Cyclic Voltammetry Study of Copper Tin Sulfide Compounds

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ABSTRACT

The Cu²⁺, Sn²⁺ and S²⁻ deposition onto indium doped tin oxide (ITO) glass substrate from aqueous solutions was studied by means of cyclic voltammetry technique. Deposition was carried out in a standard three-electrode cell consisting tin chloride, copper sulfate, and sodium thiosulfate. The deposition process was investigated at ±25 °C. The anodic and cathodic scans were recorded within the potential range which from 1000 to -1000 mV. The scan rate and multiple cycling were carried out to examine the behavior of electroactive species at the electrode surface. The thin films were characterized by X-ray diffraction (XRD) technique for structural studies. The peaks in the pattern indicate the formation of orthorhombic phase of Cu₄SnS₄.

(Keywords: copper tin sulfide, cyclic voltammetry, metal chalcogenide, thin films)

INTRODUCTION

Efforts are being made currently in finding new materials for energy conversion and other photo-electrochemical uses. Two important factors that should be considered in producing these materials are the band gap energy matching the solar spectrum and the competitiveness of production cost. The first criteria met by several materials such as Si and GaAs, which are being used currently. However, the cost is extremely high for large-scale production. The reduction of cost is possible by looking for other materials and simplifying the manufacturing process. Among other materials of interest, are metal chalcogenides (binary-2 elements) such as CdS and CdSe [1] from Group II and Group VI elements. Another promising class of compounds, which has been less extensively studied, is tin chalcogenides, which fall into Group IV and Group VI elements in Periodic Table. The interest of this project is to synthesize new materials ternary compound (3 elements) based on tin, copper, and sulfur (CuSnS). Since, binary tin-based compounds such as SnS [2], SnSe [3] have been successfully synthesized; further studies will involve the ternary compounds based on tin.

Malaysia is a tin producer country and copper is easily available. Modern thin film technology has evolved into a sophisticated set of techniques used to fabricate many products. Applications include very large-scale integrated circuits, electronic packaging, sensors, optical devices, as well as protective and decorative coating. There are three categories of thin film process; physical vapor deposition (such as sputter deposition [4] and thermal evaporation [5]); chemical vapor deposition (such as metal-organic chemical vapor deposition [6] and plasma enhanced chemical vapor deposition [7]); and chemical methods (such as chemical bath deposition [8] and electro-deposition [9]).

Cyclic voltammetry is considered to be one of the most versatile electro analytical techniques currently available. It is generally the first experiment to be run when dealing with any electrochemically active species. The basic theory behind cyclic voltammetry is to measure the current response at the electrode surface to a specific range of potentials in an unstirred solution. The present work involves study of ternary chalcogenide metal compound comprising of copper, tin, and sulfur by employing cyclic voltammetry technique. Here, we report a
study of the electrochemical behavior of ternary compound under different voltammetric conditions. The experiment outlined below demonstrates the determination of the following: the peak current and peak potential, the diffusion coefficient, electrochemical reversibility, scan rate and scan cycle. The composition of copper tin sulfide, which deposited on the ITO substrate, will be identified by XRD methods.

EXPERIMENTAL DETAILS

The analytical grade reagents such as copper sulfate (CuSO₄), tin chloride (SnCl₂·2H₂O), and sodium thiosulfate (Na₂S₂O₃·5H₂O) were used as the precursor compounds to deposit ternary metal chalcogenide. Tin chloride was first dissolved in concentrated hydrochloric acid (HCl) and then diluted with the deionized water to required volume. The pH values of aqueous solution were adjusted by adding 1 M of hydrochloric acid. The voltammetric experiments were performed with a BAS, (Bioanalytical System, and West Lafayette, IN, USA). A conventional three-electrode potentiostated system was used with an indium tin oxide (2cm x 1cm) as working electrode; a platinum wire (1 mm) as counter electrode and an Ag/AgCl (3M NaCl) as a reference electrode. All the experiments were carried out in room temperature (25 ± 1°C). Solutions were degassed with nitrogen for ten minutes prior to recording the voltammogram. The electrochemical behaviors of ternary compound were investigated under different cyclic voltammetric conditions such as different scan rate, scan cycle. The X-ray diffraction (XRD) was recorded at 2° per minute using a Philips PM 1730 Diffractometer for the 2θ ranging from 20° to 60° with CuKα (λ = 1.5418 Å) radiation. Signals of the samples were identified and matched with the standard values from the Joint Committee on Powder Diffraction Standard (JCPDS) data.

