Electrosynthesis and photoelectroactivity of polycrystalline *p*-zinc selenide

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Abstract. The photoelectroactivity of polycrystalline zinc selenide films prepared by
electrochemical codeposition in zinc sulphate solutions of different concentrations containing
the \(I^-/I_2\) redox couple has been investigated. Measured photopotentials, photocurrents and
the initial rate of build-up of photopotentials indicate a significant enhancement in photo-
electro-convertibility with increase in concentration, in spite of practically no change in the
flat band potentials. The photoelectroactivity of a \(p-n\) heterojunction photoelectrochemical
cell using cadmium selenide along with zinc selenide has also been studied.

Keywords. Photoelectrochemical cell; electrochemical codeposition; semiconductor photo-
electrochemistry; energy conversion.

1. Introduction

Cadmium chalcogenides are among the most studied materials for photoelectrodes
in photoelectrochemical cells (Ellis *et al* 1976; Heller *et al* 1977; Cahen and Hodes
1978). These electrodes exhibit reasonable conversion efficiencies and successfully
resist the impairment in functional activity when illuminated in aqueous polysulphide
solutions. The photoelectroactivity of zinc selenide has also been studied to some
extent (Lemasson and Gautson 1981; Lemasson *et al* 1982; Russak 1982). Zinc
selenide usually exhibits *n*-type semiconductivity. For solar energy conversion *p*-type
semiconductors with acceptable stability and compatibility are important so that
enhanced photoresponsiveness when illuminated may become possible. We have
prepared zinc selenide electrodes by electrochemical codeposition using limiting
currents to study their photoelectroactivity in aqueous zinc sulphate solution
containing the \(I^-/I_2\) redox couple. All preparations exhibit *p*-type semiconductivity.
Capacitance was measured for characterization in terms of flat band potential. The
current-voltage behaviour in dark and under illumination along with the capacitance
data were used to establish their *p*-type semiconductivity. The observed photopoten-
tials vary with light intensity and exhibit a tendency towards saturation at
higher light intensities.

2. Experimental

The procedure as reported earlier (Singh and Rai 1985; Singh *et al* 1986) was used for
preparing zinc selenide electrodes. A titanium plate (1.69 cm\(^2\)) was cleaned with
emery paper, polished with diamond paste (Madras Metallurgical Service Limited)
and washed successively with acetone and deionized water. It was then soaked for
about an hour using zinc sulphate and \(\text{SeO}_3\) of known composition. The limiting
current needed for electrochemical codeposition of zinc selenide was determined in
the usual manner (Glasston 1971; Vagramyan and Solov’eva 1961) by varying the
potential of the titanium electrode with respect to a saturated calomel electrode
using an electronically operated power supply (Hindustan Power Tronic Inc) and measuring the current between the titanium electrode and a platinum electrode. Deposition was carried out for about 4 h. The thickness of the zinc selenide film was $5 \times 10^{-4}$ cm.

A simple experimental arrangement (Ellis et al 1976) was used for testing the photoelectroactivity of the zinc selenide preparations. Zinc sulphate solution containing KI and $I_2$ was used to combine the zinc selenide electrode with a platinum counterelectrode to form the photoelectrochemical cell. A tungsten lamp (1000 W) was used for illumination and the photopotential thus generated was measured using a digital multimeter (HIL 2142, Delhi) with a least count of 0.1 mV. The photopotential build-up and decay were recorded (Anika recorder A-4) and the current-voltage characteristics both in dark and under illumination were studied using a standard potentiostat (DB Electronics, Pune model 1078). For capacitance measurements a digital LCR meter (VLCR 7, Vasavi Electronics, Secunderabad) was used.

3. Results and discussion

Photoelectroactivity data obtained using zinc selenide prepared by electrochemical codeposition in conjunction with a platinum counterelectrode are summarized in table 1. Zinc sulphate solutions of different concentrations containing the $I_2$ redox couple were used. The variations of photopotential $E_p$, and photocurrent $I_p$ with relative light intensity are shown in figures 1 and 2 respectively.

<table>
<thead>
<tr>
<th>Electrolyte solution</th>
<th>$E_D$ (mV)</th>
<th>$E_I$ (mV)</th>
<th>$E_p$ (mV)</th>
<th>$I_D$ ($\mu$A)</th>
<th>$I_L$ ($\mu$A)</th>
<th>$I_P$ ($\mu$A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 M ZnSO$_4$</td>
<td>−154</td>
<td>+171</td>
<td>325</td>
<td>0.4</td>
<td>30.5</td>
<td>30.9</td>
</tr>
<tr>
<td>2 M ZnSO$_4$</td>
<td>−300</td>
<td>+186</td>
<td>486</td>
<td>0.6</td>
<td>52.9</td>
<td>53.5</td>
</tr>
<tr>
<td>4 M ZnSO$_4$</td>
<td>−310</td>
<td>+250</td>
<td>560</td>
<td>2.5</td>
<td>69.8</td>
<td>72.3</td>
</tr>
</tbody>
</table>

Figure 1. Variation of photopotential with relative light intensity. (Δ) 1 M ZnSO$_4$ + 0.1 M KI + 50 mM $I_2$; (●) 2 M ZnSO$_4$ + 0.1 M KI + 50 mM $I_2$; (○) 4 M ZnSO$_4$ + 0.1 M KI + 50 mM $I_2$. 

Figure 2. Variation of photocurrent with relative light intensity. (Δ) 1 M ZnSO$_4$ + 0.1 M KI + 50 mM $I_2$; (●) 2 M ZnSO$_4$ + 0.1 M KI + 50 mM $I_2$; (○) 4 M ZnSO$_4$ + 0.1 M KI + 50 mM $I_2$. 

Table 1. Photoelectroactivity of zinc selenide in different solutions (each zinc sulphate solution contains 0.1 M KI and 50 mM $I_2$).