Electrosynthesis and photoelectrochemical characterization of zinc selenide doped with thallium

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Thallium-doped zinc selenide semiconductor electrode has been prepared by electrochemical codeposition. Such doped electrodes exhibit photoresponsiveness significantly higher than that of zinc selenide electrodeposits prepared and tested under similar experimental conditions. Capacitance measurements and current-voltage behaviour in dark and under illumination in conjunction with photoaction spectral studies have been used for the characterization of Tl-doped zinc selenide electrode. The results indicate that incorporation of thallium modifies zinc selenide characteristics so as to enable it to exhibit improved photoelectro-convertibility.

Metal chalcogenides are attractive systems for solar energy conversion by photoelectrochemical means1–8. Zinc selenide in view of its large band gap has not been studied much9,10 and is considered useful only for the formation of p-n liquid junction solar cells. It is usually endowed with n-type semiconductivity11. Recently we reported the preparation of p-type zinc selenide by electrochemical codeposition12. It has also been demonstrated that p-zinc selenide exhibits12,13, reasonable stability when its photoelectroactivity is tested in zinc sulphate solution containing I2/I3 redox couple. In the present investigation we have explored the possibility of enhancing photoelectroactivity of p-zinc selenide by doping it with thallium. A priori considerations suggest that incorporation of thallium should enhance p-type semiconductor of zinc selenide14.

Material and Methods

Zinc selenide and thallium-doped zinc selenide films were obtained by the method reported earlier12,13. A titanium plate (1.69 cm2) was polished with diamond paste, cleaned with emery papers (2 μ and 3 μ), and washed successively with acetone and deionized water. The plate was then kept in an electroplating solution for 1 hr for soaking. Electrodeposition was carried out by adjusting the potential of the titanium plate with respect to saturated calomel electrode, to a desired fixed value using a platinum auxiliary electrode. The potential was controlled with the help of potentiostat (DB Electronics, Poonna). A summary of the experimental conditions employed for electrodeposition is presented in Table 1.

For a comparative study of photoelectroactivity of Tl-doped zinc selenide and zinc selenide electrodes these were combined with a platinum counterelectrode to form the cell of the type (A)

\[
\begin{align*}
\text{Zinc selenide} & \quad 1 \text{M} \text{ZnSO}_{4}, \\
\text{Tl-doped zinc selenide} & \quad 0.1 \text{M} \text{KI}, \\
& \quad 50 \text{mM} \text{I}_{2} \\
& \quad \text{Pt}
\end{align*}
\]

Illumination was done with the help of a tungsten lamp (1000 watt) and photopotentials were measured using a digital multimeter HIL 2142 (HIL, New Delhi) with a least count of 0.1 mV. Photopotential buildup and decay were recorded with the help of Anika recorder A-4 (Anika, Instrument Pvt, New Delhi). Capacitance measurements were carried out using Vasvai Electronic LCR meter VLCR-7. For spectral studies Oriel (USA) monochromator-7350 was used.

Results and Discussion

It may be noted that during electrodeposition, the deposition current initially varied rapidly and subsequently attained an almost time-invariant value. A typical curve depicting decay of current is shown in Fig. 1. The attainment of steady current took only a few minutes. Table 1 includes only steady state current values.

Some representative data obtained using Tl-doped zinc selenide and zinc selenide electrodes prepared by electrochemical codeposition under comparable conditions are included in Table 2. Zinc sulphate solution (1M) containing KI (0.1M) and I2 (50 mM) was used for the determination of photoactivity of these electrodes. In our earlier work13 we have demonstrated that this electrolyte system may
Table 1—Preparation of zinc selenide and thallium doped zinc selenide electrodes by electrochemical codeposition

<table>
<thead>
<tr>
<th></th>
<th>Tl-doped ZnSe</th>
<th>ZnSe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potential (V)</td>
<td>-0.76</td>
<td>-0.76</td>
</tr>
<tr>
<td>Current (mA)</td>
<td>1.37</td>
<td>-0.10</td>
</tr>
<tr>
<td>Deposition time (h)</td>
<td>4.0</td>
<td>4.0</td>
</tr>
</tbody>
</table>

Solution composition; for Tl-doped ZnSe: 0.01 M ZnSO₄; 0.01 M SeO₂; 0.001 M Tl(NO₃)₂; for ZnSe: 0.01 M ZnSO₄; 0.01 M SeO₂.

Table 2—Photoactivity of zinc selenide and thallium doped zinc selenide

<table>
<thead>
<tr>
<th></th>
<th>ED (mV)</th>
<th>EL (mV)</th>
<th>Ep (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc selenide</td>
<td>-109</td>
<td>-79</td>
<td>30</td>
</tr>
<tr>
<td>-130</td>
<td>+12</td>
<td>142</td>
<td></td>
</tr>
<tr>
<td>Tl-doped ZnSe</td>
<td>-285</td>
<td>+60</td>
<td>345</td>
</tr>
<tr>
<td>-285</td>
<td>-40</td>
<td>245</td>
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</tbody>
</table>

Table 3—Initial rate of buildup (R_d), initial rate of decay (R_d), half decay time (t_1/2) and rate constant (k) values

