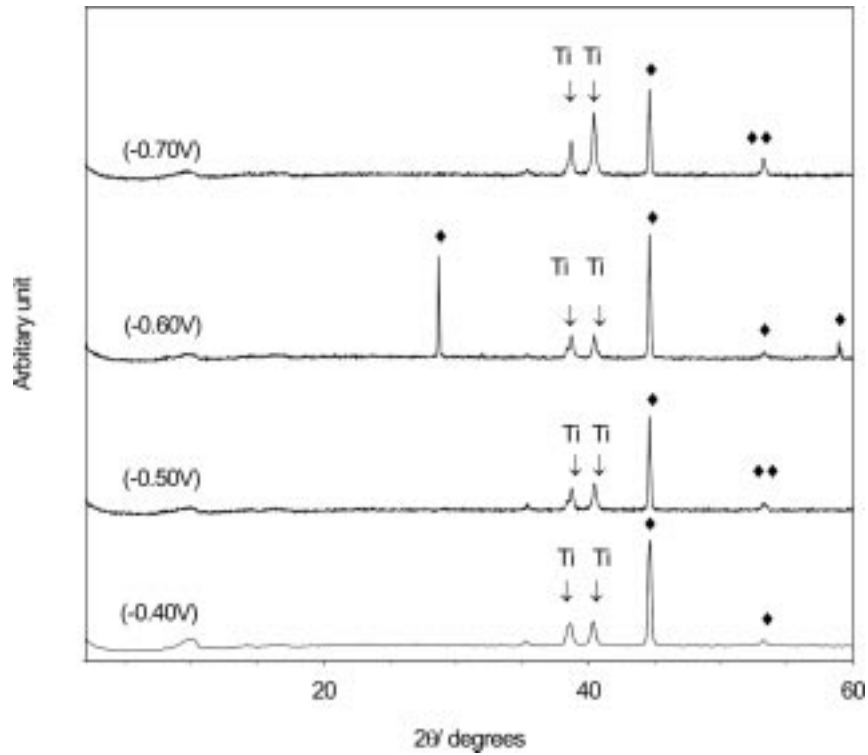


Figure 2 : XRD pattern of samples prepared at different deposition potentials

Table 1 : Comparison of the theoretical and experimental *d*-spacing data for Ni₃Se₂ deposited at different potentials.

Potentials, V	2θ (°)	<i>d</i> -spacing, Å	
		Observed values	JCPDS data (File No. 19-0841)
-0.40	44.4	2.0	2.1
	53.2	1.7	1.7
	53.5	1.7	1.7
-0.50	44.6	2.0	2.1
	53.3	1.7	1.7
	53.5	1.7	1.7
-0.60	28.7	3.1	3.0
	44.6	2.0	2.1
	53.2	1.7	1.7
-0.70	58.9	1.5	1.5
	44.4	2.0	2.1
	53.2	1.7	1.7
	53.5	1.7	1.7

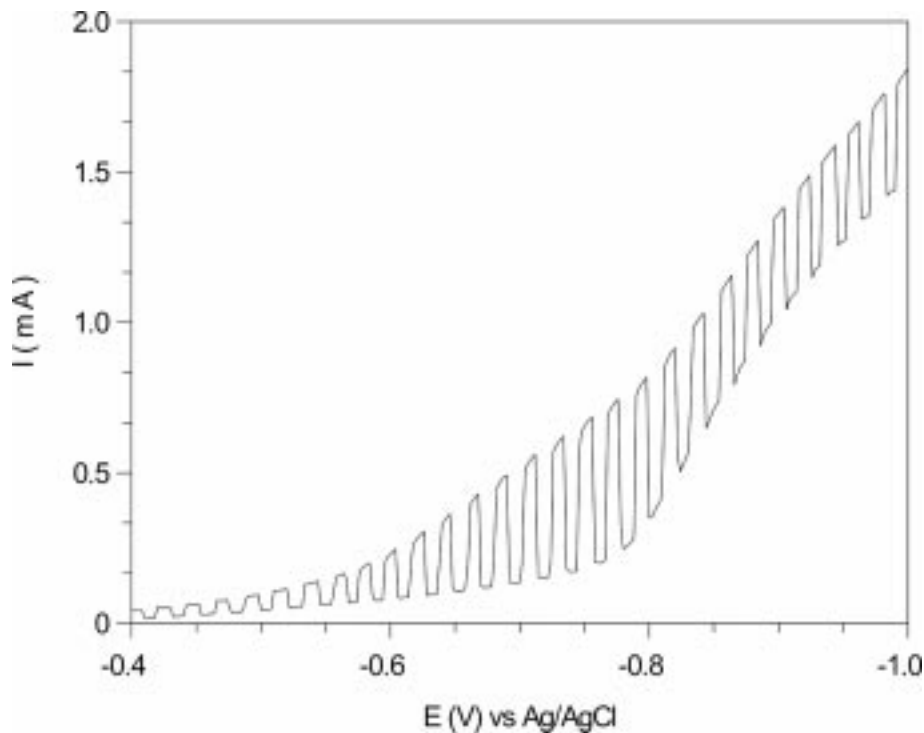


Figure 3 : Photo activity of Ni_3Se_2 film deposited at -0.50 V

the best photoactivity (Figure 3). Films prepared at other deposition potentials did not show good photoresponse as the currents produced were much lower compared to the film prepared at -0.50 V. From the result (Figure 3), the film was found to be a good semiconductor with significant photocurrent output in the cathodic polarisation region. The upper value of the current corresponds to the photocurrent when the sample employed as cathode was illuminated, while the lower value corresponds to the dark current when the illumination was interrupted by chopping. The fact that photocurrent occurs on the negative potential region indicates that electrons are minority carriers of the film and their concentration was then enhanced by the illumination. Thus, the films prepared are p -type semiconductor and can be deployed as photocathode in the PECs application to facilitate a reduction process³.

