

SURFACE MODIFICATION OF CADMIUM SULPHIDE PHOTOANODES WITH ELECTRODEPOSITED RUTHENIUM

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[Received: 1992 March]

Cyclic voltammetry, space-charge capacitance variation with electrode potential and spectral dependence of quantum efficiency have been studied for ruthenium plated cadmium sulphide single crystal electrodes in 1M NaOH–0.1M Na₂S–0.1M S electrolyte. The results were compared with those obtained for bare CdS photoelectrodes. The ruthenium covered electrode registered a lowering of the barrier height at the semiconductor–electrolyte junction while the spectral response was better for short wavelengths. The ruthenium plated cds electrode showed a poorer power output.

Key words: Cadmium sulphide, photoanode, electrodeposition of ruthenium thin film

INTRODUCTION

Semiconducting cadmium sulphide has been widely studied as a solar cell material in both solid state and photoelectrochemical (PEC) energy conversion devices. The sustained interest in this material is due to its favourable position of the band edges in aqueous electrolyte for the direct splitting of water into hydrogen and oxygen [1] which is, of course, the cherished goal of many photochemists and photoelectrochemists worldwide [2].

The photo electrochemical studies on thin film CdS photoanodes in aqueous polysulphide electrolyte have recently been reported [3–6]. In photoelectrochemistry, the interest in semiconductor surfaces treated with metal ions or in some cases plated with transition metal films has been due to improved photoeffects [7–10]. Studies with CdS electrodes modified with Zn or Ag ions have been reported [13,14].

Adam Heller [15] observed enhanced photoactivity on InP electrodes covered with Ru, Rh or Pt metal islands formed by electrodeposition. The presence of Ru on the surface is ensured with greater certainty by electrodeposition than by chemisorption. Tomkiewicz et al [16] investigated the effect of chemisorbed Ga, Ru and Zn ions on the surface of CdSe photoelectrodes. They concluded that metal ions, known to catalyze hydrogen reduction e.g., Ru³⁺, increased the cathodic dark current thus effecting an anodic shift in the open-circuit voltage, while those which were poor electrocatalysts for hydrogen evolution e.g., Ga³⁺ had the opposite effect. The effect of thin Pt overlayers on the performance of CdS photoanodes has been reported only recently [17]. In the present communication, the results on the photoelectrochemical behaviour of Ru-plated CdS electrodes are reported.

EXPERIMENTAL

CdS single crystals grown by the Piper and Pollich method have been used in the present investigations. They have resistivity of 80 ohm cm and a free electron concentration of $2.91 \times 10^{18} \text{ cm}^{-3}$. Ruthenium nitroschloride plating bath was prepared from RuCl₃·5H₂O by standard procedure [18,19]. The deposition was carried out for 15 minutes at a constant electrode potential of -0.2V (vs SCE). The plated electrodes were washed thoroughly with triple distilled water and were air dried.

The experimental arrangement used for the PEC studies was

the same as the one used before and described elsewhere [3,5]. The PEC experiments were conducted in a standard 3-electrode Corning glass electrochemical cell using a Pt foil counter electrode and a saturated calomel reference electrode. 1M NaOH- 0.1M Na₂S –0.1M S was used as the electrolyte. Space charge capacitance was measured by the lock-in technique at a frequency of 400 Hz.

RESULTS AND DISCUSSION

The thickness of the Ru coating was estimated to be 790 Å (approximately) from the plating current and the time of deposition using a value of $0.26347 \times 10^{-3} \text{ g.C}^{-1}$ for the electrochemical equivalent of Ru.

Figure 1 shows the cyclic voltammograms (cv) obtained at 50 mV. sec⁻¹ for the CdS electrode–electrolyte junction before and after Ru plating.

From the figure, it may be noted that the onset of dark cathodic current takes place at about -1.13V(SCE) for the bare electrode and considerably at less negative potentials of -0.85V(SCE) for the Ru plated electrode. The voltammogram for the bare electrode further revealed an anodic peak at -0.65V(SCE) and a cathodic peak at -1.35V(SCE) during the forward potential sweep. Two more cathodic peaks were observed at -1.63 and -0.75V(SCE) on the reverse scan. It has been recently reported [20] that CdS decomposes cathodically at potentials negative of -1.4V(SCE) and that deposition of metallic catalysts like Pt or RuO₂ shifts the onset potentials of both the oxygen reduction as well as hydrogen production by about 0.45V in the anodic direction. In the light of these observations, the anodic and cathodic direction. In the light of these observations, the anodic and cathodic peaks at -0.65 and -0.75V(SCE) (Fig. 1), can be associated with the stripping and the deposition of dissolved Cd²⁺ ions. The reduction peaks at -1.35 and -1.63V(SCE) signify cathodic decomposition of CdS. It is interesting to note that the above peaks were absent in the voltammogram obtained for the Ru plated electrode. However, a small hump at and around -1.75V(SCE) was noticed during the return anodic scan.

