

*Full Length Research Paper*

# Cyclic voltammetry studies of cadmium zinc sulfide aqueous solution

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**Cyclic voltammetry studies in aqueous solution were found to offer some noteworthy information in the electrodeposition synthesis of cadmium zinc sulfide thin film. The studies were performed at low pH, room temperature and fixed solution concentration. Suitable deposition potential ranges were obtained from this analysis. Cadmium zinc sulfide thin films were deposited at different potentials to determine optimum deposition potential. Scanning electron microscope images of deposited thin film show improved nucleation rate and crystal growth at higher deposition potential.**

**Key words:** Cadmium zinc sulfide, pH, cyclic voltammetry, synthesis.

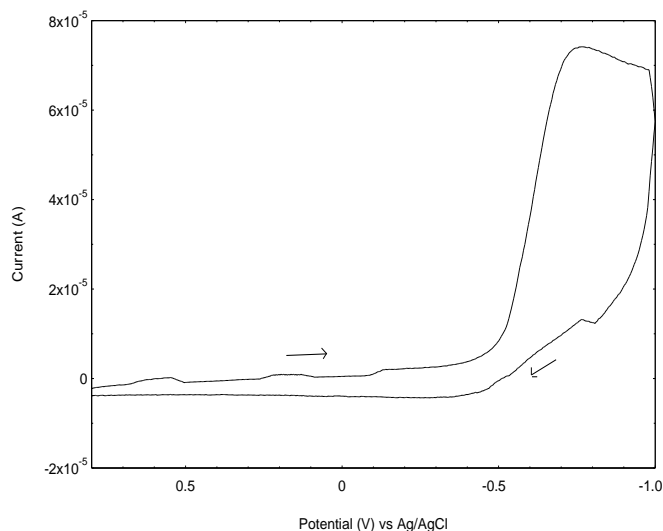
## INTRODUCTION

Cadmium zinc sulfide (CdZnS) thin films have been widely used as a wide band gap window material in heterojunction solar cells and in photoconductive devices. In solar cell systems, where CdS films have been demonstrated to be effective, the replacement of CdS with the higher band gap ternary CdZnS has led to a decrease in window absorption losses and has resulted in an increase in the short-circuit current in the solar cell (Yamaguchi et al., 1996; Jae-Hyeong et al., 2003). This CdZnS ternary compound is also potentially useful as a window material for fabrication of p-n junctions without lattice mismatch in devices based on quaternary materials like  $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$  (Yamaguchi et al., 1992) or  $\text{CuIn}(\text{S}_x\text{Se}_{1-x})_2$  (Raffaella et al., 1999). CdZnS thin films have been prepared by a variety of techniques, which include evaporation, spray pyrolysis, chemical bath deposition, dip technique and organic chemical vapor deposition. However, these techniques are plagued with their own drawbacks and difficulties. The crystallographic structure, lattice constants, optical and electrical properties and stoichiometry of the films deposited by these techniques are highly sensitive to the deposition

conditions. Among various deposition techniques, electrochemical deposition yields stable, uniform, adherent and hard films with good reproducibility by a relatively simpler process. Electrodeposition of semiconductor thin film offers the advantage over techniques in terms of controlled deposition and high material yield, and is suitable for large area deposition. Electrodeposition can be carried out using substrates with different sizes and shapes. Reactions involved occur closer to the equilibrium and the deposition process can be controlled more easily than in many high temperature gas phase methods. In addition, toxic gaseous precursors do not have to be used unlike in chemical gas phase methods. Thus, it is a simple, economical and viable technique which produces films of good quality for device applications (Saloniemi et al., 1998; Pawar et al., 2007; Manzoli et al., 2007; Switzer et al., 1995; Ihlal et al., 2007; Kois et al., 2006).

The valuable features of the electrochemical method are the convenience for producing large area surfaces, low temperature growth and the possibility to control film thickness, morphology and composition by adjusting the electrical parameters and the composition of electrolytes (Lincot et al., 2004; Bhattacharya et al., 2000; Singh et al., 1995; Friedfeld et al., 1999; Guillemoles et al., 1994). The only major limitation of electrodeposition is that the substrate has to be conductive (Zainal et al., 2004).

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**Figure 1.** Cyclic voltammogram of 0.01 M ZnCl<sub>2</sub> at pH 2 (scan rate: 5 mV/s).

## MATERIALS AND METHODS

The solutions containing dissolved 0.01 M ZnCl<sub>2</sub> (TechnoPharmChem), 0.01 M CdCl<sub>2</sub> (R & M Chemicals) and 0.01 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (SystemChemAR) were prepared using deionized water. Chemicals used in this study are analytical grade reagents. 1 M HCl (R&M Chemicals) was used to adjust solution pH and to prevent formation of hydroxyl species and insoluble compound. An EG & G PAR model 263A potentiostat/galvanostat with a three-electrode cell was used for cyclic voltammetry study. Titanium (0.8 cm diameter) was used as working electrode, platinum wire (1 mm diameter) as counter electrode and Ag/AgCl (NaCl saturated) as reference. The reference electrode was placed as close as possible to the working electrode.

