

# The formation of CdTe thin films by the stacked elemental layer method

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Cadmium telluride thin films have been produced using the Stacked Elemental Layer technique. The films were characterized using x-ray diffraction, optical transmittance and reflectance, and atomic force microscopy. The evolution of the thin film reaction and compound formation were studied using x-ray data. The results show that the growth is diffusion controlled and the activation energy is  $(82 \pm 2)$  kJ/mol. In addition, some physical properties of the films produced are reported.

## 1. Introduction

Cadmium telluride (CdTe) is one of the most promising polycrystalline materials for producing solar cells because of its high absorption coefficient ( $> 10^4 \text{ cm}^{-1}$ ) and optimum bandgap (1.5 eV).

Several techniques have been used for depositing these films [1]; all of them leads to good quality films, mainly if they are submitted to the well-known post-deposition  $\text{CdCl}_2$  heat treatment [2,3].

This work investigates the physical properties of CdTe films prepared by a more recent deposition method: the Stacked Elemental Layer (SEL) technique. This process was originally developed to produce copper indium diselenide thin films [4] but has also been used to produce CdTe films [5, 6]. It consists of sequentially depositing Te and Cd layers and then annealing the resulting stack in order to form the compound. It is particularly suitable for deposition of compound semiconductor films, as it provides good control of composition; also, it seems to be a promising method for producing highly efficient CdTe/CdS solar cells [6]. For this reason, additional investigations concerning growth mechanisms and physical properties are needed. Here, the compound formation reaction was evaluated progressively, at different temperatures, using x-ray diffraction with grazing incidence geometry.

In addition, this work briefly reports the structural and optical properties of the layers produced. A complete and very well detailed discussion about this issue is published elsewhere [7].

## 2. Experimental procedure

Bilayers and multilayers of Te/Cd were deposited onto unheated Corning 7059 glass substrates by thermal evaporation, in a vacuum system equipped with a cryogenic pump. The elemental layers, Te followed by Cd, were alternatively evaporated at  $3 \text{ \AA/s}$ ; in both cases, quartz bottles were used as heat sources. The pressure during evaporation was in the  $10^{-6}$ - $10^{-5}$  torr range. A shutter, just above one of the sources, could be displaced to cover each one of the bottles, thus selecting the desired layer to reach the substrate. Another shutter was placed just under the

substrate holder in order to avoid deposition on the substrate.

In order to establish the desired stoichiometry, the thickness of elemental layers must be adjusted; for a CdTe film, the number of atoms in Te and Cd layers must be identical; this leads to the following relationship between the thicknesses of the elemental layers:  $t_{\text{Te}} / t_{\text{Cd}} = 1.53$ . Also, a 20% increase in the thickness of the stack is expected after completion of the reaction, due to the difference between the molar volumes of the CdTe compound and the Cd/Te bilayer. In this work, Te and Cd films were  $0.20 \text{ \mu m}$  and  $0.13 \text{ \mu m}$  thick, respectively.

The synthesis of CdTe was carried out in argon, in a separate vacuum system. The chamber was initially pumped down to  $10^{-3}$  torr, purged with argon, and then filled with argon up to  $10^{-1}$  torr, in order to prevent Te and Cd loss. Bilayers were annealed from  $170 \text{ }^\circ\text{C}$  to  $250 \text{ }^\circ\text{C}$  for different times, to study the kinetic of the reaction; higher annealing temperatures ( $300 \text{ }^\circ\text{C}$  to  $500 \text{ }^\circ\text{C}$ ) were used to improve film crystallinity. Thicker films ( $\approx 2,3 \text{ \mu m}$ ) were produced from multilayers (6 pairs) annealed at temperatures ranging from  $400 \text{ }^\circ\text{C}$  to  $500 \text{ }^\circ\text{C}$  for 30 min.

The samples were analyzed by grazing incidence x-ray diffraction (GIXRD), using the  $\text{CuK}\alpha$  radiation in a Siemens D5000 diffractometer, by atomic force microscopy (AFM), using a Park Scientific Instruments Autoprobe LS, and by optical transmittance and reflectance using a Carry 2300 spectrophotometer.

