

# Anneal induced recrystallization of CdTe films electrodeposited on stainless steel foil: The effect of CdCl<sub>2</sub>\*

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Electrodeposited CdTe films were treated with a saturated solution of CdCl<sub>2</sub>, and later annealed in air at various temperatures and time durations in order to investigate the influence of post deposition CdCl<sub>2</sub> annealing treatments on the structure of the films. The XRD results showed that the CdCl<sub>2</sub> treatment has a noticeable influence on the stress, grain growth and the re-crystallization of CdTe. The value of activation energy for 20% re-crystallization in CdTe was estimated as  $1.17 \pm 0.4$  eV and  $0.99 \pm 0.1$  eV respectively for untreated and CdCl<sub>2</sub> treated CdTe films. In the early stages of annealing the re-crystallization is dominated by random orientation of the grains followed by a second phase in which once again the crystallites tend to orient in a particular direction. The Lattice constant (*a*) increases upon annealing and reaches a maximum and on further annealing for a long time it decreases and attains a value less than that of the powder sample.

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## 1. Introduction

The optoelectronic properties of CdTe based photovoltaic devices are highly dependent on the post deposition CdCl<sub>2</sub> annealing treatments. The annealing treatments promotes recrystallization, grain growth and improve the optical and electrical properties of the film and hence the device. Despite CdTe/CdS solar cells reaching efficiencies above 16% [1, 2], knowledge of basic properties of the materials and processes involved in the device fabrication is limited, including the heat treatment. An understanding of the structural changes due to post deposition treatments of the film is helpful in understanding and optimizing the performance of the photovoltaic device. There are reports regarding the effect of CdCl<sub>2</sub> annealing treatments on the structural changes of CdTe thin films and its influence on the performance of CdTe-CdS solar cells [3–8]. It was reported that the chlorine has a substantive influence on the structural changes in CdTe; reduces the lattice parameter and inhomogeneous stress, improves the crystallinity and promotes grain growth [3–5, 8]. In electrodeposited CdTe thin films the grain growth exponent *n* was found to be smaller than the ideal value of 0.5 and the re-crystallization activation energy was determined to be  $\sim 2.5$  eV [6]. All these studies were either on CdS or on transparent conducting oxide (TCO) coated glass substrates, and in such an analysis it is difficult to isolate the CdTe layer alone and investigate the effect of heat treatment on CdTe.

We have recently published the results of our studies about the effect of annealing on the structural properties of as deposited CdTe films (hereafter called untreated) on metallic substrate [9]. In this article we are presenting the study of the influence of CdCl<sub>2</sub> on the post deposition annealing and recrystallization of the electrodeposited CdTe films on stainless steel (SS) substrates. Since a 400 °C annealing in CdCl<sub>2</sub> ambient is a routine step in CdTe/CdS device fabrication, we have included for a comparison, the data of untreated film annealed at 400 °C [9] in different figures. XRD measurements were performed to investigate the effect of annealing on the stress, re-crystallization and the grain growth. Since our films were on metallic substrates, the effect of TCO layer and the heterojunction partner CdS as well as the diffusion effects at the interface between the films were eliminated.

## 2. Experimental

The details of the electrolyte as well as the electro deposition parameters for the development of CdTe thin films are described elsewhere [10, 11]. The thickness of all the CdTe films used in this study was about 1.4 μm. The CdCl<sub>2</sub> treatment was performed as follows; the CdTe films were dipped into a saturated solution of CdCl<sub>2</sub> in methanol for 5 min and the films were taken out of the solution and left on glass slides in room temperature for drying. The films were annealed at three

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different temperatures 350, 400 and 450 °C and for different time durations 0 to 60 min. The XRD data over a  $2\theta$  range of 20–115 degrees were collected using a Rigaku X-ray diffractometer. The integral intensity of 111 and 220 peaks were used to calculate the activation energy of the CdTe thin films.