<table>
<thead>
<tr>
<th></th>
<th>R_d (mV s⁻¹)</th>
<th>R_d (mV s⁻¹)</th>
<th>t_1/2 (s)</th>
<th>k (s⁻¹)</th>
</tr>
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<tr>
<td>Zinc selenide</td>
<td>81.5</td>
<td>47.5</td>
<td>2.0</td>
<td>0.18</td>
</tr>
<tr>
<td>Tl-doped ZnSe</td>
<td>183.3</td>
<td>2.6</td>
<td>2.53</td>
<td></td>
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</table>

Fig. 1—Typical electrodeposition curve

Fig. 2—Ep versus log light intensity curve [Light intensity was varied using a voltage regulator and is expressed in terms of volts used to illuminate a 1000 watt tungsten lamp. 1 M ZnSO₄ solution containing 0.1 M KI and 50 mM I₂ was used in all cases]

Fig. 3—Typical curve for validity of equation: $E_p = E_{p0} e^{-kt}$.

be used with advantage for testing the activity of zinc selenide photoelectrode.

Both zinc selenide and Tl-doped zinc selenide electrodes become anodic upon illumination indicating their p-type semiconducting nature. Thallium-doped zinc selenide, however, exhibits much improved functional activity. Incorporation of thallium is expected to enhance p-semiconductivity of zinc selenide, and enhanced photoactivity shown by the Tl-doped electrode is consistent with this expectation. Variation of photoeffect with light intensity shown in Fig. 2, indicates the formation of a good Schottky barrier. It has been shown earlier that the buildup of photopotential and its decay are much faster in the case of thallium containing zinc selenide. The initial rate of buildup, initial rate of decay of photopotential and half-time decay values of zinc selenide and Tl-doped zinc selenide electrodes are compared in Table 3. It was shown earlier that the buildup of photopotentials follows the first order
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Fig. 4—Mott-Schottky plots [- • , ZnSe; and - ○ , Tl-doped ZnSe]

Fig. 5—Functional stability of Tl-doped zinc selenide electrode under intermittent illumination

<table>
<thead>
<tr>
<th></th>
<th>$E_{fb}$ (V vs SCE)</th>
<th>$N_D$ (cm$^{-3}$)</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc selenide</td>
<td>0.69</td>
<td>3.5 x 10$^{15}$</td>
<td>2.17</td>
</tr>
<tr>
<td>Tl-doped selenide</td>
<td>0.54</td>
<td>4.22 x 10$^{17}$</td>
<td>1.75</td>
</tr>
</tbody>
</table>

Table 4—Flat band potential ($E_{fb}$), donor density ($N_D$) and band gap ($E_g$) values

kinetic Eq. (2)

$(E_p)_t = E_p^0 (1 - e^{-kt})$  

In Eq. (2) $(E_p)_t$ and $E_p^0$ denote photopotentials at time $t$ and the steady state respectively. Validity of Eq. (2) in the present case has been examined in Fig. 3. $(E_p)_t$ and $(E_p)_s$ values at different $t$ were obtained from the photopotential buildup curves. Values of rate constant ($k$) obtained from the slope of log $[E_p^0 - (E_p)_t]$ versus $t$ plots, are included in Table 3.

A comparison of the photoaction spectral studies, reveals that the threshold wavelength values in the case of zinc selenide and Tl-doped zinc selenide electrodes are 570 and 710 nm respectively. These values correspond to band gap equal to 2.17 eV for zinc selenide and 1.75 eV for Tl-doped zinc selenide. Thus incorporation of thallium results in lowering of the band gap of zinc selenide; this indicates possibility of enhancement of the capture and conversion of light into electrical energy. This is borne out by the experimental results.

The semiconductor-electrolyte interfacial region is endowed with electrical heterogeneity on account of the existence of a depletion layer on the semiconductor side. The charge distribution in the depletion layer is altered when the semiconductor potential is
varied. The capacitance, $C_{sc}$, thus depends on the electrode potential, this dependence is usually expressed in terms of Mott-Schottky relations\textsuperscript{22,23} (see Eq. 3)

$$\frac{1}{C_{sc}^2} = \frac{2}{\varepsilon \varepsilon_0 q N_D} (E - E_{fb})$$  \hspace{1cm} (3)

In Eq. (3) $N_D$ is the charge carrier density, $\varepsilon$ and $\varepsilon_0$ are the dielectric constants of the vacuum and semiconductor; $q$ is the electronic charge and $E_{fb}$, the flat band potential of the semiconductor.

$1/C_{sc}^2$ versus E plots presented in Fig. 4 support the inference that Tl-doped zinc selenide prepared by electrochemical codeposition exhibits p-type semiconductivity. This is also consistent with the current-voltage behaviour of the electrode examined in dark and under illumination. The donor density and the flat band potential values derived from the slope and intercept on the potential axis respectively of the Mott-Schottky plots (Fig. 4) are compared in Table 4 for zinc selenide and Tl-doped zinc selenide. While $E_{fb}$ values are comparable in the two cases, the donor density is substantially higher in the case of Tl-doped zinc selenide, again indicating the possibility of enhanced photoresponsiveness.

Zinc selenide\textsuperscript{24} exhibits reasonable stability and activity when tested in cadmium acetate solution containing potassium iodide and iodine. Photoelectroactivity data obtained using Tl-doped zinc selenide, presented in Fig. 5, show that no impairment in its functional activity occurs during the period of investigation.

**Acknowledgement**

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**References**