RESULTS AND DISCUSSION

Cyclic Voltammogram of Individual Copper Sulfate Electrolyte

The cyclic voltammogram of 0.05 M individual copper sulfate is shown in Figure 1. Under the influence of applied voltage, the Cu²⁺ and H⁺ ions are attracted to the negative electrode, which is called the cathode. The SO₄²⁻ and OH⁻ ions are attracted to positive electrode, called the anode. Electrons are consumed at the cathode by metallic cation as in equation below. The metal atoms are deposited in the process. An equal number of electrons are liberated at the anode by anions, thus completing the circuit. Cathodic current can be seen started at -100 mV versus Ag/AgCl followed by a steady current increase to a second cathodic peak (about –700 mV versus Ag/AgCl) on the forward scan, which may be associated with the reduction of copper ions according to reaction:

\[ Cu^{2+} + e^- \rightarrow Cu^+ \] (1)

\[ Cu^+ + e^- \rightarrow Cu \] (2)

Further current rise at more negative potential, at –900 mV versus Ag/AgCl was due to hydrogen evolution reaction can happen in acidic condition. The deposition reaction is reconfirmed by the reverse scan. Two anodic peaks observed in potential range from -200 to 850 mV vs Ag/AgCl, which may be associated with the oxidation of copper metal according to reaction:

\[ Cu \rightarrow Cu^{+} + e^- \] (3)

\[ Cu^+ \rightarrow Cu^{2+} + e^- \] (4)
Cyclic Voltammogram of Individual Tin Chloride Electrolyte

The cyclic voltammogram of 0.05 M individual tin chloride is shown in Figure 2. The scan begins from the left hand side of the current/voltage plot where no current flow. As the voltage is swept further to the right (to more reductive values) a current begin to flow at about –500 mV versus Ag/AgCl. The drastic increase in the current indicates an increase in the deposition rate of tin [10].

The reduction peak that appeared to be absent may actually be too small to be detected in higher concentration (0.05 M). This indicated that the reduction of tin chloride was irreversible. The reduction wave increases rapidly towards the more negative region due to evolution of hydrogen, which adversely affects the quality of film. The forward scan is not proceeding beyond this point to avoid any interference from the hydrogen evolution process.

\[ Sn^{2+} + 2e^- \rightarrow Sn \]  \hspace{1cm} (5)

During the reverse scan, the overlap of the current profiles indicates that co-deposition process that occurs over the tin deposited earlier in the forward scan.

This reverse scan crosses the forward scan at –470 mV versus Ag/AgCl. Thus proceeding toward the positive direction, an anodic peak was observed as shown by a well define peak at about 80 mV versus Ag/AgCl. This well-defined anodic peak confirms the complete dissolution of the tin layer deposited (Equation 6) during the cathodic scan.

The voltammogram also revealed that beyond the anodic peak, the current approaches to zero, indicating that the majority of the deposited tin has been removed from the substrate surface. Thus, the oxidation process had stopped.

\[ Sn \rightarrow Sn^{2+} + 2e^- \]  \hspace{1cm} (6)

The voltammogram shows a crossover between cathodic current branch which is characteristic of the nucleation and growth process. The cyclic voltammogram showed the curve as a flick out during the reverse scan. This phenomenon indicated that nucleation of metal occurs at a surface of substrate in the system.

Cyclic Voltammogram of Individual Sodium Thiosulfate Electrolyte

The voltammogram of 0.05 M individual sodium thiosulfate is recorded in Figure 3. The cathodic current was observed to begin at potential around –400 mV versus Ag/AgCl.