## 3. Results and discussion

### X-Ray measurements

The grazing incidence x-ray diffraction (GIXRD) technique was used to observe the gradual formation of CdTe compound from the elemental layers. The GIXRD geometry is particularly useful for thin films, since low incidence angles significantly increases the path length of the beam into the layer, leading to a better signal-to-noise ratio. In this work, all the measurements were performed with the Bragg angle,  $2\theta$ , ranging from  $20^\circ$  to  $80^\circ$  and the incidence angle,  $\theta_i$ , fixed at  $1^\circ$ . With this value of  $\theta_i$ , the penetration depth of  $\text{CuK}\alpha$  x-rays in CdTe is close to  $0.11 \text{ \mu m}$  [8, 9], that is, close to the interface Cd/Te.

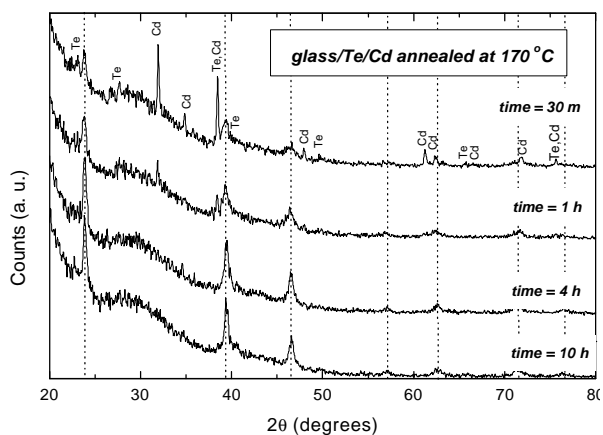


Fig. 1. XRD patterns of a glass/Te/Cd film annealed at 170 °C. Dotted lines indicate cubic CdTe peaks.

The XRD pattern of an as-deposited glass/Te/Cd film showed no CdTe peaks. The XRD patterns of a glass/Te/Cd film annealed at 170 °C for different times are given in Fig.1. Dotted lines indicate peaks belonging to the CdTe cubic structure; they grow slowly with the annealing time. The extra peaks are due to free elements, Cd and Te, which gradually disappear as a result of the reaction.

Considering that the integrated intensity of a diffraction line is proportional to the irradiated volume, one can follow the CdTe formation by measuring the CdTe peak intensity (area under the curve) as a function of time. This assumption is correct since no texture was observed in the growing film. In addition, assuming that the new planar phase layer has uniform thickness, the integrated intensity will also be proportional to the thickness of the new phase. A Voigt II function was used to fit the area under the diffraction lines. The results are seen in Fig. 2, which shows the peak intensity summation in 20°-80° range,  $A_{CdTe}$ , as a function of  $time^{1/2}$ , for samples annealed at 170 °C, 200 °C and 250 °C. These curves represent, in fact, the variation of the compound thickness with annealing time and may provide useful information about the dominant growth mechanism.

The fact that the parabolic law,  $A_{CdTe} = \sqrt{ct}$ , is satisfied in this range of temperature shows that growth of the new planar phase layer is being controlled by a diffusion process [10, 11]. Hence, the model that better describes the formation of CdTe compound from the elemental layers is a planar interface that moves parallel to the original one, in a diffusion controlled rate. The activation energy for CdTe growth,  $E_A$ , is obtained from the kinetic parameter,  $c$ , extracted from the slopes of the curves shown in Fig. 2. These values are plotted in an Arrhenius graph shown in Fig.3. The value of  $E_A$ , obtained from the slope of the straight-line fit to the experimental data, is  $(82 \pm 2)$  kJ/mol.

