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Electrodeposition of CdTe films on CdS layers deposited using magnetron sputtering and chemical bath deposition

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Abstract

This paper compares the structural and optical properties of electrodeposited Cadmium Telluride films grown on Cadmium Sulphide films prepared by two different methods: pulsed DC Magnetron Sputtering and Chemical Bath deposition (CBD). The films were characterised using Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Energy Dispersive X-ray Spectroscopy (EDS) and Spectrophotometry. The SEM and TEM characterisation revealed that the microstructure of the CdTe film was influenced by the deposition method used for the underlying thin film CdS. The CdTe films deposited on the CBD CdS films showed development of bigger crystallites compared to the films grown on the sputtered CdS layer. Thickness measurements showed that the substrate had significant influence on the growth rate of the CdTe, with the material grown on sputtered CdS having 3 times higher deposition rate. Transmission measurements showed that the material deposited on the sputtered CdS had a narrower band gap, 1.41eV, compared to that deposited on CBD CdS, 1.46eV.

Introduction

Thin film Cadmium Telluride (CdTe) technology is one of the key photovoltaic (PV) technologies. Due to its physical properties, CdTe is considered a prime candidate for a PV material and has generated great interest in its use. The CdTe material is characterised by a direct band gap (1.44eV) with a high absorption coefficient ($>5 \times 10^5/\text{cm}$). Another great advantage of CdTe is that it can be deposited by number of techniques including evaporation, sublimation, sputtering and chemical methods [1–3]. The growth of CdTe films by electrodeposition is a simple and low

cost process of producing high-quality material for PV device fabrication [4]. The cathodic electrodeposition of CdTe thin films has been successfully performed in both acidic (pH 1-3) [5], [4] and alkali aqueous solutions [7]. The most commonly used source of tellurium ions is Tellurium dioxide (TeO_2). In order to obtain a stoichiometric CdTe film, the electrolyte should contain a high concentration of the less noble component (Cd), while the concentration of HTeO_2^+ is low during the deposition and it affects the deposition rate of Te, leading to a diffusion controlled process.

A good quality CdS/CdTe interface is required to form a good p-n junction, which is a key factor for the performance of the solar cell. This study investigates how the deposition technique used for the growth of the CdS thin film affects the growth of the subsequent CdTe. Two different sets of experiments have been performed, one with the CdS thin film deposited by Chemical Bath deposition and a second one with the CdS film grown by Pulsed DC magnetron sputtering prior to the electrodeposition of CdTe film.

Experimental

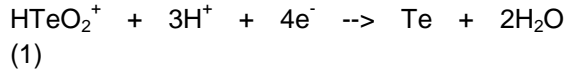
The CdS films were deposited on TEC10 glass substrate, a transparent conducting fluorine doped tin-oxide (FTO) coated glass supplied by NSG-Pilkington (<http://www.pilkington.com/>). This was cleaned in a two-step ultrasonic bath process (IPA and rinse), followed by a plasma surface treatment in a mixture of O_2 and Ar [8]. Next, thin films of CdS were grown by sputtering and CBD, details are available elsewhere [8], [9].

Thin films of CdTe were prepared by electrodeposition technique in aqueous solution. The electrolyte contained Cd^{2+} ions,

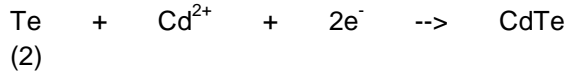
from CdSO_4 $3.8 \cdot 10^{-2}\text{M}$, and a lower concentration of HTeO_2^+ ions, from TeO_2 10^{-3}M precursor, the solution was adjusted to pH 1-2 with the addition of $\text{H}_2\text{SO}_4 >95\%$.

Two steps may represent the overall deposition process [5], [9]:

- 1) Tellurium reduction



- 2) The Tellurium reacts rapidly with Cd^{2+} ions in solution due to the free energy gain in CdTe formation, $\Delta G = -103.7\text{kJ/mol}$:



The deposition potential, E , for each, is given by

$$E = E_{\text{Te}}^0 + \frac{RT}{4F} \ln(a_{\text{HTeO}_2^+} a_{\text{Te}}) + \frac{3RT}{4F} \ln C_{\text{H}^+} \quad (3)$$

$$E = E_{\text{Cd}}^0 + \frac{RT}{2F} \ln\left(\frac{a_{\text{Cd}^{2+}}}{a_{\text{Cd}}}\right) \quad (4)$$

Electrodeposition was performed at room temperature in a conventional three-electrode cell using a Parstat 2273 potentiostat (Advanced Electrochemical System). The reference electrode was a saturated KCl silver/silver chloride electrode (Ag/AgCl) [Ag/AgCl +0.199V vs standard hydrogen electrode (SHE)] placed inside a glass tube (Figure 1) not completely closed in order to prevent the back diffusion in the solution of O_2 formed during the process. A Pt foil served as a counter electrode and the working electrode was made of a CdS thin film (~100nm) deposited either by Chemical Bath deposition [8] or by Pulsed DC Magnetron sputtering [10] on a TEC 10 glass. Depositions were performed under potential control, the potential being fixed at -0.3V and the exposed area was 6cm^2 for a deposition time of 4h.