On illumination, the voltammogram for the bare CdS revealed anodic and cathodic peaks at -0.97 and -1.36V(SCE) respectively. According to Meissner et al [20], the anodic oxidation peaks for CdS occur usually between -1.0 and 0.3V(SCE). The heights

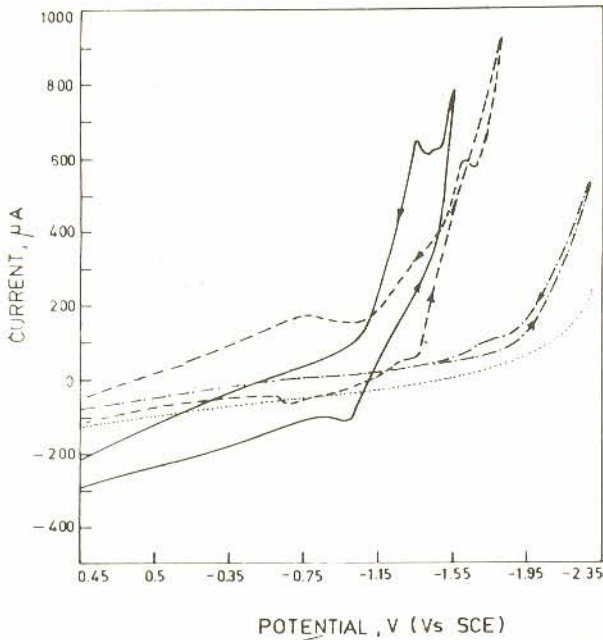


Fig. 1: Cyclic Voltammograms for the cell CdS/1M NaOH-0.1M Na₂S - 0.1M S/Pt

- in dark
- - - under illumination
- Ru coated CdS in dark
- under illumination

and potentials of these peaks depend largely on the amount of previous anodic corrosion, the amount of oxygen dissolved in the electrolyte and the time of cathodic polarization at potentials negative of -0.9V(SCE). It is therefore difficult to predict the reactions occurring at these potentials.

The variation of space charge capacitance with electrode potential is shown in Fig. 2. The extrapolated intercepts on the potential axis revealed values of flat-band potential,

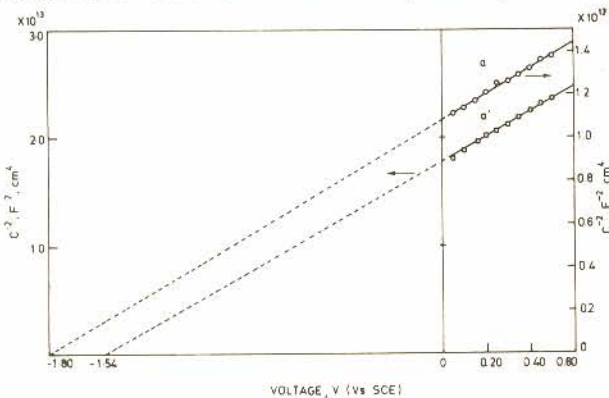


Fig. 2: Mott-Schottky plots for CdS/1 M NaOH 0.1 M Na₂S - 0.1M S/Pt at 400 Hz
a - cds
a' - Ru coated CdS

$V_{fb} = -1.80$ and $-1.54V$ (SCE) respectively for the bare and Ru covered electrodes. The observed positive shift of $0.26V$ in the value of the flat-band potential and $0.28V$ in the onset potential for oxygen reduction are in excellent agreement and generally indicates a decrease in the barrier height at the interface. The linear nature of the plots in Fig. 2 suggests that the donor ionisation was uniform over the depletion region. The ionised donor densities were found to be $2.28 \times 10^{18} \text{ cm}^{-3}$ and $1.14 \times 10^{18} \text{ cm}^{-3}$ respectively from

the slopes of the straight lines "a" and "a'" of Fig. 2. A static dielectric constant of 10.3 was assumed in these calculations. The donor densities thus obtained agreed reasonably well with the electron concentration of $2.19 \times 10^{18} \text{ cm}^{-3}$ for CdS as measured by Hall-effect experiments.

