Characterization of Cadmium Tin Oxide Thin Films as a Window Layer for Solar Cell

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ABSTRACT

Cadmium tin oxide thin (Cd$_2$SnO$_4$) films prepared by thermal evaporation technique at room temperature. The film deposited with thicknesses of 400 nm, then annealed at different annealing temperatures (350, 400, and 450 K). X-ray diffraction analysis of thin Cd$_2$SnO$_4$ films showed cubic polycrystalline structure. The surface morphological was investigated by atomic force microscopy (AFM), which revealed the crystalline nature of the films. The optical parameters of the prepared films as transmittance, optical energy gap, refractive index, extinction coefficient and the dielectric constants were found to be affected by varying the annealing temperatures.

Key World: Thin CdSnO4 film, Thermal evaporation, annealing effects.

1.INTRODUCTION

Transparent conducting oxides (TCOs) have been widely used in different areas due to their high optical transparency, low resistivity and wide energy band gap. Hence there has been great deal of work on investigating their preparation process and optimizing their properties [1]. Among the various TCO materials available, cadmium stannate (Cd$_2$SnO$_4$) is one of the potential candidates for solar cell application [2]. Cadmium tin oxide is an n-type semiconductor and has great technological interest due to their high quality electrical and optical properties superior to the conventional transparent conducting oxide materials. In addition, these films have wide applications in photogalvanic cells, liquid crystal displays, heat mirrors, transparent electrode and solar cells [1-6]. Recently it has been reported that, Cd$_2$SnO$_4$ thin films have several significant advantages in the CdTe/CdS based solar cells [3][4]. Comparing with SnO$_2$, cadmium stannate films have better adhesion in the CdTe/CdS solar cells [3]. The reduced film thickness of Cd$_2$SnO$_4$ films in the solar cell devices reduces the number of interconnects and reduces manufacturing costs [1]-[6]. Thus preparing the low cost and quality cadmium stannate thin films is an important and useful task.

Conventional TCOs, primarily SnO$_2$ films, typically have been used as the front collector in CdS/CdTe cells and modules. However, SnO$_2$ films, deposited using the commercially viable SnCl$_2$ chemistry, have a resistivity of ~ 5.8x10$^{-4}$ Ω cm. This yields films with an average transmission of 80% and a sheet resistivity of about 10 Ω/square. Although this may be satisfactory for small-area devices and first generation modules, it does not provide adequate design latitude when trying to optimize either device performance or manufacturing costs. For example, reducing the TCO resistivity by a factor of two could allow for a TCO film that retains the same sheet resistance as the inferior TCO, yet is half as thick. This would improve the transmission and ultimately improve device performance by increasing the short-circuit current density ($I_{sc}$). Alternatively, a film with transmission properties similar to those of the inferior TCO, but half the sheet resistance, could be used. This would have the advantage of reducing the number of interconnects required, thereby improving throughput, reducing interconnect losses, and reducing manufacturing costs. For these reasons, it is desirable to improve the performance of the TCO films for CdS/CdTe solar cell applications. Nozik and later Haacke et al. were the first to report Cd$_2$SnO$_4$ TCO films deposited by r.f. sputtering [5][6]. Recent improvements in r.f. sputter-deposited Cd$_2$SnO$_4$ and post-deposition processing have yielded films with superior properties [7]-[9].

CdSnO$_3$ and Cd$_3$Sn$_2$O$_9$ cadmium stannates are interesting due to their optical and electrical properties. These compounds, related to so-called optically limpid conductive oxides, are used as thin films which are transparent in visible spectrum part [10], in semiconductor technology [11], as sensitive elements of chemical sensors [12]-[14] etc. Cadmium stannate films have several significant advantages over conventional TCOs. They are more conductive, more transparent, have lower surface roughness, are pattern able, and are very stable. Cd$_2$SnO$_4$-based CdS/CdTe polycrystalline thin-film solar cells with efficiencies of 14.0% have been fabricated. Preliminary cell results have demonstrated that device performance can be enhanced by replacing the SnO$_2$ layer with a Cd$_2$SnO$_4$ TCO film. Various deposition methods such as rf sputtering, DC reactive sputtering, DC magnetron plasmation sputtering, reactive magnetron sputtering and atom beam sputtering were employed to prepare cadmium stannate films [10]-[15]. In this paper, thin Cd$_2$SnO$_4$ films have been prepared by thermal evaporation technique. The main task of this study is a search for studying the effect of the annealing temperatures on some structural, morphological, and optical properties for thin Cd$_2$SnO$_4$ films prepared by thermal evaporation method.