The XRD technique was also used to investigate the effect of higher annealing temperatures on film crystallinity. This effect can be evaluated in Fig. 4, which shows the XRD data of a glass/Te/Cd film annealed at 300

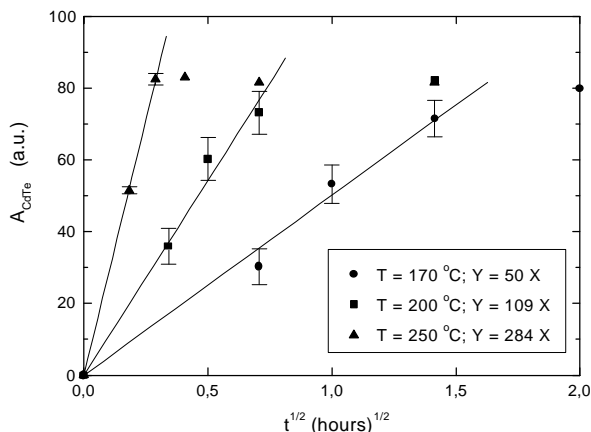


Fig. 2. Peak intensity summation (area under CdTe peaks),  $A_{CdTe}$ , as a function of  $(time)^{1/2}$ .

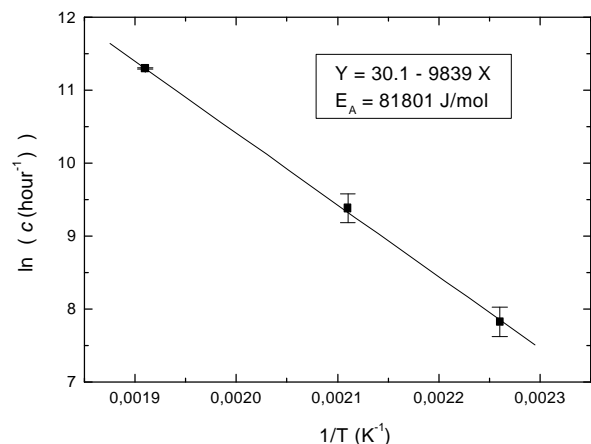


Fig.. 3. Plot of  $\ln c$  versus  $1/T$  to determine the activation energy for CdTe growth.

°C and 500 °C, for 30 min. The patterns display sharp and strong reflections, indicating that annealing temperatures above 300 °C improve film crystallinity, probably by promoting grain growth and reducing inhomogeneous stress.

**Transmittance and reflectance measurements.**

It was found that the annealing time has a (4) influence on the film absorption. Transmittance versus wavelength measurements for as-deposited and annealed glass/Te/Cd films are shown in Fig. 5. It is evident that, although XRD data have unveiled that Te/Cd reaction started at temperatures as low as 170 °C, films synthesized in 170 °C - 250 °C range do not present the characteristic absorption edge ( $\approx 830$  nm). Such a result should be expected, since the XRD spectra of films synthesized below 300 °C showed the presence of Te and Cd free phases and broad and low-intensity peaks, fact that would explain the lack of the absorption edge in these films. The above-mentioned behaviour indicates that thermal energy supplied in this range of temperature was enough to surpass the activation barrier for the reaction but not to improve crystallinity; this was only achieved when annealing was carried out above 300 °C.

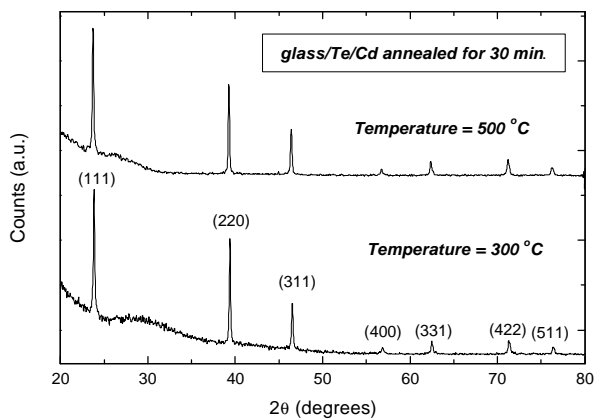


Fig. 4. XRD patterns of a glass/Te/Cd film annealed at 300 and 500°C. Dotted lines indicate cubic CdTe peaks.