From the figure, a first reduction wave can be observed at around –600 mV versus Ag/AgCl, which is due to the reduction of thiosulfate ions [11]. This reduction wave may be due to the \( S_2O_3^{2-} \) ions released during the disproportionation of \( Na_2S_2O_3 \) at the pH of 1. The second cathodic peak occurred at –750 mV versus Ag/AgCl could be attributed to the further reduction of \( S_2O_3^{2-} \) ions to release the sulfur (Equation 9).
In acidic medium, dissociation of $\text{S}_2\text{O}_3^{2-}$ takes place as:

$$2\text{S}_2\text{O}_3^{2-} + \text{H}^+ \rightarrow \text{HSO}_3^- + \text{S} \quad (9)$$

The electrons released in reaction 8 with sulfur released in reaction 9 will form $\text{S}^{2-}$ ions:

$$\text{S} + 2\text{e}^- \rightarrow \text{S}^{2-} \quad (10)$$

sodium thiosulfate) and mixture. The results reflected that the Cu$^{2+}$ and Sn$^{2+}$ compete for each other to combine with $\text{S}^{2-}$ to produce ternary compound. The cathodic current begin flowing at mV vs Ag/AgCl is due to the presence of Cu$^{2+}$ rather than Sn$^{2+}$. The copper ions are more easily reduced in the system, hence increasing the amount of copper content in ternary compound. The suddenly increased cathodic current around $-500$ mV vs Ag/AgCl may be due to the reduction of tin and thiosulfate ions.

During the oxidation process, the deposited tin easily dissolves back into solution if compared with copper which indicated by the large anodic current. Based on the cyclic voltammogram, there is no oxidation peak can be observed, suggested that the sulfur content in ternary compound is quite stable.

Figure 3: The Cyclic Voltammogram of 0.05 M Individual Sodium Thiosulfate on ITO Substrate at 25±1 C. Scan Rate = 10 mV/s in pH =1.

At potentials more negative than $-900$ mV versus Ag/AgCl, the cathodic current increased rapidly and many bubbles were formed on electrode surface. This is due to the evolution of hydrogen gas.

However, during the reverse scan, there was no anodic peak observed, which reflected that the elemental sulfur is formed in a stable state and was insoluble in the system. At potentials more positive than $-400$ mV versus Ag/AgCl, the current had ceased to flow, which indicates that the oxidized species is only slowly desorbed and diffused away from the surface of the electrode.

The chemical reaction mechanism for the formation of $\text{S}^{2-}$ in acidic bath was proposed [12] as below:

$$\text{Na}_2\text{S}_2\text{O}_3 \rightarrow 2\text{Na}^+ + \text{S}_2\text{O}_3^{2-} \quad (7)$$

Na$_2$S$_2$O$_3$ is a reducing agent. By a virtue of the half-cell reaction as:

$$2\text{S}_2\text{O}_3^{2-} \rightarrow \text{S}_4\text{O}_6^{2-} + 2\text{e}^- \quad (8)$$

Cyclic voltammogram of mixture compounds

Figure 4 showed that cyclic voltammograms for comparison between the individual compound of electrolyte (copper sulfate, tin chloride and...
The Effect of Multiple Cycling of Mixed Electrolyte

The cyclic voltammograms shows that multiple cycling appears to affect both reduction peak potential and oxidation peak potential in Figure 5a and 5b. This is due to the loss in the faradaic activity. The peak current in the first scan cycle was significantly different from those in the subsequent cycles. The increase in cathodic peak height and reduction in anodic peak height with repeat scanning confirm the formation of stable thin film. The decrease in oxidative current on extensive scan cycling may be associated with the formation of a more resistive ternary compound on the ITO substrate. Since the combination of Cu²⁺, Sn²⁺, S²⁻ to the ternary metal chalcogenide creates a very stable condition, during the oxidation reaction, not all the deposited thin film dissolved back to solution. On the other hand, the cathodic peak and anodic peak potential shift towards more negative and positive values, respectively, also can be seen in Figure 5a. This indicates the presence of a chemically irreversible electrochemical reaction. The subsequent continual scanning in a positive direction decreased peak potential indicating some polarization (Figure 5b).

Results obtained from multiple cycling showed that the first cycle of the voltammogram was usually in an unstable stage (Figure 5a, b). After repeating few cycles, achieve steady state condition in cyclic voltammetry.

The Effect of Varying Scan Rate of Mixed Electrolyte

An irreversible reaction is when the rate of electron transfer is sufficiently slow, so that the potential no longer reflects the equilibrium activity of redox couple at the electrode surface.

