Galvanostatic formation and photoelectrochemical characterization of zinc selenide and mercury containing zinc selenide films

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Electrosynthesis of zinc selenide and mercury containing zinc selenide films has been carried out under controlled galvanostatic conditions. For photoelectrochemical characterization of these preparations, photoelectro-convertibility and photoaction spectral behaviour have been investigated. Resistance of these photoelectroactive films towards electrochemical corrosion has also been examined on the basis of polarization studies and Tafel plots.

Electrochemical deposition has been recognised as an attractive technique for the preparation of photoelectroactive materials in the form of thin films. In our earlier studies, we prepared metal chalcogenides and mixed metal chalcogenides films under controlled potentiostatic conditions to investigate their photoelectroconvertibility. In this communication, we report results on (i) electrochemical formation of ZnSe and (ZnHg)Se films under galvanostatically controlled conditions, and (ii) their photoelectrochemical characterization on the basis of photoactivity measurements and photoaction spectral studies.

Examination of these preparations on the basis of polarization studies and Tafel plots shows up to a tenfold increase in their resistance towards electrochemical corrosion.

Experimental Procedure

Electrochemical codeposition of ZnSe and (ZnHg)Se was carried out using the usual three electrode system. Constant current power supply (Lake Shore Model 120, U.S.A.) was used to ensure passage of constant current. The working electrode consisting of titanium foil (Mis Titanium Equipment and Anode Manufacturing Co. Ltd., Chennai) cleaned with diamond paste using Metses Fluid (Madras Metallurgical Services Pvt. Ltd., Chennai) and washed successively with acetone and distilled water was used as the working electrode. Electrolyte solutions consisting of 0.01M zinc sulphate (CDH, India) and 0.001M selenium dioxide (Fluka Chemika, Switzerland) having pH=3.5 with and without mercuric chloride (CDH, India) were electrolysised using another titanium foil as counter electrode.

Electrodeposition was carried out for various time intervals using different current densities. Potential of the working electrode during electrodeposition was monitored with respect to a saturated calomel electrode (SCE). All the preparations were tested for their photoresponsiveness using solutions containing \( \frac{I_2}{I^-} \) redox couple. 1 kW Tungsten lamp was used as a light source. Photoaction spectral studies were carried out using Monochromator (Applied Photophysics, London). For corrosion studies Electrochemical Impedance Measurement System Model 378 (EG & G, Parc, U.S.A.) consisting of Model 273 Potentiostat/Galvanostat in combination with an IBM compatible AT personal computer and printer (Epson) was employed.

Results and Discussion

When electrodeposition of titanium supported zinc selenide films was carried out, the deposition potential initially varied somewhat rapidly with time, before attaining a time invariant magnitude as shown in Fig. 1. This alteration obviously arises on account of cumulative effect of polarization and alteration in the electrochemical character of the substrate as a result of electrolysis. Film thickness values alongwith bandgap values and other relevant electrochemical information is summarised in Table I. Film thickness, \( F_t \) values were estimated using relationship (1) assuming complete absence of occurrence of undesirable electrochemical activity.

\[
F_t = \frac{i.t.(E.W)}{F.d.A} \quad \ldots (1)
\]

where \( i= \) constant deposition current; \( r= \) deposition time,
Fig. 1 — Variation of deposition potential with time during galvanostatic formation of zinc selenide. [O — 0.4 mA/cm², △ — 0.8 mA/cm², ● — 1.2 mA/cm²]

Fig. 2 — Photoactivity of different zinc selenide coatings prepared under different experimental conditions. [O — 0.4 mA/cm², △ — 0.8 mA/cm², ● — 1.2 mA/cm², (a) 5 min (b) 10 min. (c) 15 min]

Fig. 3 — Photoaction spectrum of a representative zinc selenide preparation. Deposition current density=1.2 mA/cm², Deposition time=5 min

Fig. 4 — $E^2$ vs $\lambda$ plot for the estimation of bandgap. Deposition current density=1.2 mA/cm², Deposition time=5 min

Table 1 — Experimental conditions and corrosion characteristics of zinc-selenide preparations.