2.EXPERIMENTAL WORKS
Thin Cd$_2$SnO$_4$ films have been evaporated by using Edward (E306A) coating system under vacuum of about 2×10$^5$ mbar, from Cd$_2$SnO$_4$ powder purity of about 99.999% manufacturer by Balzers Switzerland. These films deposited on 7059 corning glass slides with 400nm thickness at room temperature (RT). The prepared films have been annealed at different annealing temperatures ($T_a$=300(RT), 350, 400, and 450 K). The thin Cd$_2$SnO$_4$ films structural analysis was examined by using Phillips X-Ray diffractometer system with CuK$\alpha$ source.

The surface morphology of the prepared films is investigated by means of atomic force microscopy (AFM). Optical transmittance spectrum was recorded using UV–Visible spectrometer in the range of 200–1100 nm.

3. RESULTS AND DISCUSSION

3.1 Structural Properties

X-ray diffraction spectra of thin Cd$_2$SnO$_4$ films, as grown and annealed at 350, 400 and 450 K are shown in figure (1). It can be observed that these prepared Cd$_2$SnO$_4$ films are polycrystalline of spinal cubic structure according to standard JCPDS, and a small amount of CdO may be responsible for the broad (400) reflection.

This figure shows crystallize with a strong peak at (311) direction. The increase of $T_a$ improves the crystal structure by increasing the intensity of the planes. Such improvement in crystal structure could be attributed to the increase in crystallite size as the small crystallites join each other’s in the planes by increasing heat treatments as shown in Table (1).

This result is in agreement with researchers Jeyadheepan et al [1], Wu et al [3] and Wang et al [16]. They found that the XRD analysis shows that the film coated on glass substrate maintained at RT was in its first state of crystallization and the small hump present in the diffraction data at 23.4° is due to the glass substrate. Also they found that the films prepared at 373, 473 and 573K were crystalline in nature having the cubic spinal phase. The films coated at substrate temperatures 373, 473 and 573K were preferentially oriented along (311) plane. Also Mostafa et al [17] have found that the effect of annealing temperatures on the structural properties of the films with same thickness 350 nm. Thick reveals a tendency of beginning crystallization, Xiaonan et al [18] have found that the crystal structures is cubic (CdO) and cubic spinal (Cd$_2$SnO$_4$), also our results in agreement with Andrew et al [19].

![Figure 1: The XRD spectrum of thin Cd$_2$SnO$_4$ films, as deposited and annealed at different annealing temperatures.](image)

They found that the as deposited films are highly crystalline with the cubic spinal Cd$_2$SnO$_4$ crystal structure, and a small amount of CdO may be responsible for the broad (400) reflection at 39°. The structure parameter of as deposited Cd$_2$SnO$_4$ and annealed films at different annealing temperatures is shown in Table (1).

<table>
<thead>
<tr>
<th>$T_a$ (K)</th>
<th>(hkl)</th>
<th>$2\theta$ (degree)</th>
<th>d (Å)</th>
<th>FWHM (degree)</th>
<th>D (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>311</td>
<td>31.895</td>
<td>2.8039</td>
<td>0.446</td>
<td>20.38</td>
</tr>
<tr>
<td>350</td>
<td>311</td>
<td>31.893</td>
<td>2.8039</td>
<td>0.428</td>
<td>21.23</td>
</tr>
<tr>
<td>400</td>
<td>311</td>
<td>31.892</td>
<td>2.8039</td>
<td>0.407</td>
<td>22.32</td>
</tr>
<tr>
<td>450</td>
<td>311</td>
<td>31.874</td>
<td>2.8054</td>
<td>0.381</td>
<td>22.35</td>
</tr>
</tbody>
</table>

3.2 Morphological Properties

Atomic force microscopy (AFM) scan image of thin Cd$_2$SnO$_4$ films at different annealing temperatures is shown in figure (2). AFM image shows that the films are well faceted crystallites, with linear transversal contains uniformly packed small
The thin Cd$_2$SnO$_4$ films have a root mean square (RMS) roughness of about 1.48 nm and 2.90 nm for 300 and 350 K respectively.