In such a case, the potential peak values will change as a function of the scan rate. The reduction peak at low scan rates (1 mV/s) is well marked. At high scan rates (which are more than 10mV/s), the peak widened and increased both in terms of peak currents and peak potentials. When the scan rate increased, the peak separation also increased (Figure 6) due to the heterogeneous kinetics and IR drop effects. The ohmic polarization (IR drop) effect is a characterization of bulk solution. This effect can be minimized by proper cell design during the experiment.
The relationship between the cathodic peak current \( i_{pc} \) and anodic peak current \( i_{pa} \) corresponding to square root of scan rate is presented on the Figure 7. The variation is linear but the lines do not pass through the origin. The linearity is expected for a reduction processes that happen under the mass transfer control. However the additional process, other than diffusion, also happens, showed by the intercept, which is higher than zero.

The peak current increases linearly with the square root of the scan rate (Table 1) reflects conditions of diffusion control of the charge transport process. The rate of electron transfer is controlled by the rate of supply of material to the electrode by the diffusion process.

We can observe that increased peak current when the scan rate was increased. As shown in Randles-Sevcik equation below [13], the peak current depends on the square root of scan rate in a cyclic voltammetry process.

\[
i_p = \left(2.69 \times 10^5\right) n^{3/2} ACD^{1/2} v^{1/2}
\]  \hspace{1cm} (11)

Table 1: Voltammetric Data of the Peak Current as a Function of Scan Rates. The Deposition Bath Contains CuSO\(_4\), SnCl\(_2\), H\(_2\)O, and Na\(_2\)S\(_2\)O\(_3\), H\(_2\)O at Same Concentration, 0.05 M Respectively, at 25±1 °C.

<table>
<thead>
<tr>
<th>( v^{1/2} ) ([\text{mV/s}]^{1/2} )</th>
<th>( i_{pa} ) ([\text{mA}] )</th>
<th>( i_{pc} ) ([\text{mA}] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>2.504</td>
<td>1.201</td>
</tr>
<tr>
<td>3.16</td>
<td>2.115</td>
<td>2.494</td>
</tr>
<tr>
<td>4.47</td>
<td>2.159</td>
<td>2.408</td>
</tr>
<tr>
<td>7.75</td>
<td>2.964</td>
<td>3.982</td>
</tr>
<tr>
<td>10.00</td>
<td>2.636</td>
<td>6.516</td>
</tr>
</tbody>
</table>

Where \( i_p \) is the peak current in A; \( n \) is the number of mole of electrons transferred per mole of electroactive species; \( A \) is the area of the electrode in cm\(^2\); \( D \) is the diffusion concentration coefficient in cm\(^2\)/s; \( C \) is the concentration in mol/cm\(^3\); and \( v \) is the scan rate of potential in V/s.

The anodic peak potential, \( E_{pa} \) and cathodic peak potential, \( E_{pc} \) shifted progressively towards positive (except 100 mV/s) and negative potential, respectively, with increasing scan rates as shown in Figure 8 and Table 2, respectively.
Figure 8: The Plot of Peak Potential Versus Scan Rate Obtained for Electrodeposited Cu₄SnS₄ Thin Films on ITO Substrate. The Deposition Bath Contains CuSO₄, SnCl₂.2H₂O, and Na₂S₂O₃.5H₂O at Same Concentration, 0.05M Respectively, at 25±1°C. Scan Rate = 1, 10, 20, 60,100 mV/s in pH =1.

Table 2: Voltammetric Data of the Peak Potential as a Function of Scan Rates. The Deposition Bath Contains CuSO₄, SnCl₂.2H₂O, and Na₂S₂O₃.5H₂O at Same Concentration, 0.05M Respectively, at 25±1°C.

<table>
<thead>
<tr>
<th>v/mVs⁻¹</th>
<th>Eₚ⁺/mV</th>
<th>Eₚ⁻/mV</th>
<th>ΔEₚ/mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>18</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>10</td>
<td>-53</td>
<td>31</td>
<td>84</td>
</tr>
<tr>
<td>20</td>
<td>-200</td>
<td>50</td>
<td>250</td>
</tr>
<tr>
<td>60</td>
<td>-301</td>
<td>117</td>
<td>418</td>
</tr>
<tr>
<td>100</td>
<td>-429</td>
<td>76</td>
<td>505</td>
</tr>
</tbody>
</table>

This shows the characteristic of a partly diffusion controlled process. The negative shift of the anodic peak potential was observed at the scan rate of 100 mV per second due to an easier dissolution of the deposited thin film.