<table>
<thead>
<tr>
<th>Electrode Number</th>
<th>Deposition current-density (mA/cm²)</th>
<th>Deposition time, (min)</th>
<th>Film thickness $\times 10^4$ (cm)</th>
<th>Bandgap, (eV)</th>
<th>Polarization Resistance $R_p$ ($\Omega$) $\times 10^4$</th>
<th>Corrosion Rate $R_c$ (g/sec) $\times 10^{10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.4</td>
<td>5</td>
<td>2.82</td>
<td>2.3 ± 0.15</td>
<td>8.93</td>
<td>2.17</td>
</tr>
<tr>
<td>2</td>
<td>0.4</td>
<td>10</td>
<td>5.64</td>
<td>10.43</td>
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<tr>
<td>3</td>
<td>0.8</td>
<td>15</td>
<td>8.46</td>
<td>14.70</td>
<td>1.31</td>
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</tr>
<tr>
<td>4</td>
<td>0.8</td>
<td>5</td>
<td>6.65</td>
<td>10.53</td>
<td>1.83</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.8</td>
<td>10</td>
<td>11.30</td>
<td>12.80</td>
<td>1.50</td>
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<tr>
<td>6</td>
<td>1.2</td>
<td>15</td>
<td>18.95</td>
<td>20.68</td>
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<tr>
<td>7</td>
<td>1.2</td>
<td>5</td>
<td>8.47</td>
<td>14.60</td>
<td>1.32</td>
<td></td>
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<tr>
<td>8</td>
<td>1.2</td>
<td>10</td>
<td>16.94</td>
<td>22.0</td>
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<tr>
<td>9</td>
<td>1.2</td>
<td>15</td>
<td>25.41</td>
<td>23.8</td>
<td>0.81</td>
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</tbody>
</table>
$E.W.$ = Equivalent weight of the electrodeposit; $F$ = Faraday constant; $A$ = Area of the deposited film; and $d$ = density of the electrodeposit.

These galvanostatically formed electrodeposits were studied for their photoelectroconvertibility using 0.5 M ZnSO$_4$ solution containing 0.1 M KI and 0.2 mM I$_2$ solution. The results are presented in Fig. 2. The observed photoactivity varies with deposition current-density in all cases. Photoaction spectrum of one of the well behaved preparations is included in Fig. 3. Bandgap values were obtained on the basis of $E^\gamma$ vs $\lambda$ plots$^8$. A representative plot is shown in Fig. 4 which yields bandgap value equal to 2.1 eV.

The galvanostatically formed ZnSe preparations were also subjected to polarization studies with a view to ascertain their ability to withstand electrochemical corrosion. Polarization resistance values were obtained on the basis of examination of current-voltage behaviour of the electrodeposits$^{10,11}$. A typical curve is given in Fig. 5. Polarization resistance values along with corrosion rates estimated using the prescribed procedure$^{12,13}$ are summarised in Table 1. These galvanostatically formed films exhibit somewhat improved resistance towards corrosion in comparison to potentiostatically formed films studied earlier$^{14,15}$.

Inclusion of mercury in metal chalcogenides in some cases, has been shown to improve photoelectroconvertibility of the deposits in a substantial measure$^{16-18}$. With the view to explore this possibility in the present case, 0.01 M ZnSO$_4$ and 0.001 M SeO$_2$ solutions containing variable concentration of HgCl$_2$ were subjected to electrolysis under controlled galvanostatic conditions. Experimental conditions along with film thickness values for (ZnHg)Se electrodeposits are summarised in Table 2. Photoelectrochemical behaviour of these preparations depicted in Fig. 6 shows that unlike zinc selenide which in all cases exhibited $p$-type semiconductivity,
some of the Hg containing zinc selenide preparations exhibit $n$-type semiconductivity as well. In some cases under identical conditions, some preparations are endowed with $p$-type behaviour while some others show $n$-type character. Inclusion of Hg thus alters photoelectrochemical character of the zinc selenide films. Increased inclusion of Hg results in lowering of bandgap. A plot of bandgap against concentration of HgCl$_2$ in the electroplating solution shown in Fig. 7, indicates formation of a solid solution$^{19,20}$ till concentration of HgCl$_2$ approaches $6 \times 10^{-5} \text{M}$. These observations are consistent with the photoactivity exhibited by different preparations (Fig. 6). No improvement in photoelectrochemical behaviour is observed beyond $6 \times 10^{-5} \text{M}$ HgCl$_2$. Corrosion
Characteristics of these preparations were investigated by studying their current-voltage behaviour to construct Tafel plots. Corrosion-currents and corrosion rates estimated\textsuperscript{10,11} using these data are included in Table 2. Inclusion of Hg is seen to result in considerable improvement in the resistance of the electrodeposits towards electrochemical corrosion.

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References