### Table 2: The grain size and roughness from AFM and XRD for thin Cd$_2$SnO$_4$ films

<table>
<thead>
<tr>
<th>$T_a$ (K)</th>
<th>Grain size (AFM)</th>
<th>Grain size (XRD)</th>
<th>Roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>140.05</td>
<td>20.38</td>
<td>1.48</td>
</tr>
<tr>
<td>350</td>
<td>256.92</td>
<td>21.23</td>
<td>2.90</td>
</tr>
</tbody>
</table>

Figure 2: 2 and 3-D AFM images of thin Cd$_2$SnO$_4$ films (a) as deposited (b) annealed at 350K.

It shows that the morphology of the thin Cd$_2$SnO$_4$ films has larger number of grain size and are homogeneously distributed, which indicates the crystalline nature of the film. Due to the heating grain growth will takes place which gives the crystalline and good surface morphology [2]. These results are in good agreement with XRD characteristics. The crystal morphology and molecular orientation change with annealing temperatures. The average grain size increases as annealing temperature increases.

These structural characterizations confirm that the annealing temperature allows us to control the structural organization of Cd$_2$SnO$_4$ thin films molecules in their solid state, from which a large improvement of the properties can be expected. Table (2) shows the grain size increases by increasing the annealing temperatures. The morphology of these films, has also confirmed the appearance of polycrystallites and increasing grain size when annealing temperature is raised. The difference in grain size may be attributed by the difference in temperature. This is caused due to the nucleating behavior of the substance. The root means square (rms) roughness of the prepared film at different substrate temperatures are shown in Table (2). From the application point of view, the higher efficiency devices are obtained from the film of greater roughness.

### 3.3 Optical Properties

The optical properties of as deposited Cd$_2$SnO$_4$ thin film and annealed films at different annealing temperatures ($T_a=350, 400, 450$ K) of $0.4\mu$m thickness deposited on glass substrate have been determined from UV-VIS spectrum in the region $(0.2-1)\mu$m. The absorption and transmission spectra have been studied; also the energy gap and optical constant have been determined. In general, we can observe that increasing $T_a$ shifts the peak of transmittance spectrum to the blue shift (shorter wavelength) compared to the as deposited film as shown in figure (3). The shift in the peak position films may be attributed to the crystallite of film structure by increasing the grain size which is confirmed by XRD results. Also we studied the spectrum of absorption as shown in the Fig.(4), it is obviously that its behavior is opposite to that of the transmittance spectrum.

Figure 3: The transmittance spectra of thin Cd$_2$SnO$_4$ films.  
Figure 4: The absorption spectra of thin Cd$_2$SnO$_4$ films.
We can observe that the transmittance increases, whereas the absorbance decreases with increasing annealing temperatures from RT to 450K as shown in Table(3). This is due to crystallization of film structure by increasing the grain size, and slightly, the absorption edge shift to smaller wavelength (higher photon energy) with increasing Ta from RT to 450K.

<table>
<thead>
<tr>
<th>T&lt;sub&gt;a&lt;/sub&gt; (K)</th>
<th>T</th>
<th>A</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
<td>0.058</td>
<td>0.873</td>
<td>0.067</td>
</tr>
<tr>
<td>350</td>
<td>0.131</td>
<td>0.739</td>
<td>0.129</td>
</tr>
<tr>
<td>400</td>
<td>0.263</td>
<td>0.544</td>
<td>0.191</td>
</tr>
<tr>
<td>450</td>
<td>0.381</td>
<td>0.415</td>
<td>0.203</td>
</tr>
</tbody>
</table>

Table 3: The values of A, T and R for thin Cd<sub>2</sub>SnO<sub>4</sub> films at λ=0.4 μm

Fig.(5) shows the absorption coefficient (α) of as deposited Cd<sub>2</sub>SnO<sub>4</sub> thin film and treated films at different annealing temperatures (350, 400, 450 K). From this figure, α decreases with increasing annealing temperatures for all samples as shown in Table (4). This is due to the increasing value of energy gap with annealing temperatures.