### 3. Results and discussion

#### 3.1. Grain growth

The average diameter ( $D$ ) of the CdTe grains were calculated by measuring the full width at half maximum (FWHM) of the peaks and using the Scherrer relation [12, 13]. The effect due to instrumental broadening was eliminated using the data of polycrystalline silicon. The variation of grain size with the annealing time and temperature is presented in Fig. 1. The solid lines correspond to the untreated sample and the dotted lines represent the CdCl<sub>2</sub> treated samples. It can be seen that at the early stages of annealing, a rapid re-crystallization happens and the grains attain the maximum size in less than 5 mins, afterwards the grain size slowly decreases until 30 mins of annealing and beyond 30 mins the grains show a tendency to slightly increase in size. A comparison between the two types of samples shows that the CdCl<sub>2</sub> influences the grain growth not only by increasing the grain size but also in reducing the process time. Further, it was observed that in the presence of CdCl<sub>2</sub>, the annealing temperature has only little influence on the grain size compared to the untreated samples which shows a significant dependence on annealing temperature [9]. Hence it can be observed that CdCl<sub>2</sub> treatment helps to lower the annealing temperature of the CdTe films and improves the grain size. From Fig. 1 it is clear that a CdCl<sub>2</sub> treatment followed by annealing at 350 °C for 5 min is sufficient to produce grain growth in the case of CdTe films electrodeposited on SS substrate.

The AFM pictures of the (a) as deposited, (b) untreated but annealed at 350 °C for 5 min and (c) CdCl<sub>2</sub> treated and annealed at 350 °C for 5 min are shown in

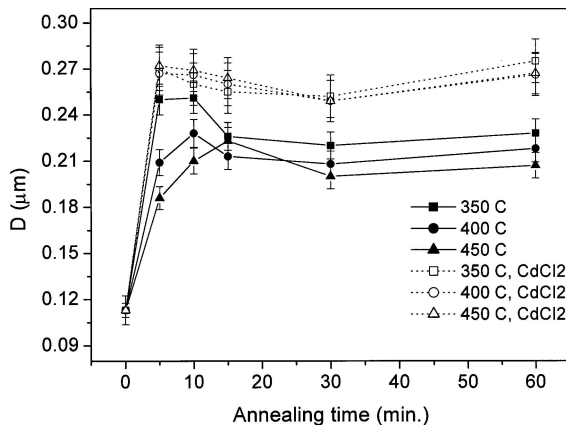


Figure 1 The change of the average grain size  $D(\text{\AA})$  with respect to the annealing time. The films were annealed in air at 350, 400 and 450 °C. The solid lines correspond to the samples annealed without a CdCl<sub>2</sub> treatment [9]. The legend CdCl<sub>2</sub> stands for the samples treated with CdCl<sub>2</sub>. The markers are experimental data and the line is a guide to the eye.

