Successively pulse plated cadmium selenide films and their photoelectrochemical behaviour

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Abstract. In successive pulse plating, the pulse deposition is repeated after a definite duration of plating preceded by a mild cleaning of the electrode and with a fresh deposition bath for the same duration. In this study, CdSe films were deposited on Ti substrates by successive pulse plating from a bath containing CdSO₄ and SeO₂ at a current density of 80 mA cm⁻² and a duty cycle of 3.3% for a duration of 30 min. The films heat-treated to 550°C for 20 min in argon atmosphere, were polycrystalline with a hexagonal structure. At an illumination of 60 mW cm⁻², a conversion efficiency of 4.5% for the photoetched film and 1.7% for the chemically etched one were determined.

Keywords. Cadmium selenide; pulse plating.

1. Introduction

n-CdSe has been used as a photoanode in photoelectrochemical (PEC) cells to give a high power conversion efficiency, both in single crystal and polycrystalline forms. In recent years, there has been considerable work in the study of polycrystalline electrodes for PEC cells, since 70% of the single crystal efficiency can be obtained with low cost polycrystalline films. Vacuum evaporation, spray pyrolysis, chemical bath deposition, slurry coating, electrodeposition etc have been employed earlier for the preparation of these films. We report here the results on successively pulse plated CdSe films.

Metal deposits obtained by pulse plating show distinct advantages like improved deposit distribution, adhesion and lower impurity content compared to conventional dc electrodeposition. The properties of the deposit can be varied by varying the current density and duty cycle. Higher nucleation rates are possible with pulse plating (Rehrig *et al* 1977; Popov *et al* 1980; Lam *et al* 1983). Crack-free hard deposits with low porosity and low internal stress are obtainable with pulsing (Devaraj *et al* 1989a, b). An increased average grain size and uniform grain distribution (compared to conventional electrodeposition) are noticed in pulse plated films.

The main purpose of carrying out successive pulse plating (pulse deposition repeated after a definite duration of plating preceded by a mild cleaning of the electrode and with a fresh deposition bath for the same duration) is to obtain higher film thicknesses which, in turn will yield higher grain size (Saitoh *et al* 1976) due to better nucleation sites, yielding higher conversion efficiencies (Lanza and Hovel 1980; Pandey *et al* 1991) for photoelectrochemical cells.

This paper reports the comparative PEC results obtained with successively pulse plated CdSe films with those obtained by conventional pulse plating. The improvements in the output parameters have justified the expectations.

2. Experimental

CdSe films (3 μm thick) were pulse plated cathodically at room temperature on Ti substrates employing a bath of 0.5 M CdSO_4 and 0.005 M SeO_2 , which was kept stirred. Graphite was used as the other electrode with an inter-electrode distance of 2 cm. A current density of 80 mA cm^{-2} was employed with an on-time of 1 sec and off-time of 29 sec making the duty cycle 3.3%. Then, the substrates along with the deposited films were taken out, washed well with triple distilled water and introduced in a fresh bath solution of the same composition for a second pulse deposition (which we call successive pulse plating). The other parameters such as current density, duty cycle etc were kept constant for the successive pulse deposition and repeated for the same duration of 30 min. The thickness of the films were found to be 5 μm .

The films were heat treated at 550°C for a duration of 20 min in argon atmosphere, and characterized by X-ray diffraction using CuK_α radiation. Optical absorption studies were carried out employing a Hitachi U 3400 UV-VIS-NIR spectrophotometer. Surface morphology was examined by 35 CF JEOL scanning electron microscope.

The PEC cell consisted of the photoelectrode and a graphite counter electrode with 1 M alkaline polysulphide as the electrolyte. The light source was an Oriel 250 W tungsten halogen lamp. The photon flux reaching the electrode surface was measured by a CEL Suryamapi. After heat treatment, the electrodes were etched chemically in 1 : 3 HCl for 5 sec and rinsed in triple distilled water. Photoetching was performed by shorting the photoelectrode and the counter electrode in 1 : 3 HCl for different durations in the range of 5 to 60 sec under an illumination of 60 mW cm^{-2} . $C-V$ measurements were carried out in polysulphide electrolyte using an EG and G PARC impedance system at different frequencies. Quantum efficiencies at different wavelengths in the range 550–820 nm were measured employing an Applied Photophysics $f/3.4$ monochromator with a resolution of 0.2 nm.

3. Results and discussion

The X-ray diffraction pattern of a successively pulse plated film is shown in figure 1. The diffractograms indicate the polycrystalline nature of the film with all the major peaks corresponding to hexagonal CdSe. Peaks corresponding to elemental Se or Cd are not present. Surface morphology of the films indicate an average grain size of 3 μm . The grain size is found to increase from 1 to 3 μm after successive pulse deposition.

