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## High temperature electrodeposition of CdS thin films on conductive glass substrates

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**Abstract.** We study the possibility of preparing thin CdS films on conductive glasses by high temperature molten salt electrocrystallization. The CdS films have been electrodeposited on ZnO or ITO coated glass substrates in solution of CdCl<sub>2</sub> and Na<sub>2</sub>SO<sub>3</sub> in fused LiCl–KCl eutectic. They consist only of hexagonal phase  $\alpha$ -CdS irrespective of the crystal structure of the substrates (hexagonal for ZnO and cubic for ITO). CdS films deposited on ZnO coated glass consist of single platelets oriented with the (0001) face parallel to the substrate. They are yellow in colour and show good adhesion to the substrates at higher current density ( $>0.4 \text{ mA cm}^{-2}$ ) and long deposition time ( $>30 \text{ min}$ ). The films of CdS deposited on ITO/glass are more dense under identical conditions which is explained by the lower resistivity of the ITO layers in comparison with ZnO layers.

### 1. Introduction

Thin films of CdS have been used as a junction partner in solar cells for many years. A great progress has been recently reached in high efficiency photovoltaic polycrystalline thin film heterostructures based on CdTe and CuInSe<sub>2</sub> (CIS) [1]. They have typical configuration glass/conductive oxide/n-CdS/p-CdTe (CIS)/contact. Tuttle *et al* [2] achieved an efficiency of 17.7% for a CIS solar cell. Aramoto *et al* [3] and Bhattacharya *et al* [4] demonstrated solar cell efficiency of 16% and 13.7% for CdTe and CIS, respectively. In these systems the n-CdS thin film constituted an integral component. The wide bandgap (2.42 eV) of the latter serves as a window layer after which a narrow bandgap p-type light absorbing semiconductor layer is deposited. Zinc oxide (ZnO) or indium tin oxide (ITO) layers on glass served as conductive layers. The latter transmit wavelengths longer than 400 nm.

A series of low cost methods: close space sublimation [5], screen printing [6, 7], chemical bath deposition [8–12], electrodeposition from aqueous [13–16] and organic solutions [17], solution growth [18] etc, have been used to fabricate CdS layers on conductive glasses. A critical step in all these methods is chemical (in hydrogen or argon ambient) and heat treatments carried out at temperatures higher than 400 °C leading to recrystallization of the films, increase in grain size and improvement of the adhesion. High temperature electrodeposition in molten alkali halides is a promising low cost method for fabrication of thin semiconductor films on various substrates as post-deposition treatment of the films is unnecessary. The wide potential span ( $\sim 3 \text{ V}$ ) in molten salts, the high ion conductivity, low viscosity, high exchange current densities and their ability to dissolve many inorganic compounds make them ideal electrolytic media for electrocrystallization of semiconductor compounds. The present work reports the

first results of cathodic deposition of CdS thin films on ZnO and ITO covered glass substrates by electrolysis in fused LiCl–KCl eutectic.

## 2. Experiment

The LiCl–KCl eutectic ( $T_m = 352\text{ }^\circ\text{C}$ ) used as a solvent has been purified in a separate set-up. The procedure consisted of vacuum drying first at room temperature and after that at  $400\text{ }^\circ\text{C}$ , followed successively by saturation with high purity hydrogen chloride gas, argon and prolonged pre-electrolysis to remove the heavy ions [19]. It was then melted in a three-electrode electrochemical cell placed in a resistant furnace (figure 1). The experiments were carried out in a glove box in argon atmosphere with low level of moisture ( $<20\text{ ppm}$ ) and oxygen ( $<5\text{ ppm}$ ). The electrochemical cell consisted of a cathode (substrates of conductive oxide layers coated on glass of size  $15 \times 10\text{ mm}^2$ ), a spectrophotometric graphite anode and an Ag/Ag<sup>+</sup> reference electrode. The latter consisted of a silver wire immersed in a solution of AgCl ( $1 \times 10^{-2}$  mole fraction) in purified LiCl–KCl eutectic, contained in a pear-shape glass bulb with a thin wall end [20].