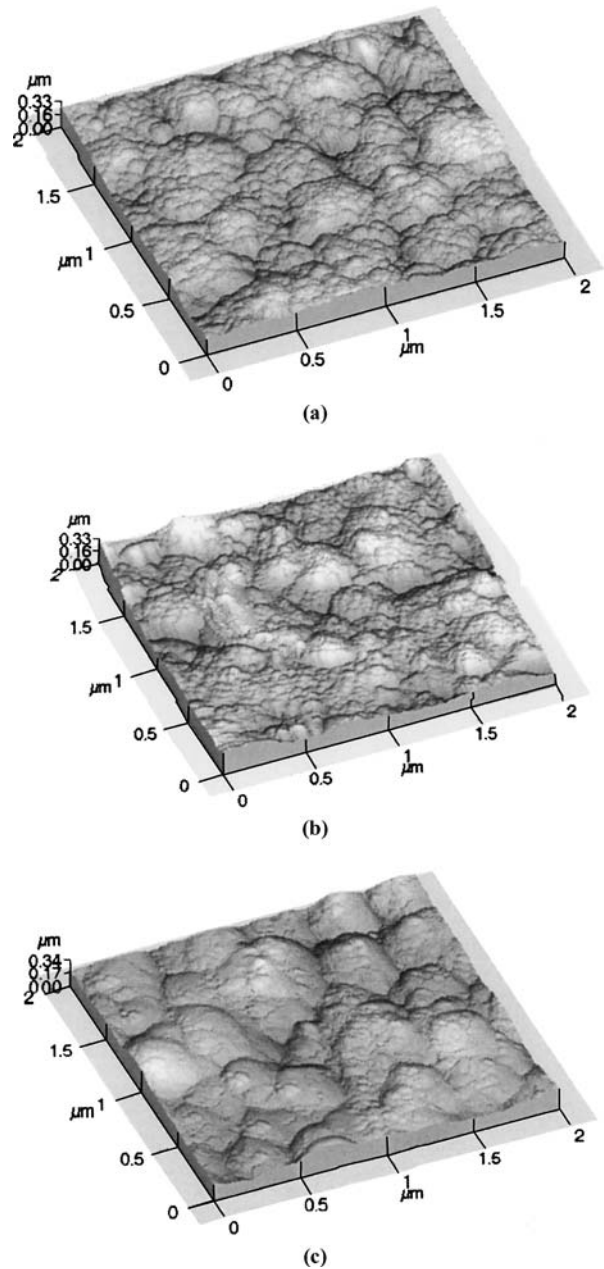


Figure 2 AFM pictures of (a) as deposited CdTe film, (b) untreated but annealed in air at 350 °C for 5 min and (c) CdCl<sub>2</sub> treated and annealed in air at 350 °C for 5 min.

Fig. 2. The as deposited film shows morphology with agglomerations of small grains, giving a cauliflower like appearance. Annealing of the untreated film did not made many changes, but the CdCl<sub>2</sub> treated film shows significant changes in appearance; the small grains in each agglomerate coalesced together producing larger grains. The above three samples were cut from the same film used for the XRD measurements.

The time dependent grain growth was studied by applying the parabolic grain growth law [14],

$$(D^2 - D_0^2)^{1/2} = At^n \quad (1)$$

where  $D_0$  and  $D$  are the average grain sizes before and after annealing,  $t$  is the annealing time,  $A$  is a constant and  $n$  is the grain growth exponent (the ideal value of  $n$  above the half melting temperature is 0.5). We have estimated the values of  $n$  in the case of untreated films

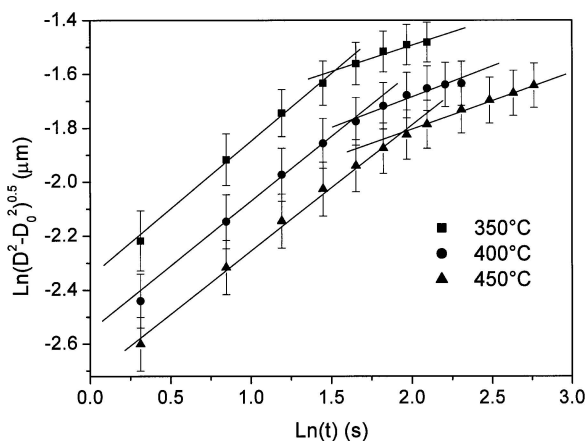


Figure 3 The fit of the generated data to the parabolic grain growth law (Equation 1). The data was generated by applying a polynomial curve fitting for the first phase in Fig. 1 where the grain size increases with annealing time.

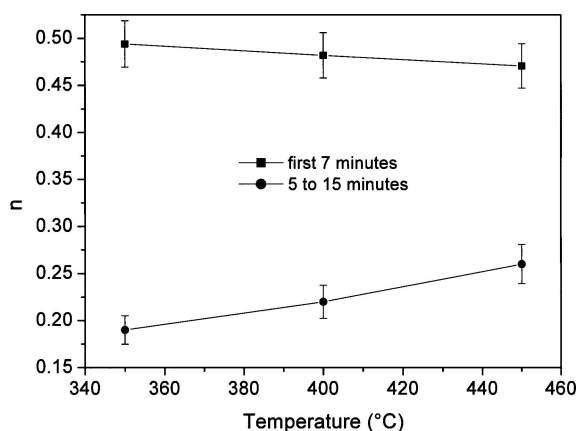


Figure 4 Plot of grain growth exponent  $n$  against temperature as a function of annealing duration. The markers are the actual data and the line is a guide to the eye.

for three different temperatures; 350, 400 and 450 °C using the data of the early stages of annealing when the grain growth occurs (0 to 15 minutes in Fig. 1). In order to facilitate this calculation we have made a polynomial curve fitting using the data of the first phase in Fig. 1 where the grain size increases with annealing time and various points were taken from the polynomial fit. A plot of  $\text{Ln}((D^2 - D_0^2)^{1/2})$  against  $\text{Ln}(t)$  is shown in Fig. 3 and the slope of the graph corresponds to the value of  $n$  for each annealing temperature. From figure it is clear that the grain growth follows two exponents, one in the first 7 minutes and a second one in the 5 to 15 mins interval depending on the annealing temperature.