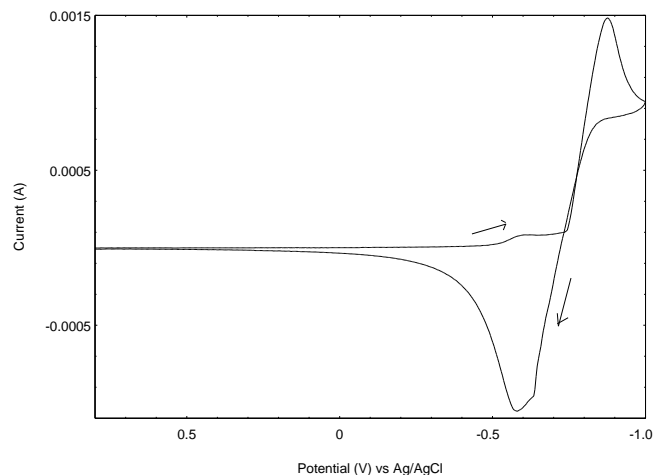
### Cyclic voltammetry studies

Cyclic voltammetry (CV) study was used to evaluate the reduction and oxidation reactions and obtain suitable deposition potential range. Cyclic voltammetry studies were carried out at a sweep rate of 5 mV s<sup>-1</sup> with the potential scanned from +1.00 to -1.00 V versus Ag/AgCl and reversed. This process was carried out at room temperature (27°C) and in unstirred solutions. Purified N<sub>2</sub> gas was purged into the electrolyte for at least 2 min to remove dissolved oxygen before starting the experiment (Zainal et al., 2005). In order to achieve optimum deposition conditions, cyclic voltammetry (CV) was performed at pH 2. The reactant solutions were analyzed individually and after mixing.

## RESULTS AND DISCUSSION

### Cyclic voltammetry of ZnCl<sub>2</sub>

Figure 1 shows the cyclic voltammogram of 0.01 M ZnCl<sub>2</sub> solution. During the forward scan, cathodic current remains low up to -0.40 V versus Ag/AgCl. However, cathodic current increases gradually from -0.45 V versus Ag/AgCl onwards indicating reduction of Zn<sup>2+</sup> ions onto



**Figure 2.** Cyclic voltammogram of 0.01 M CdCl<sub>2</sub> at pH 2 (scan rate: 5 mV/s).

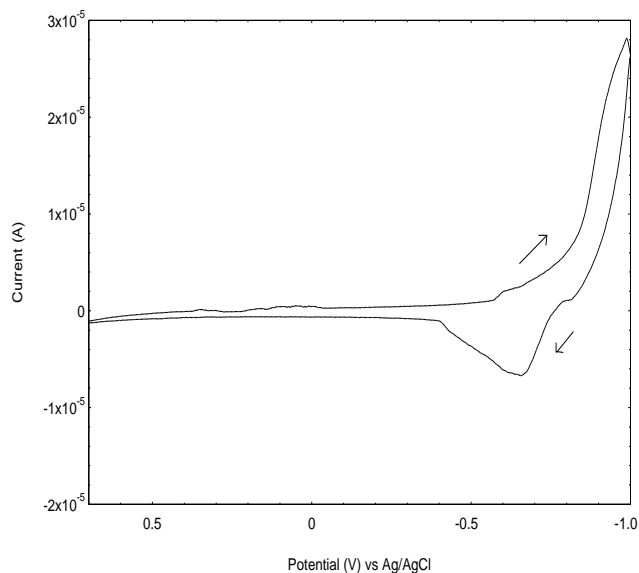
the substrate surface. The cathodic current reached a maximum value at -0.75 V and reduced after this value. The scan was not extended beyond -1.00 V versus Ag/AgCl. Further rise in potential would lead to hydrogen evolution reaction (Zainal et al., 2003):