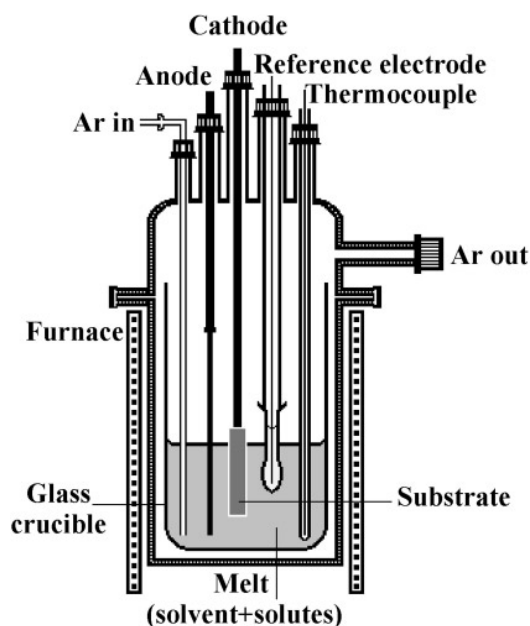


Figure 1. Experimental set-up.

Anhydrous solutes  $\text{Na}_2\text{SO}_3$  ( $1 \times 10^{-4}\text{ M}$ ) and  $\text{CdCl}_2$  ( $1 \times 10^{-3}\text{ M}$ ) were added to the LiCl–KCl as sources of sulphur and cadmium, respectively. Higher concentration of the solutes caused homogeneous precipitation of CdS in the solution. The same result is confirmed by Minoura *et al* [21] during their investigation of the cathodic deposition of CdS onto a graphite substrate.

The electrodeposition of CdS was carried out under conditions of a constant current density in the range  $0.2\text{--}1.0\text{ mA cm}^{-2}$  at temperatures  $410$  and  $450\text{ }^\circ\text{C}$ . These conditions were selected from our previous experiments of electrodeposition of CdS on Cu and Ag substrates [22]. Dry argon was introduced above the melt during the experiments.

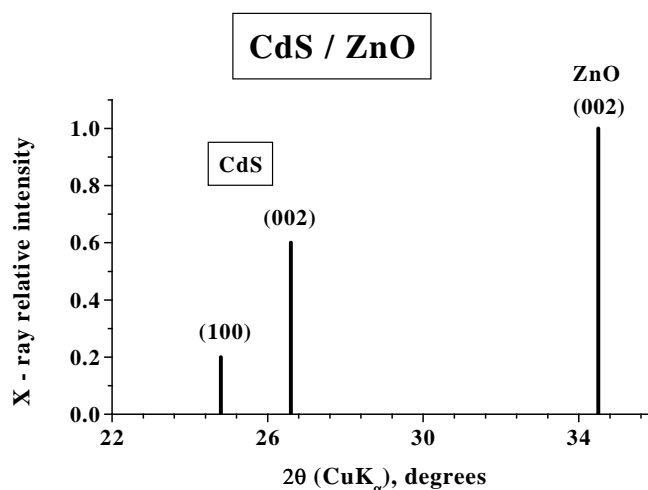
ZnO substrates represented aluminium doped ZnO (ZnO:Al) films deposited on glass substrates by R.F. magnetron sputtering (13.56 MHz) [23]. The film thickness was about 300 nm and the electrical resistivity was of the order of  $10^{-3} \Omega \text{ cm}$ . ITO substrates represented  $\text{In}_2\text{O}_3:\text{Sn}$  films prepared by d.c. sputtering on glass substrates [24] with resistivity  $2 \times 10^{-4} \Omega \text{ cm}$  at the working temperature [24]. The optical transmission in the visible range was about 90% for ZnO/glass [23] and 80% for ITO/glass [25]. Prior to the deposition the substrates were cleaned with deionized boiling water and then by an isopropylalcohol ultrasonic bath followed by degreasing in isopropylalcohol vapour.

The crystalline structure of the films were identified by x-ray diffraction analysis using  $\text{Cu K}\alpha$  radiation. The morphology of the surface was studied by scanning electron microscopy (JEOL JSM 5300).

### 3. Results

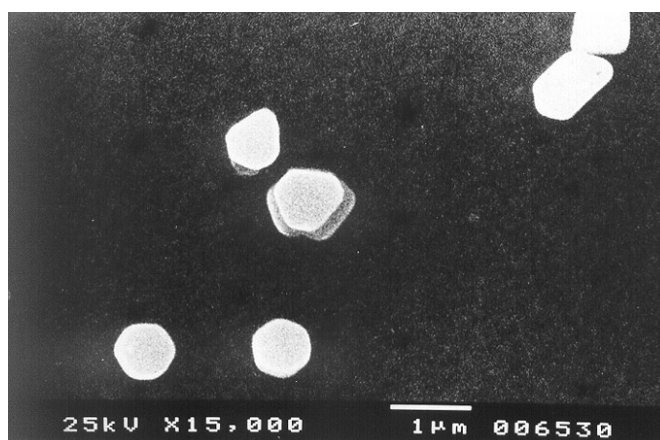
#### 3.1. CdS films on ZnO/glass substrates