The power output characteristics of the PEC cells employing the regular pulse deposited and successively deposited films are shown in figure 2. While for the regular pulse deposited films, a V_{oc} of 435 mV, J_{sc} of 3.2 mA cm^{-2} , fill factor (FF) of 0.43 and efficiency (η) of 1% are obtained, for the successively pulse plated films a V_{oc} of 450 mV, J_{sc} of 5 mA cm^{-2} , FF of 0.46 and η of 1.7% are obtained. From the $I-V$ curves, series resistance (R_s) values of 58 ohms and 40 ohms and shunt resistance (R_{sh}) values of 1.66 kohms and 3 kohms have been obtained for the two cases respectively. The enhanced output for the successively pulse plated films is due to their increased grain size. After a 60 sec photoetch of the successively pulse plated films, the output parameters are: $V_{oc} = 475 \text{ mV}$, $J_{sc} = 11.7 \text{ mA cm}^{-2}$, FF

$= 0.48$ and $\eta = 4.8\%$. The cell shows an R_s of 18 ohms and high R_{sh} of 3.5 kohms. For the present study, a large number of films [50] had been prepared. The variation in efficiency among the cells was from 4.5% to 4.8%. Other measurements carried out on the successively pulse plated films are V_{oc} , quantum efficiency, minority carrier diffusion length, diffusion layer width and the conductivity.

Figure 1. X-ray diffraction pattern of the CdSe film.

Figure 2. Power output characteristics of the CdSe film. a. single pulse deposited, b. successive pulse deposited and c. after photoetching.

Mott-Schottky plot for a frequency of 10 kHz in 1 M polysulphide electrolyte is shown in figure 3. The linearity of the plot suggests that the impurities are uniformly ionized (Ramprakash *et al* 1988). From the extrapolated intercept on Y-axis, a flat band potential (V_{fb}) of +1.19 V vs SCE was obtained. The plot indicates *p*-type behaviour for the films. *p*-type behaviour has also been reported by Hodes *et al* (1992) for the quantum box CdSe semiconducting films and the reason for the *p*-type behaviour has not been well understood. From the slope of the plot, a value of $5.65 \times 10^{16} \text{ cm}^{-3}$ has been deduced for the carrier density.

Quantum efficiency (ϕ) was evaluated from the spectral response measurements by employing the following expression (Segui *et al* 1991)

$$\phi = \frac{1240 J_{sc}}{\lambda P}, \quad (1)$$

where J_{sc} is current density expressed in A cm^{-2} ; λ the wavelength expressed in nm and P the radiant power absorbed in the photoactive region, expressed in W cm^{-2} . Figure 4 shows the variation of quantum efficiency in the wavelength range 550–820 nm.

A peak quantum efficiency of 0.61 is observed in the region 650–700 nm, agreeing with the band gap of the material.

From Gartner's photocurrent equation for a metal–semiconductor junction, quantum efficiency, ϕ , (Russak *et al* 1980) follows the relation

$$\phi = 1 - (e^{-\alpha W}/1 + \alpha L_p), \quad (2)$$

Figure 3. Mott-Schottky plot of successively pulse plated CdSe film in 1 M polysulphide at 10 kHz.

where W is the depletion layer width given by

$$W = [(2\epsilon\epsilon_0/qN_D) (V - V_{fb})]^{1/2}, \quad (3)$$

q is the electron charge, α the absorption coefficient, L_p the diffusion length of the minority carriers, ϵ the dielectric constant of the semiconductor, ϵ_0 the permittivity of free space, V the electrode potential, V_{fb} the flat band potential and N_D the doping density. By choosing a wavelength of relatively weak absorption so that $L_p \ll 1$ and $W \ll 1$ (Pandey *et al* 1991), the following relationship is obtained

$$\phi = L_p.$$

Hence

$$\phi^{-1} = (L_p)^{-1}.$$

A plot of ϕ^{-1} vs α^{-1} is shown in figure 5. L_p is obtained from the inverse of the slope and is found to be $0.98 \mu\text{m}$. This value of L_p is in close agreement with the value of $0.8 \mu\text{m}$ reported (Russak *et al* 1980) for a CdSe film obtained by the dc electrodeposition technique.

In order to obtain W , (2) can be rearranged as

$$W = -\ln [(1 - \phi) (1 + \alpha L_p)] / \alpha \quad (4)$$

Substituting the corresponding values of α and ϕ when $W \ll 1$, we obtain $W = 0.3 \mu\text{m}$. The maximum reported value (Gutierrez and Salvador 1987) of W for CdSe films is $0.7 \mu\text{m}$. The reported conversion efficiencies are 11.7% for a PEC cell

Figure 4. Variation of quantum efficiency (ϕ) with wavelength (λ) for the PEC cell employing successively pulse plated CdSe films.

Figure 5. Variation of inverse quantum efficiency (ϕ^{-1}) with reciprocal of absorption coefficient (α^{-1}) for the PEC cell.

with a chemically deposited polycrystalline CdSe film (Savado and Mandal 1992) with surface modification and 7.3% with the film obtained by the dc electrodeposition technique (Szabo and Cocivera 1986) and 7.4% with the films obtained by brush plating technique (Murali *et al* 1994).

From the measurement of cross-plane resistance of the CdSe film, the conductivity has been found to be $0.02 \text{ ohm}^{-1} \text{ cm}^{-1}$. Employing the values of N_D , the mobility of the electrons is found to be $2.4 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$. This value is in agreement within the range of values reported (Wynands and Cocivera 1992) for the electrodeposited CdSe films.

4. Conclusion

The results of the present study indicate that successive pulse plating improves PEC characteristics. There is reason to expect that quantum efficiency and power conversion efficiency can be enhanced further by optimizing the heat treatment and etching steps and also pulse parameters.

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