FABRICATION OF ULTRA-THIN CdTe LAYERS BY THE CLOSE-SPACED SUBLIMATION TECHNIQUES FOR CdTe/CdS SOLAR CELLS

M. R. KARIM, M. T. RAZA, Z. A. ALOTHMAN, H. A. ALTURAIM, N. AMIN

Center of Excellence for Research in Engineering Materials (CEREM), Advanced Manufacturing Institute, King Saud University, Riyadh 11421, Saudi Arabia

Department of Industrial Engineering, College of Engineering, King Saud University, Riyadh 11421, Saudi Arabia

Department of Chemistry, College of Science, King Saud University, Riyadh 11421, Saudi Arabia

Centre for Nanoscale Science & Technology (CNST), Flinders University of South Australia, South Australia 5042, Australia

Department of Electrical, Electronic and System Engineering, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, 43600 Bangi, Malaysia

Close-spaced sublimation (CSS) of ultra-thin (~3–4 µm) CdTe layers for deposition on CdS-coated glass has been performed using a custom-designed CSS system. The deposition characteristics of CdTe have been studied on three types of CdS: firstly, CdS by Sputtering; secondly, CdS by CBD; and thirdly, CdS:O by Sputtering. Surface morphology was then studied using FESEM. XRD was performed to confirm the crystal properties of the film. UV-VIS spectrophotometry was used for determining the optical absorption and transmission characteristics of the film, which was further used to calculate the band gap of the deposited film.

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1. Introduction

Cadmium Telluride (CdTe) is a group II–IV compound semiconductor, very suitable for the photovoltaic applications due to its near ideal band gap 1.45 eV and its optical absorption coefficient, which is greater than 1x10^5 cm^{-2}, meaning that 90% of incoming light is likely to be absorbed in the first few microns [1]. The ideal window partner for CdTe deposition is CdS, which acts as an n-type semiconductor in PV devices. CdS has been found to be the most effective hetero-junction partner for CdTe in high-efficiency solar cells because CdTe and CdS are miscible, and a reaction between these two materials during the cell fabrication process leads to the formation of an interfacial layer of CdS_{1-x}Te_{x} [2]. The thicker CdS layer results in lower cell efficiency, therefore 100-nm thick film of CdS have been found to be optimum for high-efficiency solar cells. It is well known in material science that the quality and characteristics of the growth layer hugely depends on the substrate layer (anchoring film). The influence of the substrate on the growth of CdTe has been analyzed at length in a previous study [3]. In the past, CdTe layers have been deposited by different techniques like sputter deposition [4], electrophoretic deposition [5], chemical bath deposition [6] and high-vacuum evaporation [7]. The close-spaced sublimation technique is reported to be the most effective method for CdTe deposition with CdTe/CdS thin film solar cells because the highest-efficiency lab-scale CdTe solar cells were created with CdTe.

* Corresponding author: mkarim@ksu.edu.sa
deposited by CSS \[8\]. The deposition of CdTe by CSS is based on reversible dissociation of CdTe at high temperature \[9\].

CSS equipment was custom-designed with the chamber consisted of a hollow quartz glass cylinder. Heat lamps surrounded the chamber from the top and bottom. The source and substrate holder were made of graphite blocks. These blocks were placed inside the chamber with the help of rods connected from one side and suspended in its center. Finally, a vacuum pump was used to evacuate the CSS chamber to the desired pressure.

A pressure gauge and thermocouples were attached for monitoring the chamber’s pressure and temperature, respectively. A controller unit was also attached for controlling the power supply for the heat lamps. Leakage was avoided by putting an O-ring in the gap between the steel housing and glass tube. Every joint was sealed to ensure a leak-proof chamber. The custom-designed CSS equipment is shown below in scheme A.

\[\text{Scheme A: The custom-designed CSS system.}\]

Therefore, in this work we attempted to determine the quality of single CdTe layer grown on a CdS film, deposited using three different methods. Moreover, we observed that efforts of growing CdTe by CSS on bare glass (not coated with any material) were in vain, because the amorphous surface of the glass does not support the deposition of CdTe films.