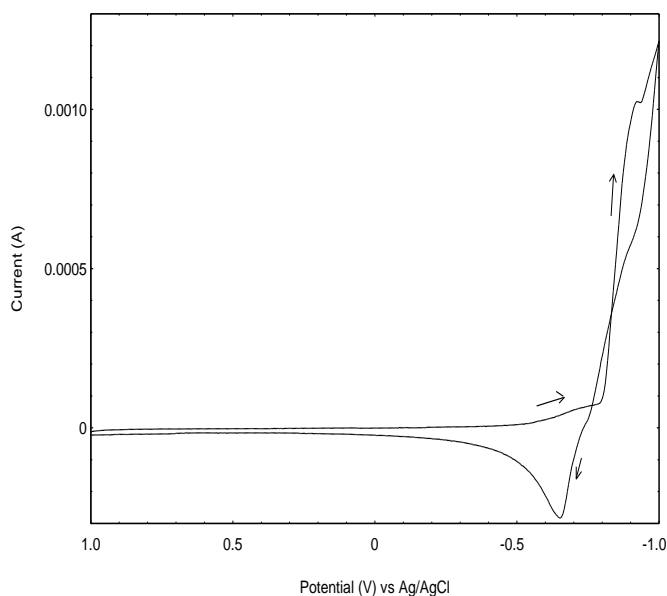
During the reverse scan, co-deposition occurred on the Zn material deposited earlier as shown by the presence of cathodic current. However, the cathodic current remained low. There was an absence of an anodic stripping peak during the reverse scan indicating that the material deposited onto the working electrode surface did not dissolve into the electrolyte. From the CV plot, we can conclude that suitable deposition potential for 0.01 M ZnCl<sub>2</sub> solution is in the range of -0.60 to -0.80 V.

### Cyclic voltammetry of CdCl<sub>2</sub>

Figure 2 shows the cyclic voltammogram of 0.01 M CdCl<sub>2</sub> solution. During the forward scan, cathodic current remained low until -0.50 V versus Ag/AgCl. As the potential was increased to more negative regions, the cathodic current increased rapidly to a maximum at -0.85 V versus Ag/AgCl indicating Cd material being deposited on the substrate. The cathodic current was reduced after this potential as the potential was swept to more negative region. However, the potential was reversed when it reaches -1.00 V versus Ag/AgCl to avoid hydrogen evolution reaction. During the reverse scan, cathodic current still remained high indicating deposition of Cd material onto the substrate. When the potential reached -0.50 V, anodic current increased indicating oxidation of Cd into the solution. From the CV plot, we can conclude that suitable deposition potential for 0.01M CdCl<sub>2</sub> solution



**Figure 3.** Cyclic voltammogram of 0.01 M  $\text{Na}_2\text{S}_2\text{O}_3$  at pH 2 (scan rate: 5 mV/s).



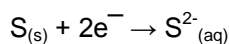
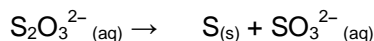
**Figure 4.** Cyclic voltammogram of 0.01 M  $\text{ZnCl}_2$ , 0.01 M  $\text{CdCl}_2$  and 0.01 M  $\text{Na}_2\text{S}_2\text{O}_3$  mixture at pH 2 (scan rate: 5mV/s)

is in the range of -0.50 to -0.90 V versus Ag/AgCl.

### Cyclic voltammetry of $\text{Na}_2\text{S}_2\text{O}_3$

Figure 3 shows the cyclic voltammogram of 0.01 M  $\text{Na}_2\text{S}_2\text{O}_3$  solution. The cathodic current increased slowly when the potential reaches -0.60 V versus Ag/AgCl. The cathodic current increased further as the potential was

swept into more negative region, which suggests  $\text{S}_2\text{O}_3^{2-}$  reduction process (Ghazali et al., 1998):