The electrodeposition was performed at  $450^\circ\text{C}$ . The x-ray diffraction spectrum for CdS films deposited on ZnO/glass substrate at a low current density of  $0.2 \text{ mA cm}^{-2}$  for a short deposition time (3 min) is shown in figure 2. It consists only of two sharp peaks of CdS at  $2\theta = 24.8^\circ$  and  $26.5^\circ$  which correspond to diffraction from the (100) and (002) planes of the hexagonal phase  $\alpha$ -CdS. This is an evidence for the preferential orientation of the films with the  $c$ -axis perpendicular to the substrate. A scanning electron microscopy (SEM) picture (figure 3) shows that the films deposited at the above conditions consist of isolated ( $\approx 1 \mu\text{m}$ ) platelike crystallites.

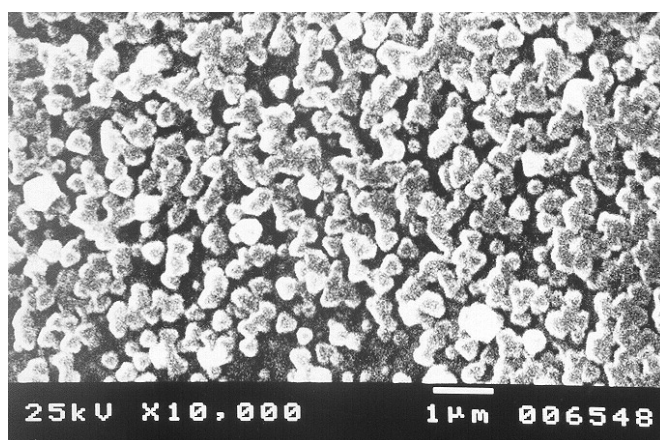


**Figure 2.** XRD pattern of CdS films grown on ZnO/glass substrate at  $450^\circ\text{C}$ ,  $0.2 \text{ mA cm}^{-2}$  for 3 min.

The increase of the deposition time (30 minutes) and the current density ( $>0.4 \text{ mA cm}^{-2}$ ) leads to a growth of more densely coated CdS films (figure 4). The x-ray diffraction pattern (figure 5) shows that the films are polycrystalline and consist of hexagonal phase  $\alpha$ -CdS only. An intensity ratio analysis indicates the tendency of the (101) plane to grow parallel to the substrate in addition to the (0001) plane. The films obtained under these conditions are yellow in colour and show good adhesion to the substrate.



**Figure 3.** SEM micrograph of CdS films on ZnO/glass substrate prepared at low current density ( $0.2 \text{ mA cm}^{-2}$ ) and short deposition time (3 min).



**Figure 4.** SEM micrograph of the surface morphology of CdS films on ZnO/glass substrate prepared at high current density ( $0.4 \text{ mA cm}^{-2}$ ) and long deposition time (30 min).

### 3.2. CdS films on ITO/glass

The electrodeposition was carried at  $410^\circ\text{C}$  because at this temperature the ITO films show the lowest resistance [24]. The x-ray diffraction pattern for CdS films deposited on ITO/glass substrate is shown in figure 6. The ITO films are polycrystalline with the cubic modification of  $\text{In}_2\text{O}_3$ . The CdS films are also polycrystalline and the x-ray peaks belong to the hexagonal phase  $\alpha$ -CdS. An SEM micrograph of the surface of CdS films prepared at low current density of  $0.2 \text{ mA cm}^{-2}$  and longer deposition time (30 minutes) is shown in figure 7. The grain size in these films is smaller than  $0.3 \mu\text{m}$ . The films obtained under these conditions are continuous as compared with the films deposited on ZnO coated glass substrates under similar conditions (see figures 3 and 4). They also show good adhesion to the substrate. Comparing figures 4 and 7 shows that the films on ITO substrates are more dense than on ZnO substrates. The higher density of the CdS films deposited on ITO/glass could be explained with the lower resistivity of ITO layers as compared with the ZnO layers.