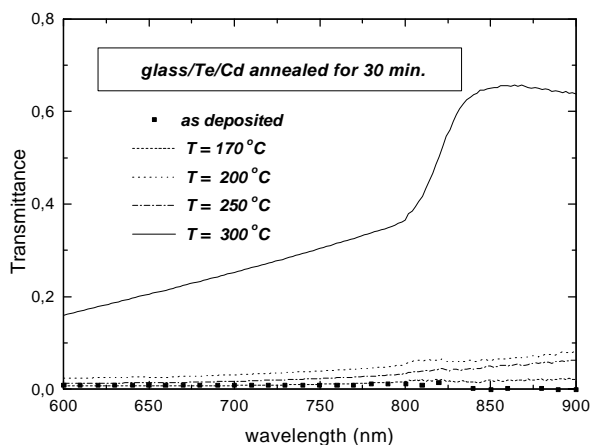


Fig. 5. Transmittance spectra of as deposited and annealed glass/Te/Cd films.

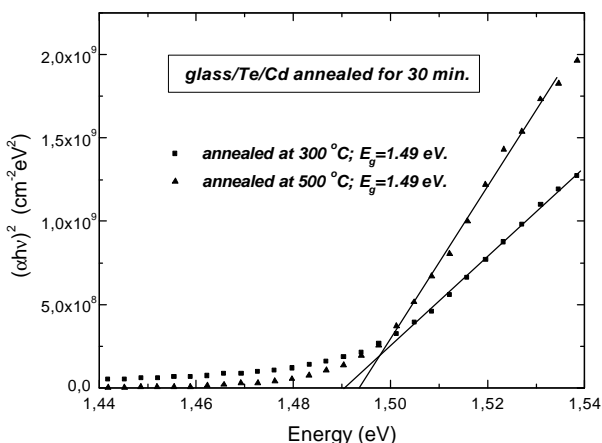


Fig. 6. Bandgap energy of CdTe films synthesized at 2 temperatures.

The data shown in Fig. 5 in conjunction with reflectance measurements led to the determination of the absorption coefficient,  $\alpha$ , as a function of wavelength [12]. The variation of  $(\alpha h\nu)^2$  with energy,  $h\nu$ , is shown in Fig. 6, for two temperatures. The bandgap energy is obtained by intercepting the linear portion of the absorption curves to

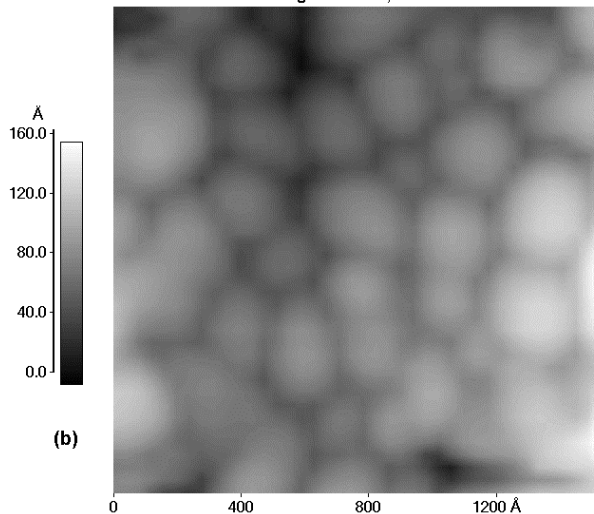
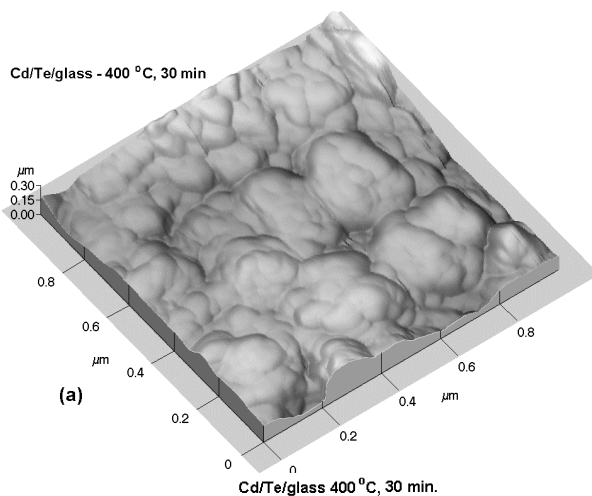