The normalized spectral response over the wavelength range 400–700 nm (Fig. 3) showed a gradual increase in the response with increase in wavelength. The maximum of the response occurred at 500 nm for the bare Ru plated CdS PEC cells. The latter exhibited a better short wavelength response particularly over the wavelength region of 460–520 nm where CdS absorbs most of the radiation. At 500 nm, the quantum efficiency is approximately 1.6 times higher for the Ru plated CdS PEC cell. This is expected, for Ru has been shown [15] to reduce recombination losses and thereby enhance the collection efficiency of the photogenerated charge carriers. The variation of the response over the sub-band gap region also supports this view. As is well known, the magnitude of the response in this wavelength region is indicative of the density of surface states which mediate the charge transfer to the electrolyte. The Ru plated CdS PEC cell thus showed lower sub-band gap response as expected and also has a response cut-off at 610 nm compared to 680 nm for the bare CdS PEC cell.

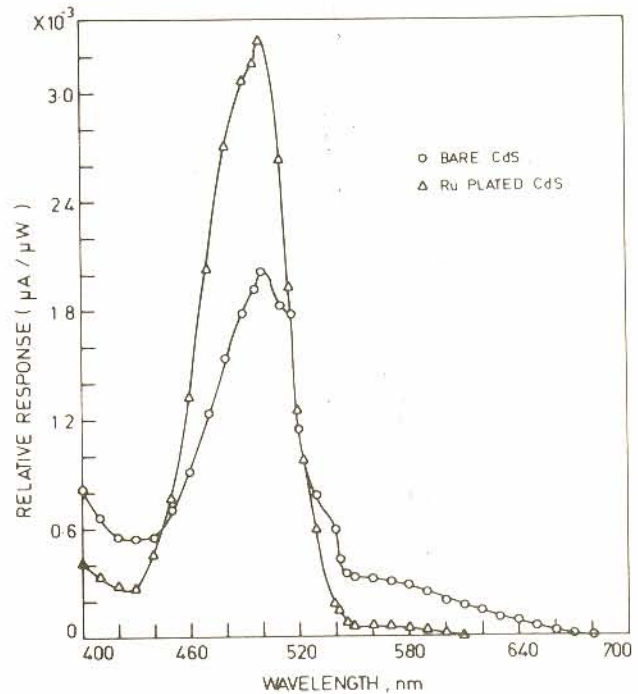


Fig. 3: Spectral response for the CdS PEC cell
○ ... ○ CdS
△ ... △ Ru plated CdS

The power output characteristics for the two PEC cells are compared in Fig. 4. At $30 \text{ mW} \cdot \text{cm}^{-2}$ tungsten-halogen illumination, $V_{oc} = 0.33$, $J_{sc} = 0.94 \text{ mA} \cdot \text{cm}^{-2}$ and fill-factor, $FF = 0.31$ were obtained for the PEC cell using the bare CdS photoanode. For the cell using the Ru plated CdS electrode, the power output was poor and the values of V_{oc} , J_{sc} and FF were $0.08V$, $0.35 \text{ mA} \cdot \text{cm}^{-2}$ and 0.31 respectively.

CONCLUSION

The electrodeposited Ru on CdS showed an electrocatalytic effect by shifting the onset potentials for oxygen reduction to more

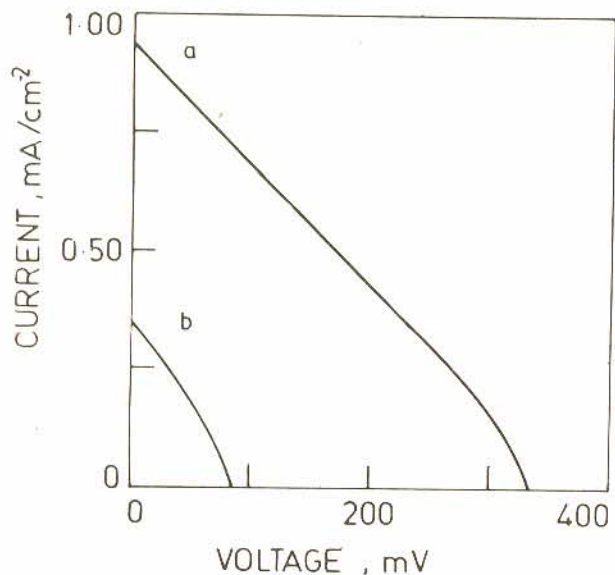


Fig. 4: I-V curve for (a) CdS (b) Ru coated CdS

positive values. The spectral response studies indicated better short wavelength response for the PEC cell using the Ru plated CdS photoanode. The positive shift observed in the value of the flat-band potential for the Ru covered electrode indicated a decrease in the barrier height at the CdS-electrolyte junction.

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