A gradual increase in the peak separation (ΔEₚ) for the peak couple in Figure 9 indicated that the reaction involved became more irreversible as the scan rate increased. It was due to the motion of charge between fixed redox groups which were severely hampered by the slow motion of counter ions. Meanwhile, the peak separation at the low scan rate is close to a reversible value.

In a slow voltage scan, the diffusion layer will grow much further from the electrode in comparison to a fast scan. Consequently the flux to the electrode surface is considerably smaller at the slow scan rate. As the current is proportional to the flux toward the electrode, the magnitude of the current will be lower at a slow scan rate.

X-ray Diffraction study

Figure 10 shows the X-ray Diffraction pattern of the Cu₄SnS₄ films. The peaks in the pattern indicate the formation of the orthorhombic phase of Cu₄SnS₄. The results are well matched with the Joint Committee on Powder Diffraction Standards (JCPDS) values (Reference code: 01-071-0129) shown in Table 3.

There are six peaks at 2θ = 28.6°, 30.2°, 35.2°, 47.4°, 50.7° and 56.3° corresponding to d-spacing values 3.12, 2.95, 2.54, 1.92, 1.81 and 1.63 Å and attributed to the (102), (221), (420), (040), (711) and (423) planes with (221) being the most intense detected.

Raising the scan segments to 80 times, however, resulted in the disappearance of the (221), (420), (711) planes and the appearance of plane at d-spacing 1.92 and 1.63 Å which are related to (040) and (423), respectively. As the scan segments were increased to 80 times, the crystalline plane also changed. However, the
Figure 10: XRD Patterns of Cu₄SnS₄ at Different Scan Cycles on ITO Substrate. The Deposition Bath Contains CuSO₄, SnCl₂·2H₂O, and Na₂S₂O₃·5H₂O at Same Concentration, 0.05 M Respectively, at 25±1 C. Scan Rate = 10 mV/s in pH 1.

Table 3: Comparison of the JCPDS d-spacing Data for Cu₄SnS₄ to Experimentally Observed Values for the Samples Deposited at Different Scan Cycles.

<table>
<thead>
<tr>
<th>Sample (scan cycles)</th>
<th>2 theta (°)</th>
<th>d-spacing (Å)</th>
<th>h k l</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Observed Values</td>
<td>JCPDS data</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>30.2</td>
<td>2.95</td>
<td>2 2 1</td>
</tr>
<tr>
<td></td>
<td>35.2</td>
<td>2.55</td>
<td>4 2 0</td>
</tr>
<tr>
<td></td>
<td>45.2</td>
<td>2.01</td>
<td>2 0 1</td>
</tr>
<tr>
<td></td>
<td>50.6</td>
<td>1.80</td>
<td>7 1 1</td>
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<tr>
<td>10</td>
<td>30.2</td>
<td>2.96</td>
<td>2 2 1</td>
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<td></td>
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<td>2.55</td>
<td>4 2 0</td>
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<td></td>
<td>50.4</td>
<td>1.81</td>
<td>7 1 1</td>
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<td>20</td>
<td>28.6</td>
<td>3.12</td>
<td>1 0 2</td>
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<td></td>
<td>30.3</td>
<td>2.95</td>
<td>2 2 1</td>
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<td></td>
<td>35.4</td>
<td>2.54</td>
<td>4 2 0</td>
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<tr>
<td></td>
<td>50.7</td>
<td>1.80</td>
<td>7 1 1</td>
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<td>40</td>
<td>28.6</td>
<td>3.12</td>
<td>1 0 2</td>
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<td></td>
<td>47.4</td>
<td>1.92</td>
<td>0 4 0</td>
</tr>
<tr>
<td></td>
<td>56.3</td>
<td>1.63</td>
<td>4 2 3</td>
</tr>
</tbody>
</table>

Cu₄SnS₄ material remains almost the same and did not induce any structural changes.

CONCLUSIONS

The Cu²⁺, Sn²⁺ and S²⁻ deposition on indium tin oxide (ITO) glass substrate from aqueous solutions containing 0.05 M copper sulfate, tin chloride, and sodium thiosulfate was studied by means of the cyclic voltammetry technique. The acidic condition is believed to be critical for the formation of Cu₄SnS₄ thin films especially at pH 1. This is due to the reduced hydroxyl species and dissociation of sodium thiosulfate releasing the sulfur. The orthorhombic phase of Cu₄SnS₄ was identified in XRD.

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