Fig. 7. Typical surface morphology of CdTe films a) representative AFM image of a Cd/Te film synthesized at 400 °C; b) detail of an agglomerate of grains.

the energy axis. The value 1.5 eV does not depend upon annealing temperature and is in good agreement with literature [5, 6]. The tendency of the absorption edge to become more abrupt at higher annealing temperatures is certainly related to the observed improvement in the crystallinity of these films.

**Atomic force microscopy**

The surface morphology of CdTe films grown by the SEL technique is typically as seen in Fig. 7a, which shows an AFM image of glass/Te/Cd sample annealed at 400 °C. It is uniform and composed of agglomerates of very small grains (roughly 20 nm). The morphological aspects are better seen in Fig. 7b, which shows the interior of an agglomerate. Neither the temperature nor the time used for synthesizing the compound influenced this morphology. This behavior may indicate the presence of a high barrier for grain boundary migration and also that the thermal energy supplied by annealing was just enough to promote the reaction between the layers.

The morphology of nanograins has recently been reported in literature for CdTe films deposited by physical vapor deposition and sputtering [3]. As reported elsewhere

[7], the film morphology is significantly changed by heat treatment in the presence of CdCl<sub>2</sub>/methanol solution. After this treatment, the agglomerates of nanograins are substituted by larger grains (average size is 400 nm) whose surface is completely smooth.

#### 4. Conclusions

The physical properties of CdTe thin films produced by SEL method have been investigated. XRD and optical analysis showed that CdTe formation starts at 170 °C, but useful optical properties are only achieved when the reaction is carried out above 300 °C. AFM images showed an uniform morphology, composed by agglomerates of nanograins. The isothermal reaction between Cd and Te was studied using the GIXRD technique. The growth rate of CdTe follows a parabolic relation between the thickness and the annealing time, indicating that growth is diffusion controlled. The activation energy for CdTe growth was determined to be  $(82 \pm 2)$  kJ/mol over the temperature range of 170 °C to 250 °C.

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#### References

- [1] T. L. Chu and S. S. Chu, *Progress in Photovoltaics: Research and Applications* **1**, 31 (1993).
- [2] B. E. McCandless and R. W. Birkmire, *Solar Cells* **31**, 527 (1991).
- [3] H. R. Moutinho F. S. Hasoon, F. Abulfotuh, and L. L. Kazmerski, *J. Vac. Sci. Technol. A* **13(6)**, 2877 (1995).
- [4] M. J. Carter, I. I'Anson, A. Knowles and R. Hill, *Proc. 19th IEEE Photovoltaic Specialists Conference*, 1275 (1987).
- [5] M. T. Bhatti, K. M. Hynes, R. W. Miles and R. Hill, *Int. J. Solar Energy* **12**, 171 (1992).
- [6] R. W. Miles, M. T. Bhatti, K. M. Hynes, A. E. Baumann and R. Hill, *Material Science and Engineering* **B16**, 250 (1993).
- [7] L. R. Cruz, L. L. Kazmerski, H. R. Moutinho, F. Hasoon., R. G. Dhere and R. R. de Avillez, *Thin Solid Films*, in press.
- [8] T. Slimani, P. Goudeau and A. Naudon, *J. Appl. Cryst.* **24**, 638 (1991).
- [9] R. W. James, *The Optical Principles of the Diffraction of X-Rays* (G. Bell & Sons Ltd., London, 1950).
- [10] G. V. Kidson, *J. Nuclear Materials* **3(1)**, 21 (1961).
- [11] U. Gosèle and K. N. Tu, *J. Appl. Phys.* **53**, 3252 (1982).
- [12] J. I. Pankove, *Optical Process in Semiconductors* (Dover Publications, Inc., NY, 1971).