To determine the type of optical transition, we have examined (αhν)<sup>1/2</sup>, (αhν)<sup>1/3</sup>, (αhν)<sup>3/2</sup>, and (αhν)<sup>2</sup>, versus hν then we found that the last relation yielded a linear dependence, which describes allowed direct transitions. From Fig.(6) the energy gap is determined by plotting Tauc equation and taking the extrapolation of the linear portion, where (α ≥10<sup>4</sup> cm<sup>-1</sup>) of the (αhν)<sup>2</sup> as a function of hν curve to α=0.

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Figure 5: The absorption coefficient of thin Cd<sub>2</sub>SnO<sub>4</sub> films with different annealing temperatures.

The direct energy gap value was found to be as shown in the Table (4), which nearly in agreement with the other literatures [3-6]. The value of optical energy gap increases with increasing annealing temperatures for all samples. This is due to the growth of grain size and the decrease in defect states near the bands and this is turn increased the value of Eg. The value of Eg increases. This is due to eliminate the defect and decreasing the defect state inside Eg.

The optical behavior of materials is generally utilized to determine its optical constants for example the refractive index (n). Fig.(7) shows the variation of refractive index of as deposited thin Cd<sub>2</sub>SnO<sub>4</sub> films and annealed at different annealing temperature (350, 400, 450K). It is interesting to see that refractive index increases with increasing annealing temperatures. This behavior is due to increase in the reflection which the refractive index depend on it.

The behavior of extinction coefficient (k) is nearly similar to the corresponding absorption coefficient as shown in Fig.(8) at different T<sub>a</sub>. We can see from this figure that k decreases with increasing T<sub>a</sub> from RT to 450 K. This attributed to the same reason, which mention previously in absorption coefficient.

Table 4: The values of α and E<sub>g</sub> for thin Cd<sub>2</sub>SnO<sub>4</sub> films

<table>
<thead>
<tr>
<th>T&lt;sub&gt;a&lt;/sub&gt; (K)</th>
<th>α x10&lt;sup&gt;6&lt;/sup&gt; (cm&lt;sup&gt;-1&lt;/sup&gt;) at 0.4 μm</th>
<th>E&lt;sub&gt;g&lt;/sub&gt; (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
<td>6.655</td>
<td>2.0</td>
</tr>
<tr>
<td>350</td>
<td>5.576</td>
<td>2.1</td>
</tr>
<tr>
<td>400</td>
<td>4.183</td>
<td>2.3</td>
</tr>
<tr>
<td>450</td>
<td>3.189</td>
<td>2.4</td>
</tr>
</tbody>
</table>

Figure 6: (αhν)<sup>2</sup> as a function of photon energy for thin Cd<sub>2</sub>SnO<sub>4</sub> films with different annealing temperatures.
The variation of real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) dielectric constants with different annealing temperatures are shown in figures 10 and 11. The behavior of $\varepsilon_1$ is similar to refractive index because the smaller value of $k^2$ comparison of $n^2$, while $\varepsilon_2$ is mainly depends on the $k$ values, which are related to the variation of absorption coefficient. It is found that $\varepsilon_1$ increases with $T_a$, while $\varepsilon_2$ decreases with increasing $T_a$.

Table (5) shows the optical constants which involve refractive index, extinction coefficient, and dielectric constants.

4. Conclusion
Cd$_2$SnO$_4$ films with 0.4μm thickness deposited on glass substrates and treated at different annealing temperatures (350, 400, and 450 K) have been prepared successively by vacuum evaporation technique. We conclude from the experimental data the following:
- The structure for prepared films at different $T_a$ is polycrystalline with cubic structure.
- AFM image shows that the films is well faceted crystallites, with linear transversal contains uniformly packed small grains.
- The increasing in $T_a$ shifts the peak of transmittance spectrum to the shorter wavelength (blue shift) compared to the as deposited film.
- The absorption coefficient decreases with increasing $T_a$ for all samples.
- The optical energy gap is direct transitions with (r) equal to (1/2).
- The $E_g$ increases with the increasing $T_a$.
- The refractive index, and real dielectric constant increase with $T_a$, whereas the extinction coefficient and imaginary dielectric constant decrease with increasing $T_a$.
References


AUTHORS

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