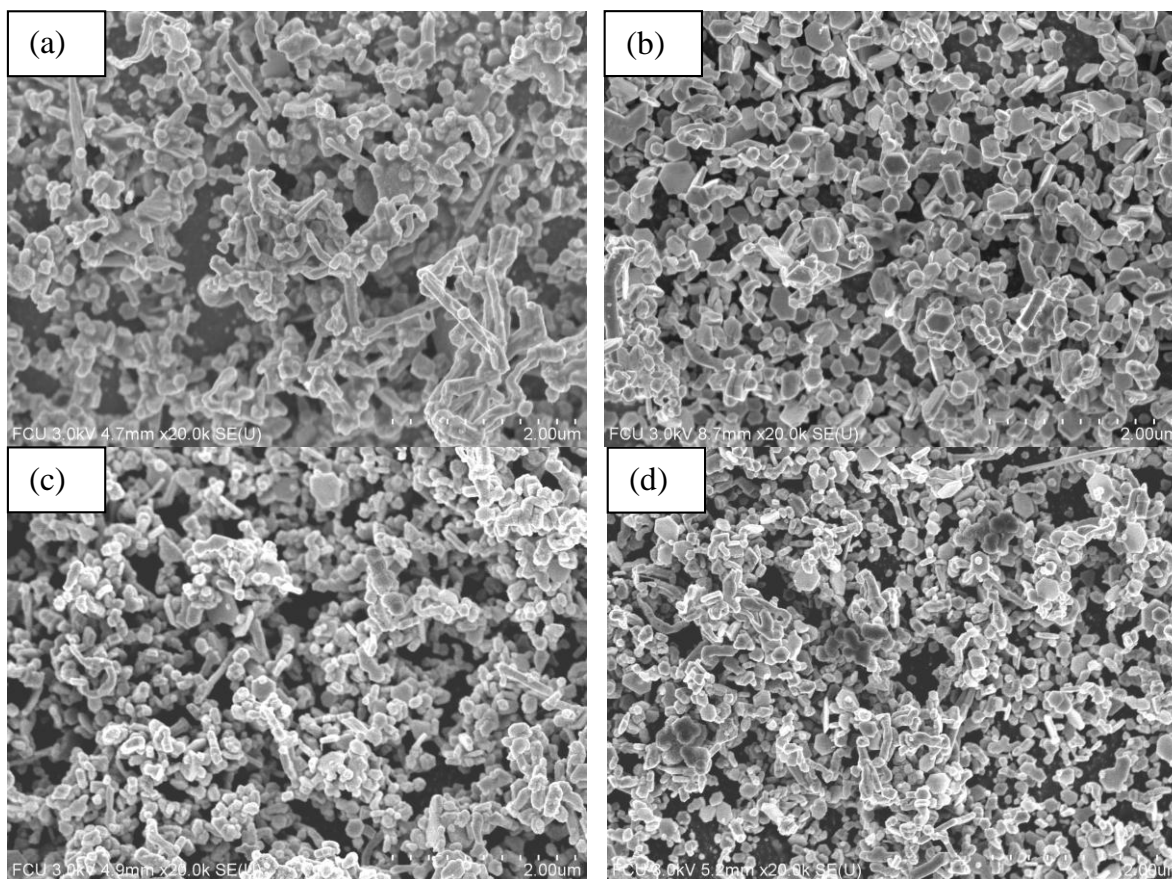


The potential was reversed when it reaches -1.00 V versus Ag/AgCl to avoid hydrogen evolution reaction. During the reverse scan, presence of anodic peak confirms dissolution of sulfur into the solution. We can conclude that suitable deposition potential for 0.01 M  $\text{Na}_2\text{S}_2\text{O}_3$  solution starts from -0.60 V versus Ag/AgCl.

### Cyclic voltammetry of solution mixture

Once the suitable deposition potential range have been identified for individual elementals, cyclic voltammetry of these mixtures were performed to find the suitable deposition potential for cadmium zinc sulfide thin film. Figure 4 shows the CV for 0.01 M  $\text{ZnCl}_2$ , 0.01 M  $\text{CdCl}_2$  and 0.01 M  $\text{Na}_2\text{S}_2\text{O}_3$  mixture at pH 2. The forward scan remained low until -0.80 V versus Ag/AgCl. The rapid increase in the cathodic current after this potential could be due to the formation of cadmium zinc sulfide compound. A further increase in the current could be observed as the potential reaches -0.95 V versus Ag/AgCl indicating the start of hydrogen evolution reaction. During the reverse scan, co-deposition continues to occur as could be seen from the presence of cathodic current. However, the reverse scan cathodic current remained lower compared to initial current during forward scan because in the latter, deposition takes place on substrate surface. In the former, deposition takes place onto material which was deposited earlier. When the potential reached -0.70 V versus Ag/AgCl, anodic peak was present indicating dissolution of deposited material into the solution. The suitable deposition potential range of this compound was found to be from -0.70 to 0.85 V versus Ag/AgCl. Based on the information obtained from CV, thin films of cadmium zinc sulfide were deposited at potentials of -0.65, -0.70, -0.75 and 0.80 V versus Ag/AgCl. Other deposition parameters such as concentration and pH remained unchanged. The deposition period was fixed at 20 min. Figure 5 shows the SEM images of these films deposited at different potentials. The films deposited at -0.65 V shows random distribution of particle sizes and shapes. The substrate surface was not covered completely at this deposition potential.

The polydispersed nature of particle size could be due to incomplete nucleation and particle growth rate. This is further supported from the data obtained from CV plot indicating a weak rise in cathodic current at this potential. When the deposition potential is increased to -0.70 V, surface coverage have increased. Particle sizes are less



**Figure 5.** SEM of thin films deposited at potential: (a) -0.65 V, (b) -0.70 V, (c) -0.75 V and (d) -0.80 V; solution concentration remained at 0.01 M; pH 2 and deposition period at 20 min.

polydispersed and random nucleation sites could be observed which promotes particle growth from many sites. At higher potential (-0.80 V), more compact particle formation could be observed. The particle sizes and shape distribution looks more uniform compared to films deposited at other potentials. The uniformity in particles shape is due to higher nucleation rate and uniform particle growth.

## Conclusion

Deposition potentials from -0.70 to -0.85 V versus Ag/AgCl was found to be suitable to deposit cadmium zinc sulfide thin films at acidic medium in room temperature (27°C). Lower deposition potentials were not suitable as the nucleation rate was too slow producing irregular particle growth.

## ACKNOWLEDGEMENT

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