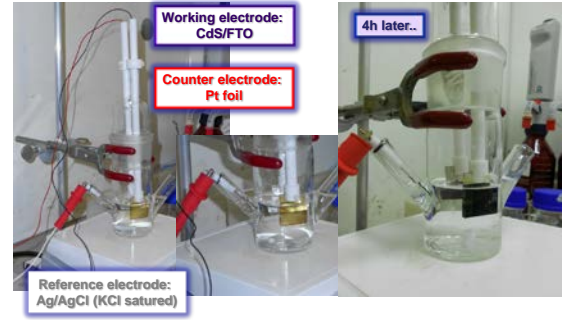


Figure 1: Three-electrodes cell for CdTe Electrodeposition.

The chemical composition, microstructure and optical properties of the resultant CdTe films were investigated. The microstructure was studied with a high resolution field emission gun scanning electron microscope (FEGSEM), Leo 1530 VP FEG-SEM. Jeol JEM 2000FX operating at 200kV was used for TEM images, for morphological analysis of grain structure. Bruker D2 Phase benchtop was used to determine the crystal structure of CdTe films.

The transmission, reflection and energy gap (E_g) measurements were carried out using a Varian Cary® UV-Vis 5000 spectrophotometer. The instrument is equipped with an integrating sphere and set of gratings, which allow the collection of transmission information from wavelengths in the range from 185nm to $3.3\mu\text{m}$. The energy band gap E_g , was calculated as a graphic extrapolation by using the Tauc plot [11].

Discussion

It was observed that CdTe film grows at different rate depending on the underlying CdS film. The CdTe film deposited on CBD grown CdS was only ~340nm thick compared to almost a $1\mu\text{m}$ thick film grown on the Pulsed DC magnetron sputtered CdS. This is clearly shown in the TEM cross section images in Figure 2. Despite the difference in thickness, the cross-sectional view of both samples shows a compact and dense CdTe film (Figure 2).

The CdTe deposited on the CBD CdS initially grew small crystals following the underlying film, but once it had grown to 50nm, thick bigger grains started to form (up to 50 nm in diameter). The CdTe deposited on the

sputtered CdS showed small crystallites across the entire thickness, (Figure 2(b)). The surface morphology of the deposited films is shown in Figure 3.

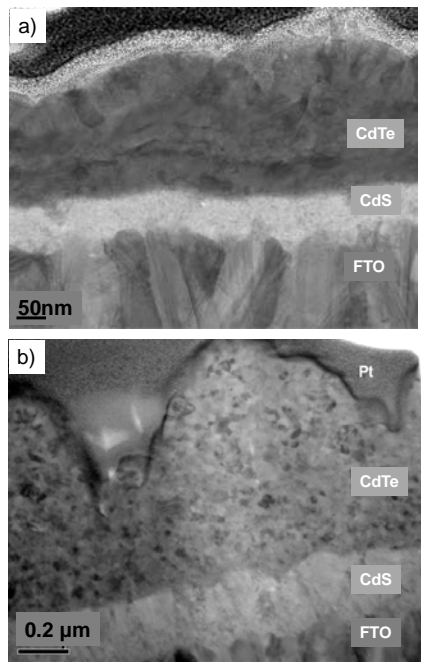


Figure 2: TEM cross sections of CdTe films electrodeposited for 4h at -0.3V on CdS CBD deposited on TEC 15 (a), CdS deposited by Pulsed DC magnetron sputtering (b)

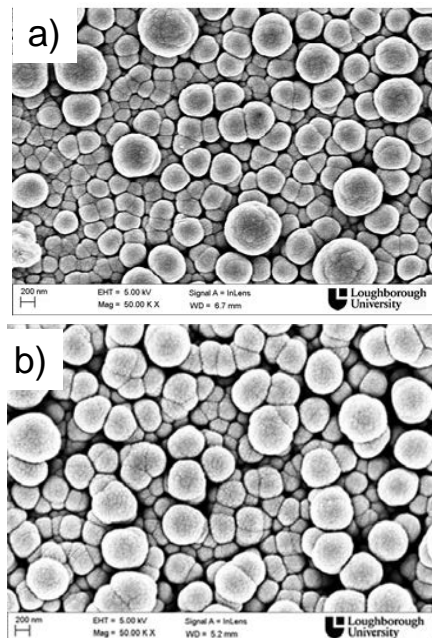


Figure 3: SEM images of CdTe electrodeposited on CdS deposited by chemical bath (a), and Pulsed DC magnetron sputtered CdS (b).

