Increasing the Conductivity of Cadmium Telluride Films

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Abstract
The structural, optical and electrical properties of vacuum-evaporated CdTe thin films were investigated as a function of post-deposition annealing without and with CdCl$_2$ treatment at 300°C for 15 min. X-Ray diffraction studies of the as-deposited films revealed polycrystalline in nature with cubic structure. The intensity of the (111) peak increased with the CdCl$_2$ annealing treatment, and there is an increasing in the grain sizes after the CdCl$_2$ annealing treatment with voids around the grain boundaries from the surface morphologies after the CdCl$_2$ annealing treatment. The optical band gap values, $E_g$, were 1.56, 1.54 and 1.38 eV for film deposited at room temperature and after annealing without and with CdCl$_2$ treatment at 300°C for 15 min respectively. Furthermore, the activation energy decreases after heat treatment without and with CdCl$_2$ for CdTe thin films.

Keywords: Cadmium telluride; CdCl$_2$ treatment; optical / electrical properties; X-ray diffraction; Thin films

1. Introduction
Cadmium telluride is one of the most promising polycrystalline materials for thin film solar cells due to its physical properties: It has a direct band gap (approximately 1.56 eV at room temperature) with a high absorption coefficient (larger than $10^5$ cm$^{-1}$ at wavelengths around 700 nm), so that only thin film layers (a few microns) are needed for the absorption of the most of the solar spectra photons with energy higher than the band gap, and it can be obtained as
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p-type [1,2]. Thin films of II–VI semiconductors are currently used in many semiconductor devices such as photo-electrochemical cells, field effect transistors, detectors, photodiodes, photo-conductors and photovoltaic solar cells [3]. For fabrication of the CdTe films a variety of preparation techniques have been employed such as vacuum evaporation [4-6], spray pyrolysis [7], electrodeposition [8], electroless deposition [9], R.F. sputtering [10], close-space sublimation [11], pulsed laser deposited [12], chemical molecular beam deposition [13]. The vacuum evaporation method has some advantages such as: the amount of impurities included in the growing layer will be minimized, the tendency to form oxides will be considerably reduced and finally straight line propagation will occur from the source to substrate [3]. In the present work, vacuum evaporation for depositing CdTe thin films is reported. The effect of annealing and CdCl₂ heat treatment at 300°C for 15 min on structural, optical and electrical properties of vacuum evaporation CdTe thin films has been studied, using X-ray diffraction (XRD) (Shimadzu XRD-6000 X-ray diffractometer, CuK radiation).

The optical properties were measured by the UV/VIS/NIR double beam spectrophotometer in the wavelength range of 200 to 1100 nm. The D.C. conductivity measurements were made using a model 602 Keithley electrometer.

3. Results and discussion
3.1. Structural analysis
Figure 1 shows the XRD pattern of as-deposited CdTe thin films of thickness 500 nm. The spectrum of as-deposited films (grown on to glass substrates and kept at room temperature) showed preferential growth of film crystallites corresponding to textured (111) growth. The other phases (220) and (311) were absent in these films. The (111) direction is the close-packing direction of the zinc-blende structure and this type of ordering is often observed in polycrystalline films grown on heated amorphous substrates [14,15].

Figure 2 presents the XRD spectrum of the CdTe thin film annealed at 300°C for about 15 min. Annealing at 300°C results in a
decreasing in the (111) peak intensity together with the appearance of the (220) and (311) peaks. The observed decreasing in the intensity may be due to the change in stoichiometry, and a certain degree of randomization in the film texture with an annealing depends on the character of the substrates are used [16,17].

The CdCl$_2$ treated CdTe thin layers are further annealed at 300°C for about 15min showing changes in the XRD spectrum, as given in Figure 3. The intensity of the (111) peak increased with the CdCl$_2$ heat treatment and the additional diffraction peaks which observed were possibly due to CdCl$_2$, Cd [18].

The crystallite size ($D$) were calculated by using the Scherrer formula [16] from the full-width at half-maximum (FWHM) ($w$) of the XRD peaks:

$$D = \frac{0.94 \lambda}{w \cos \theta}$$

where $\lambda$ is wavelength of the X-rays and $\theta$ is Bragg angle.

Estimated average grain sizes which obtained from the diffraction peaks associated with the (111) planes of cubic CdTe, were found to increase from 37 nm for as-deposited to 45 nm for the CdCl$_2$ treatment films. This suggests that some limited grain growth had occurred during the CdCl$_2$ treatment [18].

For the as-deposited samples, the value of ($a$) (6.468 Å) is smaller than that corresponding to a powder sample (6.481 Å). The smaller value of ($a$) is due to the recrystallized lattice. A further decreasing in the ($a$) lattice parameter has been observed in the CdCl$_2$-treated samples achieving a value of ($a$) (6.447 Å). For as-deposited samples a large value of ($a$) was noticed this means, the film is subjected to a compressive stress in plane parallel to the substrate surface. This stress is caused by the lattice mismatch and/or differences in thermal expansion coefficient between the CdTe and the underlying substrate. The observed lower value of ($a$) for films treated with CdCl$_2$ is an evidence for stress relieving in CdCl$_2$ treated samples [1,16].

