

# STUDIES OF RECRYSTALLIZATION OF CdTe THIN FILMS AFTER CdCl<sub>2</sub> TREATMENT

H.R. Moutinho, M.M. Al-Jassim, F.A. Abulfotuh, D.H. Levi, P.C. Dippo, R.G. Dhere, and L.L. Kazmerski  
National Renewable Energy Laboratory, Golden, Colorado

## ABSTRACT

CdTe thin films deposited by physical vapor deposition (PVD) and close-spaced sublimation (CSS) have been treated with CdCl<sub>2</sub> at 350° and 400°C. Atomic force microscopy (AFM) analysis showed that the films started recrystallizing during the 350°C CdCl<sub>2</sub> treatment. These results were confirmed by the presence of two lattice parameters, detected in X-ray diffraction (XRD) analysis. The PVD films treated at 400°C were completely recrystallized and grain growth was observed. The formation of Cd(S<sub>1-x</sub>Te<sub>x</sub>) alloy in these films was evidenced by the appearance of extra peaks close to the CdTe peaks in the diffraction patterns. No major changes were observed in the structural properties of CSS CdTe films treated at the same conditions. It was concluded that the effect of the CdCl<sub>2</sub> treatment in the CdTe films is to promote recrystallization and grain growth, but only if enough lattice-strain energy is available (as is the case for PVD films). Time-resolved photoluminescence (TRPL) analysis showed, for PVD and CSS films, an increase in minority-carrier lifetime with the treatment, mainly at 400°C, probably due to elimination of deep levels within the band gap.

## INTRODUCTION

CdTe is a very promising material for use in thin-film solar cells. CdTe/CdS solar cells have reached efficiencies up to 15.8% [1]. Nevertheless, knowledge of basic properties of the materials and processes involved in device fabrication is limited, including the critical heat treatment with CdCl<sub>2</sub>/methanol solution. Although this subject has been studied by many authors in the past years [2,3], the exact effects of this treatment are still not completely clear. An area of disagreement between different studies involves the development of the microstructure with the CdCl<sub>2</sub> treatment. For instance, grain growth is observed in some cases [4], but not in others [5]. In this study, we clarify the effects of the CdCl<sub>2</sub> treatment on the structural properties of CdTe thin films, and explain why samples deposited by different methods behave differently. We have used AFM and XRD analyses to study the effects of the CdCl<sub>2</sub> heat treatment, at different temperatures, on the physical properties of

PVD and CSS CdTe thin films. The PVD samples were deposited on both CdS and ITO substrates, in order to isolate the effects of S and Te interdiffusion on the properties of the films. Finally, we report results of minority-carrier lifetime measurements on CdTe films before and after CdCl<sub>2</sub> heat treatment.

## EXPERIMENTAL PROCEDURE

The 2- $\mu$ m thick PVD CdTe films were deposited on substrates heated at 250°C, with a deposition rate of 0.02  $\mu$ m/min, and with a base pressure of 10<sup>-5</sup> Torr. The films were deposited on two substrate structures: CdS/ITO/glass and ITO/glass. The 3- $\mu$ m thick CSS films were deposited on substrates heated at 590°C, with a deposition rate of 6  $\mu$ m/min, and with a N<sub>2</sub> background pressure of 0.1 Torr. The substrate structure used was CdTe/SnO<sub>2</sub>/glass.

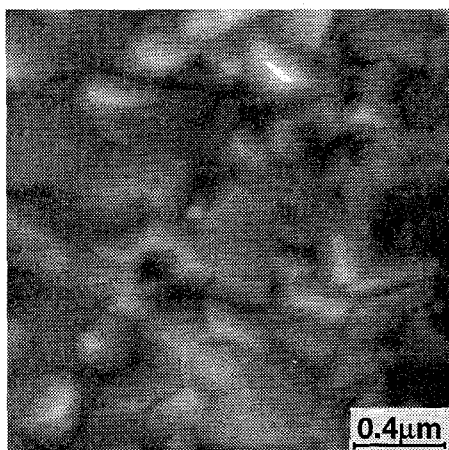
The AFM analysis was performed in contact mode, using 100-Å radius Si tips, in an Autoprobe LS AFM from Park Scientific Instruments. The XRD analysis was done in two XRD diffractometers: a Scintag, model X1, and a Rigaku, model RU-200V, both using K $\alpha$  radiation. The setup for the TRPL analysis has been described elsewhere [6].