Deposition was carried out on an ITO-coated glass substrate to study the optical behaviour of the Ni_3Se_2 films. Figure 4 shows the optical absorbance data of the film vs. wavelength obtained from UV-visible spectrophotometer. An absorption could be observed between 300 to 600 nm. This indicates that the film is active in the visible portion of the spectrum. Band gap energy and transition type can be derived from mathematical treatment of the data obtained from the optical absorbance vs. wavelength with Stern relationship (1) of near-edge absorption^{15,16}:

$$A = \left[k(h\nu - E_g)^{n/2} \right] / h\nu \quad (1)$$

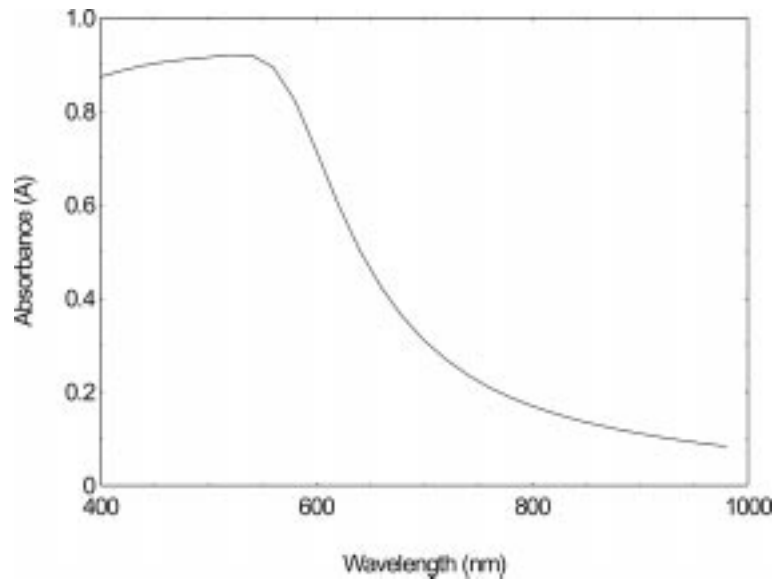


Figure 4 : Optical absorbance versus wavelength of Ni_3Se_2 deposited on ITO glass

where ν is the frequency, h is the Planck's constant, k equals a constant while n carries the value of either 1 or 4. The bandgap, E_g , could be obtained from a straight line plot of $(Ah\nu)^{2/n}$ as a function of $h\nu$. Extrapolation of the line to the base line, where the value of $(Ah\nu)^{2/n}$ is zero, will give E_g . A linear trend is apparent where n in the Stern relationship equals 4 (Figure 5). The line segments required to by bypass the energy of the gap lies at about 1.4 eV.

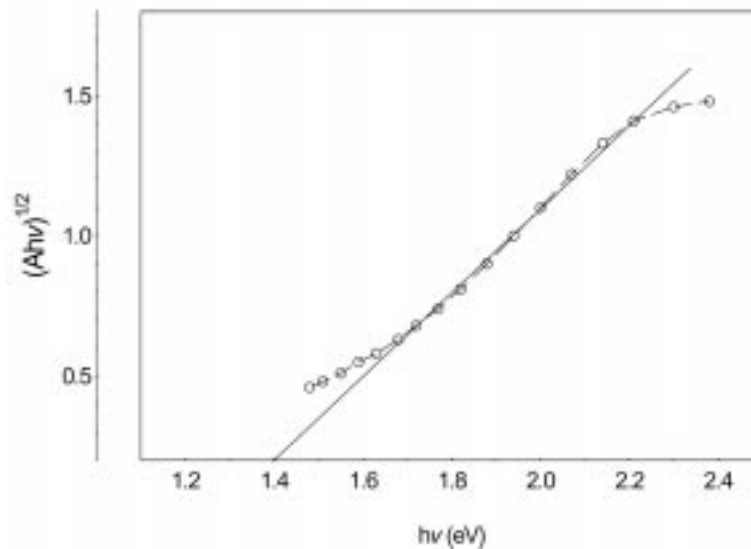


Figure 5 : Plot of $(Ah\nu)^{1/2}$ vs $h\nu$ of Ni_3Se_2 film

4. CONCLUSION

Ni_3Se_2 films could be prepared by the method explained. The presence of EDTA was found to induce better films formation. Deposition at -0.50 V was found to be optimum for the preparation of Ni_3Se_2 in this set up concluded from the XRD data and the photoresponse test.

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