Figure 4 shows XRD patterns taken for a CdTe thin film electrodeposited on TEC10. EDS analysis showed the composition of the film, consisting of 57% of Te and 43% of Cd (inset).

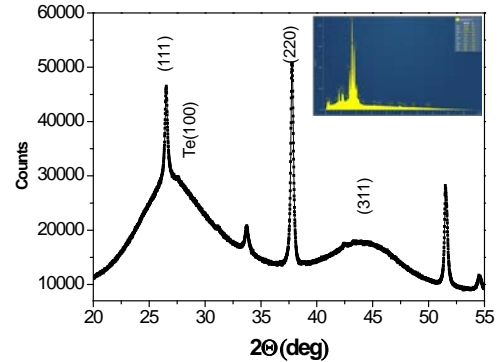


Figure 4: XRD pattern of CdTe ED on TEC10. Inset: EDS spectrum.

Optical analysis was performed on the two prepared samples; Figure 5 shows the transmittance spectra measured for the CdTe films deposited on sputtered and Chemical Bath deposited CdS films. Both spectra showed a high absorption of light. The higher transmittance of the CdTe on CBD CdS, around 13%, is a result of the thinner film thickness.

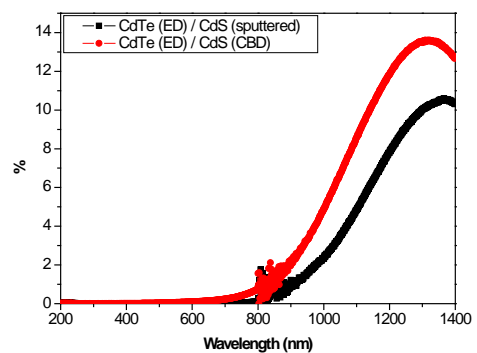


Figure 5: Transmittance curves of as-electrodeposited CdTe on Sputtered and CBD CdS

The Tauc plot analysis showed that the energy gap (E_g) for CdTe grown on chemical bath deposited CdS was 1.46eV, compared to 1.41eV for the CdTe film grown on sputtered CdS (Figure 6).

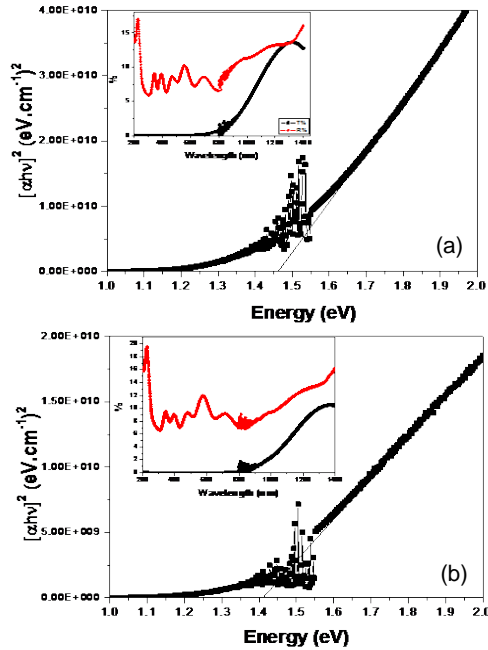


Figure 6: Energy band gap, Transmittance and Reflectance curves, as inset, for CdTe electrodeposited on chemical bath deposited (a) and Pulse DC sputtered (b) CdS.

Conclusions

CdTe thin films were grown on CdS films prepared by CBD and Pulse DC magnetron sputtering. The results show that the deposition technique used for the CdS layer affects the growth and properties of the CdTe film. The CdS film not only affects structural and morphological properties of the CdTe film but also determined the deposition rate of CdTe. The CdTe films deposited on the sputtered and CBD CdS initially grow in a similar way forming small crystallites. The film deposited on the CBD CdS showed much bigger crystallites once 50-100nm thick film was deposited.

Transmission measurements showed that the films deposited on the CBD CdS had wider band gap of 1.46eV compared to 1.41eV measured for the films deposited on CdS films prepared by pulsed DC magnetron sputtering.

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