The treatment on the samples was done with a saturated solution of CdCl<sub>2</sub> in methanol. After the application of the solution on the film surface, the samples were heated at 350° or 400°C for 30 minutes in a Lindberg one-zone tube furnace.

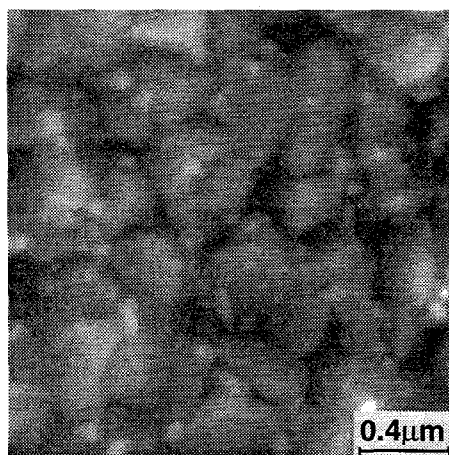
## RESULTS AND DISCUSSION

### Atomic Force Microscopy

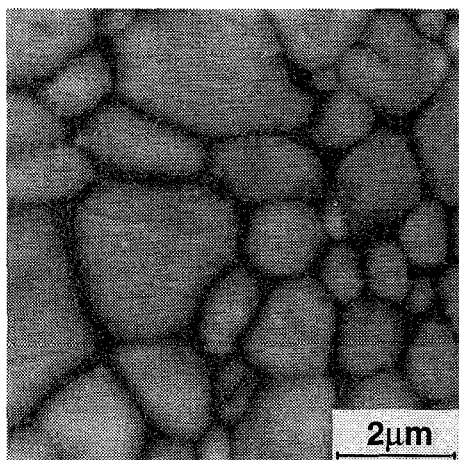
The untreated PVD CdTe films were uniform and had well-defined grains, as observed in Fig. 1a. The treatment at 350°C did not change the morphology of the films, but promoted the appearance of small grains, distributed mainly at the grain boundaries (Fig. 1b). These grains are due to the partial recrystallization of the CdTe film during the treatment at this temperature. The small grains belong to the new recrystallized structure, which grows at the expense of the original high-stressed film. To our knowledge, this is the first time that direct



(a)



(b)



(c)

Fig. 1. PVD CdTe films: (a) untreated, (b) and (c) after CdCl<sub>2</sub> heat treatment at 350° and 400°C, respectively.

evidence of recrystallization in CdTe films is presented. After the treatment at 400°C the recrystallization was complete, and there was significant grain growth (Fig. 1c). No differences on the morphology of these films were observed as a function of substrate structure. The average grain size increased from 0.26 μm, for an untreated sample, to 1.4 μm, for a sample treated at 400°C.

The untreated CSS CdTe films presented grains much larger than the untreated PVD CdTe films (Fig. 2). In contrast to the former material, CSS CdTe films did not show significant changes in morphology after the treatment at 350° or 400°C. This is evidenced in the value for the average grain size, which was 1.4 μm for an untreated film, and did not change significantly after the CdCl<sub>2</sub> treatment. Finally, no signs of recrystallization were observed in these films.

### X-ray Diffraction

The diffraction patterns for the PVD and CSS films showed peaks belonging to the cubic CdTe phase and to the underneath substrate structure.

The untreated PVD films had strong preferential orientation in the (111) direction, and only the (111), (333), and (444) peaks were present in the diffraction patterns. This strong texture was attributed to the substrate structure, which provided low-energy sites for the nucleation of the film, and also a reference plane for the growth itself. After the CdCl<sub>2</sub> treatment at 350°C, the (111) texture decreased, and peaks belonging to the other crystalline planes appeared in the XRD pattern. For samples treated at 400°C, the preferential orientation disappeared, and all the diffraction peaks were visible in the diffraction pattern.

For the study of in-plane stress in the CdTe films, we calculated values of the lattice parameter, *a*. The method used for the accurate determination of *a* was the one described by Taylor [7] and Nelson [8], where the

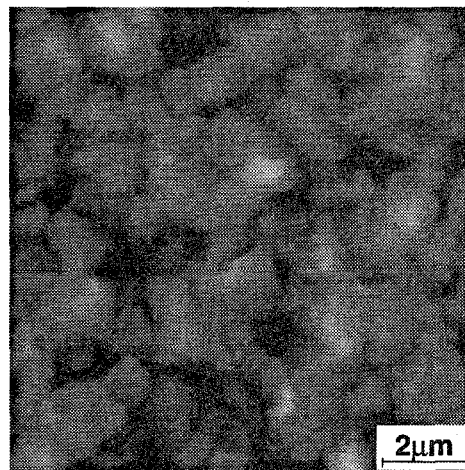


Fig. 2. AFM image of an untreated CSS CdTe film.