Fig. 4 is the plot of grain growth exponent  $n$  against temperature as a function of annealing duration. In the case of an ideal grain growth as expressed in Equation (1) the value of  $n$  is expected to be about 0.5. From Fig. 4 it is clear that during the first few minutes of the annealing process, the grain growth obeys the parabolic law, but for longer annealing times it deviates significantly from the ideal case. We have observed a significant difference in the behavior of grain growth exponent with respect to temperature of our CdTe films and that reported in the literature. It was observed that in the case of CdTe films electrodeposited

on CdS/SnO<sub>2</sub>/glass substrates, the value of  $n$  has a very significant dependence on annealing temperature [6]. But in our CdTe films electrodeposited on SS substrates, the dependence of  $n$  (Fig. 4) on temperature is negligible; in the parabolic grain growth region (first 7 mins) the exponent  $n$  shows only a difference of 0.024 in the entire temperature range. On the other hand the grain growth exponent shows a strong dependence on annealing time, changes from 0.49 to 0.19 for time durations greater than 5 min. This difference in behavior between films on SS and CdS/SnO<sub>2</sub>/glass can be due to the difference in the stress induced by the two types of substrates. We were not able to perform a similar curve fitting (as in Fig. 3) in the case of CdCl<sub>2</sub> treated samples due to lack of experimental data in the initial stages of annealing.

### 3.2. Lattice Parameter

The variation of lattice parameter ( $a_0$ ) as a function of temperature and annealing time for CdTe thin films deposited on SS is shown in Fig. 5. The lattice parameter was calculated using the method developed by Nelson and Taylor [15,16]. For the as-deposited samples, the value of  $a_0$  ( $a_{\text{as-deposited}} = 6.485 \text{ \AA}$ ) is larger than the powder sample ( $a_{\text{powder}} = 6.481 \text{ \AA}$ ), which suggests that the as-deposited film is submitted to a compressive stress in the plane parallel to the substrate surface [9]. This stress is caused by the lattice mismatch and differences in thermal expansion coefficients between the CdTe film and substrate. It can be seen that the lattice parameter has a dependence on temperature and annealing time, in the initial stages of annealing the lattice value increase with annealing time and reaches a maximum value in 5 to 10 minutes depending on the temperature and then decreases. This behavior suggest that during annealing, the films first go through a compressive stress and for longer annealing durations the stress changes from compressive to tensile. In the case of films annealed at temperatures 400 °C and higher, the

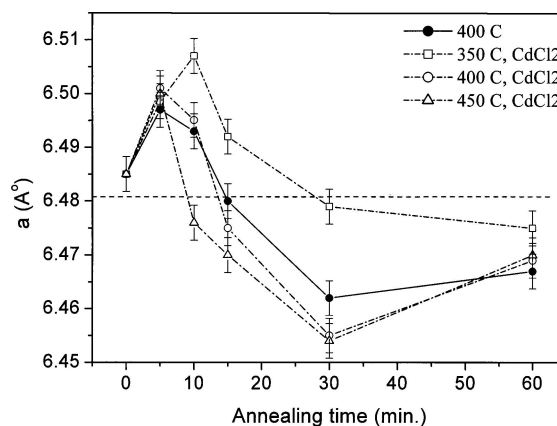


Figure 5 Graph showing the dependence of lattice constant on annealing time and temperature of CdTe thin films electrodeposited on SS substrate. The legend CdCl<sub>2</sub> stands for the samples treated with CdCl<sub>2</sub>. For a comparison, the data of the untreated sample (solid circle) annealed at 400 °C is also presented [9]. The lines connecting the markers is a guide to the eye and the broken horizontal line corresponds to the stress free value of the lattice constant ( $a_{\text{powder}} = 6.481 \text{ \AA}$ ).