Effects of heat treatment steps on the morphology of the CdTe film were investigated by optical microscope. Figure 4(a), (b), (c) show the surface morphologies of films deposited at room temperature, annealed and then CdCl$_2$ heat treated at 300°C for 15min, respectively. It can be seen from figure 4(c) that surface morphologies are changed significantly. The grain sizes are increased after the CdCl$_2$ heat treatment, but contain voids around the grain boundaries. The creation of new grains is due to the relaxation of excessive strains in the lattice. The coalescence of small grains into bigger ones is caused by the CdCl$_2$ heat treatment [1].

3.2. Optical analysis

Figure 5 shows transmission spectra for typical as-deposited, annealed and CdCl$_2$ treated + annealed CdTe thin films. All the samples show optical transparency (T≥80%) in the spectral region (800-1100)nm. The transmittance decreases in the band gap region for the CdCl$_2$-treated films. From the transmittance spectra the
absorption coefficient ( ) can be calculated from the relation [19] .

\[ \alpha = 2.303 \frac{A_o}{t} \quad \text{(2)} \]

where \( A_o \) is absorption, \( t \) is thickness of the film .

The optical band gap values of the CdTe films were obtained from transmission measurements and by plotting \( ( h \epsilon)^2 \) against \( (h \epsilon) \). The absorption spectra of CdTe films are shown in fig.6 (a), (b) and (c) the linear nature of the plot after the absorption edge indicates the presence of direct transition .

The extrapolated of the linear portion to the x-axis gives the values of optical band gap, \( E_g \), are 1.56, 1.54 and 1.38 eV for films deposited at 300K and annealed without and with \( \text{CdCl}_2 \) treatment at 300°C for 15min respectively. The data of fig.6 clearly show the progressive sharpening of the absorption edge upon heat treatment particularly for the \( \text{CdCl}_2 \) treated sample .

The reason for the sharpening might be due to a change in the stoichiometry or intrinsic defect population of the heat treated samples [16,20] .

3.3. Electrical analysis

The temperature dependence of the electrical conductivity ( ) is given by [20] :-

\[ \sigma = \sigma_o \exp(-\Delta E / KT) \quad \text{(3)} \]

Where \( \sigma_o \) is the pre-exponential factor, \( \Delta E \) is the activation energy , \( K \) is Boltzmann's constant and \( T \) is the absolute temperature .

The dark electrical conductivity \( \sigma \) of CdTe films with different treatments was measured as a function of the sample temperature in the range from 300 to 433K . Fig.7 shows the plot of \( \ln \sigma \) versus \( 1000/T \) for CdTe films, both as deposited and annealed at 300°C for 15min with and without \( \text{CdCl}_2 \). Each graph can be divided into two distinct linear parts, which indicates the existence of two activation energies for the conduction free charge carriers, \( E_i \) at temperatures below 383±10K and \( \Delta E_2 \) at temperatures above 383±10K .

In the low temperature region, the calculated activation energy \( E_i \) decreased by annealing or \( \text{CdCl}_2 \) treatment, while the room temperature conductivity increased . The decreasing in \( E_i \) from 0.480 to 0.142 eV and the \( E_2 \) from 0.727 to 0.646 eV , may be attributed to the improvement of the film crystallinity, and the larger grain size particularly in the low temperature region as indicated by XRD measurements .

4. conclusions

In this research, thermally evaporated CdTe films are polycrystalline in nature and had cubic zincblende structure with resistivity higher than \( (10^7 \, \text{ohm.cm}) \), the lowest resistivities were obtained when \( \text{CdCl}_2 \)-dip was included into the processing . XRD showed contrast in appearence and disappearence of planes in crystal structure after annealing and \( \text{CdCl}_2 \) heat treatment , also optical band gap of films became sharper upon \( \text{CdCl}_2 \) treatment .

We conclude that \( \text{CdCl}_2 \) behaves as a fluxing agent for
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recrystallization, which improves the grain size and polycrystalline nature of the CdTe film. The lowest resistivity after CdCl₂ treatment makes it easy to achieve an ohmic contact to CdTe thin film, thus enabling its use in solar cell and optical detector.

References

Figure (1) XRD spectrum of as-deposited CdTe thin film
Figure (2) XRD spectrum of CdTe thin film annealed at 300°C for 15 min.

Figure (3) XRD spectrum of CdTe thin films after CdCl₂ treatment and after annealed at 300°C for 15 min.
Figure (4) image of surface morphology of CdTe thin films (a) as-deposited, (b) annealed and (c) CdCl$_2$ treated film at 300°C for 15min.
Figure (5) Transmittance spectrum of the as-deposited CdTe thin films, annealed and CdCl₂ treated films.
Figure (6) Absorption spectra of CdTe thin films (a) as-deposited, (b) annealed and (c) CdCl$_2$ heat treated.

Figure (7) Temperature dependence of D.C. conductivity $\sigma$ for CdTe films, as-deposited, annealed at 300°C for 15min and CdCl$_2$ treated at 300°C for 15min.