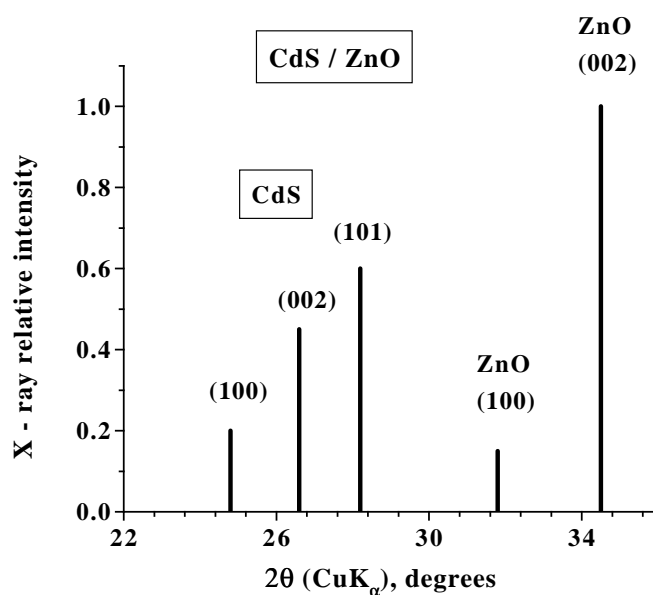


Figure 5. XRD pattern of CdS films grown on ZnO/glass substrate at 450 °C, 0.6 mA cm<sup>-2</sup> for 30 min.

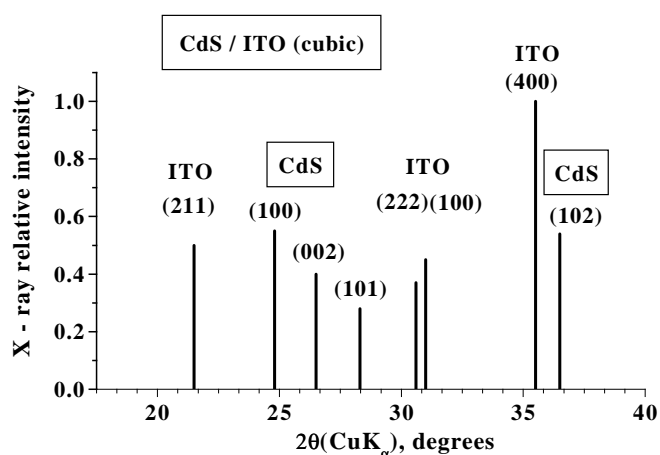
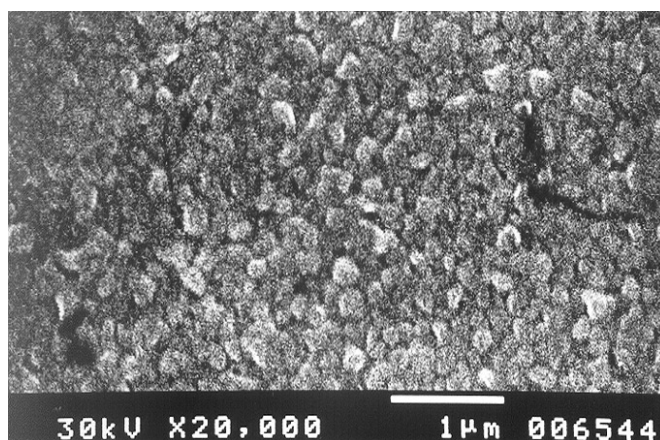


Figure 6. XRD pattern of CdS films grown on ITO at 410 °C, 0.2 mA cm<sup>-2</sup> for 30 min.

#### 4. Conclusion

As far as the authors are aware, the present study represents the first attempt at preparation of CdS thin films on different conductive oxide coated glass substrates by electrodeposition in a fused salt solution. In general, the films with the hexagonal modification  $\alpha$ -CdS were identified to deposit irrespective of the crystal structure of the substrate and the experimental conditions. This is an important result as it is well known that best solar cells are obtained with hexagonal CdS films. The films exhibit a yellow colour in contrast to the orange colour commonly shown by chemical bath deposited CdS [8]. Qualitative energy dispersive



**Figure 7.** SEM micrograph of the surface of CdS films on ITO/glass substrate prepared at low current density ( $0.2 \text{ mA cm}^{-2}$ ) and at long deposition time (30 min).

x-ray analysis shows that the ratio of Cd and S concentrations in the films is close to the stoichiometric value at all experimental conditions. The electrodeposited CdS films have good adhesion to the oxide substrates. The surface morphology of the films is similar to the surface morphology of CdS films obtained by chemical bath deposition [8–12], solution growth [18] and electrodeposition in aqueous solutions [14]. However, in all methods mentioned above a post-deposition annealing and chemical treatment is needed. A study of optical and electrical characteristics and the utility of the deposited CdS for heterojunction formation is under way.

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