lattice parameter goes through a minimum value around 30 min and afterwards shows a tendency to increase. In the figure, the first point (zero time) corresponds to the as deposited film. The influence of CdCl<sub>2</sub> treatments on the lattice parameter is very clear in Fig. 5. As the annealing temperature increases, the magnitude of the maximum value of the lattice decreases and also the maximum value is attained in shorter time for higher temperatures. In the early stages of annealing the lattice parameter of the CdCl<sub>2</sub> treated samples are higher than that of the untreated samples [9], but for longer annealing times the lattice parameter of the CdCl<sub>2</sub> treated films become smaller than that of the untreated films.

In the case of CdTe films electrodeposited on CdS/SnO<sub>2</sub>/glass substrates, it was reported that upon annealing, the lattice parameter decreases with time and attains a minimum value which is lower than that of the powder sample [4, 6]. The films on CdS/SnO<sub>2</sub>/glass substrates didn't show an increase of the lattice value as we observe in our films on SS. This suggests that the substrate has a strong influence on the post deposition annealing and the lattice parameter. However, irrespective of the substrate, the lattice parameter of the as deposited films is always larger than that of the powder (stress free) sample.

### 3.3. Recrystallization

The change in relative intensities of the XRD peaks is a measure of recrystallization in the film causing changes in the preferred orientation of the crystallites. This can be analyzed by calculating the normalized integral intensity ratio,  $R_n$ , of the (220) and (111) peaks [6, 9].

$$R_n = \frac{\left(\frac{I_{220}}{I_{111}}\right)_{\text{film}}}{\left(\frac{I_{220}}{I_{111}}\right)_{\text{powder}}} \quad (2)$$

where  $I_{220}$  and  $I_{111}$  are the integral intensities of (220) and (111) diffraction peaks respectively.  $R_n = 1$  indicates random orientation for the crystallites, and  $R_n = 0$  indicates perfect orientation (texture) along (111) direction. The effect of CdCl<sub>2</sub> on re-crystallization is very clearly demonstrated in Fig. 6, in all the cases the CdCl<sub>2</sub> treatment promotes re-crystallization significantly. It can be observed that at the initial stage of annealing the  $R_n$  increases indicating that the orientation of the planes tend to be random (recrystallization dominates) and after certain time depending on the annealing temperature the orientation of planes once again tend to obtain the (111) direction (preferred grain growth dominates). Similar behavior was observed by Bin Qui *et al*, but their data was limited up to 375 °C. [6].

We have estimated the re-crystallization activation energy using the relation [6, 9],

$$t = \frac{1}{A} e^{\frac{E_{ar}}{kT}} \quad (3)$$

where  $A$  is a constant,  $E_{ar}$  is the activation energy of re-crystallization, and  $t$  is the time required for some fraction of re-crystallization to happen. The re-

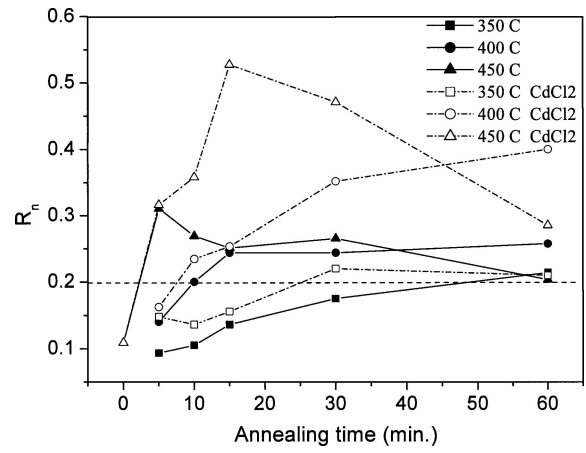


Figure 6 Graph showing the variation of the normalized XRD intensity ratio ( $R_n$ ) of the (220) and (111) peaks with annealing time. The data for both untreated [9] (solid markers) and CdCl<sub>2</sub> treated (this study) samples are presented. The legend CdCl<sub>2</sub> corresponds to the samples treated with CdCl<sub>2</sub>. The markers are experimental data and the line is a guide to the eye. The broken horizontal line corresponds to 20% recrystallization of the crystallites and it is assumed that above this the recrystallization is dominated by random orientation of the grains.