\section*{2. Experimental details}

The CdS layer was grown using two different techniques, namely sputtering and chemical bath deposition. Sputtering is a very time-intensive and costly process, but it ensures a smooth and uniform film, whereas chemical bath deposition is very cheap, easy, and fast. CdS layers grown by both processes were annealed at 350\(^\circ\)C for 30 minutes, using CdCl\(_2\), for improving film’s crystallinity.

CdS by CBD: Chemical bath deposition was performed using 20 ml of 0.025 M cadmium chloride, 20 ml of 0.20 M thiourea, 50 ml of 0.50 M potassium hydroxide, and 20 ml of 1.50 M ammonium nitrate. All these chemicals were dissolved in DI water. These solutions were mixed and heated to 75\(^\circ\)C on a hot-plate magnetic stirrer. Thiourea was added once temperature of the mixed solution reached 75\(^\circ\)C. A roughly 100-nm thick CdS film was obtained after 20 minutes of deposition. The as-deposited film was ultrasonically cleaned to remove loose particles from the surface then dried by flushing with N\(_2\) gas.

CdS by Sputtering: Bare soda-lime glass was cleaned in an ultrasonic bath using ethanol-acetone-ethanol then DI water for five minutes each. The glass was then dried in a stream of dry N\(_2\) gas. CdS layers were sputtered on these glasses at a substrate temperature of 260\(^\circ\)C with 35 watts of RF power and 15 mTorr of Ar pressure. The prepared films were once again cleaned by dry N\(_2\) gas and sent for characterization.

CdS:O by sputtering: Commercial FTO-coated soda lime glasses were cleaned in an ultrasonic bath, degreased by ethanol-acetone-ethanol then DI water for five minutes each. Degreased glasses were dried with dry N\(_2\). CdS layers of 150 nm were sputtered on these FTO-coated glasses
at a substrate temperature of 300°C with 30 watts of RF power and 18 mTorr of Ar pressure. The prepared films were annealed in a vacuum furnace at 350°C for 30 min. The chamber pressure maintained in the range 300–320 Torr by continuous N₂ (mixed with O₂) gas flow as well as evacuation during annealing. At the end of the annealing process, the samples were left in the annealing chamber until the chamber temperature returned to room temperature.

CdTe growth on CdS coated substrates:

CdTe powder was filled in the slot provided in the source holder and this powder was compacted by compressing it with a clean glass sheet. The chamber was then evacuated to a vacuum pressure of around 10 mTorr. First, the source was sintered at 650°C to create a smooth solid surface for uniform sublimation deposition on the substrate. A CdS-coated substrate was placed on the source holder with a gap of 2 mm. The operating conditions for fabricating a 3-4 µm thick CdTe layer on the three types of CdS samples are summarized in Table 1.

**Table 1: Operating temperature and pressure for the custom-designed CSS system**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Source temp (°C)</th>
<th>Substrate temp (°C)</th>
<th>Time of deposition (min)</th>
<th>Vacuum (Torr)</th>
<th>Source to subst. gap (mm)</th>
<th>Ar-gas Pressure (Torr)</th>
<th>Thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS by Sputtering</td>
<td>615</td>
<td>590</td>
<td>3</td>
<td>10⁻³</td>
<td>2</td>
<td>2-3</td>
<td>4.0</td>
</tr>
<tr>
<td>CdS by CBD</td>
<td>615</td>
<td>590</td>
<td>3</td>
<td>10⁻³</td>
<td>2</td>
<td>2-3</td>
<td>3.8</td>
</tr>
<tr>
<td>CdS:O by Sputtering</td>
<td>615</td>
<td>590</td>
<td>3</td>
<td>10⁻³</td>
<td>2</td>
<td>2-3</td>
<td>4.1</td>
</tr>
</tbody>
</table>

3. Results and discussion

The surface microstructure was studied with the Field Emission Scanning Electron Microscope (FESEM), model JSM-7600 (JEOL, Japan). The FESEM images of samples prepared in the three different conditions are shown in Fig. 1. Fine grains of the polygonal structure were observed. The grain size varied from 0.60 to 1.40 µm, with an average grain size of 0.8 µm. The FESEM images for all three types of anchor surface under investigation depict similar morphology. The only difference is seen in the CdS:O sample, where the average grain size in smaller than the other two. The average grain size for this sample is around 0.60 µm.