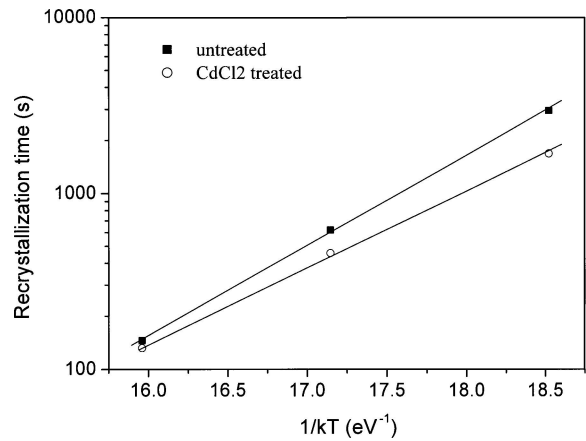


Figure 7 The fit of the experimental data to Equation (3). The recrystallization time was taken from Fig. 6 and it corresponds to the 20% recrystallization of the crystallites in the films.

crystallization process has a dependence on CdCl<sub>2</sub> annealing treatment and time duration (Fig. 6). A significant difference can be noticed between the films annealed at 450 °C and those annealed at lower temperatures. High temperature annealing of both CdCl<sub>2</sub> treated and untreated films shows that in the beginning the re-crystallization is dominated by random orientation of the grains followed by the second process which tend to orient the crystallites in a particular direction. On the other hand annealing at lower temperatures shows only the first phase indicating that a total re-crystallization happens only above 400 °C irrespective of the CdCl<sub>2</sub> treatment. However the extent of re-crystallization is significantly influenced by the CdCl<sub>2</sub> treatment. Using Equation (3), a graph of Ln( $t$ ) against  $1/T$  gives a straight line (Fig. 7) and the activation energy can be estimated from the slope of the graph.

Assuming that recrystallization dominates at  $R_n \leq 0.2$  [9], the time for 20% recrystallization was estimated from Fig. 6 and used to plot Fig. 7. The values of the activation energy of recrystallization for CdCl<sub>2</sub> treated

and untreated films were obtained as  $0.99 \pm 0.1$  eV and  $1.17 \pm 0.1$  eV respectively. This value is lower than the value (2.44 eV) of Cd diffusion in CdTe at minimum cadmium vapor pressure [17]. The reported value of  $E_{ar}$  in the literature for CdTe films electrodeposited on CdS/SnO<sub>2</sub>/glass and treated with CdCl<sub>2</sub> [6] is  $2.5 \pm 0.3$  eV.

#### 4. Conclusion

We have studied the influence of CdCl<sub>2</sub> annealing treatment on the recrystallization and grain growth of CdTe thin films electrodeposited on stainless steel substrates. It was observed that the CdCl<sub>2</sub> promotes recrystallization and grain growth. Annealing at 350 °C for 5 min in CdCl<sub>2</sub> ambient is sufficient to produce the grain growth, but a total recrystallization happens only after annealing at 450 °C. At the initial stages of annealing when the grains grow in size, the grain growth process obeys the parabolic law. The substrate surface has a significant influence on the re-crystallization of CdTe, in the case of CdTe deposited on stain less steel substrate, the grain growth exponent is independent of temperature but depends on annealing time. The lattice parameter of the as deposited CdTe film is larger than that of the powder sample indicating that the as deposited film is under compressive stress. Contrary to the reported observation in literature, we have observed that the re-crystallization process during annealing has two stages, in the beginning the re-crystallization is dominated by random orientation of the grains followed by a second process in which once again the crystallites tend to orient in a particular direction. The value of activation energy for 20% re-crystallization in CdTe was estimated as  $1.17 \pm 0.4$  eV and  $0.99 \pm 0.1$  eV respectively for untreated and CdCl<sub>2</sub> treated CdTe films.

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