![Fig. 1. FESEM of CdTe deposited on (a) sputtered CdS, (b) CdS CBD, & (c) sputtered CdS:O, and (d) EDX results for the CdTe film showing Cd and Te composition](image-url)
The EDX result was obtained using an OXFORD instrument connected to the FESEM. The elements were quantified and the values are shown in fig. 1(d), were found around 48 and 52% for Cd and Te, respectively. This value is almost same for all the three samples, i.e. CdTe/CdS by sputtering, CdTe/CdS by CBD, and CdTe/CdS:O by sputtering. The three CdS anchoring surfaces do not have an effect on the Cd and Te quantity being deposited. Only one result has been shown below for brevity.

The as-deposited CdTe film was annealed with cadmium chloride at 400°C temperature to enhance its crystal properties. A saturated CdCl₂ solution was prepared in methanol and applied on the CdTe film by dipping for one minute. Then, the sample was put in an annealing chamber equipped with IR lamps. A mixture gas of 99% N₂ and 1% O₂ was supplied to the chamber after creating a 10 mTorr vacuum in the chamber. The pressure inside the chamber during annealing was kept at 300 Torr. The IR lamps were then turned on, taking around 10 minutes to reach 400°C. The sample was kept at this temperature for 30 minutes. The heater was then turned off and the sample was removed after cooling in the chamber. The morphology shows that recrystallization has taken place. Small white spots are the residual trace of CdCl₂ particles, which were later removed by etching with methanol-bromine. The grains are reoriented and activated as show in Fig. 2. Average grain size increased considerably from 800 nm to 1.6 μm. The post-annealing microstructure obtained was nearly identical for the three anchor surfaces under investigation. Only a SEM image is shown for brevity.

![FESEM image of CdTe film after CdCl₂ annealing at 400°C for 30 minutes.](image)

The UV–VIS–NIR spectrophotometer, Shimadzu UV3600, Japan, was used for generating transmission spectra. The transmission pattern for all the three samples are nearly identical (Fig. 3). The CdS:O samples show a shift in cut off wavelength from 820 to 830 nm which indicates a band gap of 1.516 eV, whereas the sputtered and CBD sample both have a band gap of 1.497 eV.

![Transmission characteristic of the CdTe film.](image)

XRD was performed using a D8 DISCOVER, Bruker, Germany. The 2θ range was 5–80° with 5° per minute scanning. XRD patterns for all the films under investigation are shown in Fig. 4. Polycrystalline films with cubic structure are evident in the figure, which is also reported [10]. At 2θ = 23.5°, a cubic phase with lattice (111) is clearly present in all three types of film under
investigation. However, the peak is very high in CdTe on sputtered CdS. While in the other two, i.e. CdTe on CBD and CdTe on sputtered CdS:O, the peaks are also significant at 39° and 46.5° which refer to (220) and (311) lattice vectors, respectively.

![XRD graph](image)

**Fig. 4.** XRD graph for the CdTe on three different types of CdS coated substrate of a) before and b) after annealing.

### 4. Conclusion

It is evident that the type of substrate coating used has an influence on CdTe film deposition, especially given that XRD analysis confirms differences in the microstructure. The annealing of the film also affects the surface morphology significantly, as the grain size become larger after CdCl$_2$ heat treatment, however the XRD results do change significantly after annealing. Band gap was also shown to change for different substrates.

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### References