value of lattice parameter obtained from each peak in the diffraction pattern is plotted versus the function  $[(\cos^2\theta/\sin\theta)+(\cos^2\theta/\theta)]$ . The relationship between these two parameters is linear and the accurate value of  $a$  is obtained from the intercept of the curve generated by a linear regression of the points in the graph and the y-axis. The lattice parameter for PVD CdTe films deposited on CdS, before and after CdCl<sub>2</sub> treatment, were obtained from Fig. 3. For the untreated samples, we notice that the value of  $a$  (6.498 Å) is larger than the one for a powder sample (6.481 Å), which suggests that the film is submitted to a compressive stress in the plane parallel to the substrate surface. This stress has been observed before [9], and is caused by the lattice mismatch and/or differences in thermal expansion coefficients between the CdTe and the underlying film. After the treatment at 350°C, two values of  $a$  for a single sample are observed. The larger value (6.489 Å) corresponds to the original lattice (larger grains in Fig. 1b), and it is smaller than the value for an untreated sample because some of the stress in this part of the material has been relieved, probably by a process of recovery. Notice that the line in Fig. 3b corresponding to this value of  $a$  is formed only by the (111), (333), and (444) reflections, meaning strong (111) texture, and is related to the untreated film. The smaller

value of  $a$  ( $\cong$ 6.481 Å) is due to the recrystallized lattice (small grains in Fig. 1b). Because the new grains do not have any relation to the substrate, the recrystallized lattice has no preferential orientation. This explains the decrease in texture observed in the samples treated at 350°C and the points in the graph in Fig. 3b for all orientations. In this graph, the (111) related reflections due to the recrystallized lattice are not accounted for because they overlap with the corresponding reflections for the original lattice, and, since at this stage the amount of recrystallization is small, most of the signal comes from the original lattice, being difficult to extract values of  $a$  for the recrystallized lattice. An additional observation is that the value of the lattice parameter for the recrystallized lattice is the same as the one for a powder sample. This was expected, because the new material is not influenced by the substrate structure. Finally, we observed from the diffraction patterns for the PVD samples grown on CdS and treated at 400°C that an additional peak appears for each CdTe reflection. These extra peaks belong to the Cd(S<sub>x</sub>Te<sub>1-x</sub>) alloy, which is formed by the interdiffusion of S and Te at the CdS/CdTe interface [10]. The reason to assign these peaks to Cd(S<sub>x</sub>Te<sub>1-x</sub>) is because they are present for every CdTe peak, being very close to each of these peaks, which indicates the existence of a similar lattice with just a slightly different value of lattice parameter. Furthermore, this additional peak is not observed in the PVD samples treated at 400°C but deposited on ITO. Using peak deconvolution, we fitted the peaks to split Pearson functions and were able to isolate the peaks for each material and calculate the respective lattice parameters (Fig. 3a). As expected, the lattice parameter for the recrystallized CdTe did not show any in-plane stress. The lattice parameter for the CdTe alloy was 6.468 Å. Using Vegard's law [11], we calculated the amount of S in the alloy to be equal to 2%.

The evolution of the (333)/(511) peak with treatment is shown in Fig. 4. The movement of the peak to the right corresponds to the change in lattice parameter (decrease in in-plane stress) with treatment. Comparing the peaks for the untreated sample and the sample treated at 350°C, we notice that the width of the peak decreased, indicating that inhomogeneous stress [12] also decreased with the CdCl<sub>2</sub> heat treatment. This fact was also observed in PVD samples deposited on ITO, where it was observed that the lowest amount of inhomogeneous stress occurred in samples treated with CdCl<sub>2</sub> at 400°C. In Fig. 4, the presence of the extra peak due to the formation of Cd(S<sub>x</sub>Te<sub>1-x</sub>) in the sample treated at 400°C is evident.

The XRD analysis of the CSS samples showed that the untreated films did not have texture, and no significant differences were noticed after the treatment. The untreated samples presented a lattice parameter equal to 6.498 Å, indicating in-plane homogeneous stress. This stress decreased after the treatment at 350°C and decreased even further after the treatment at 400°C. Nevertheless, in contrast to the PVD samples, even after

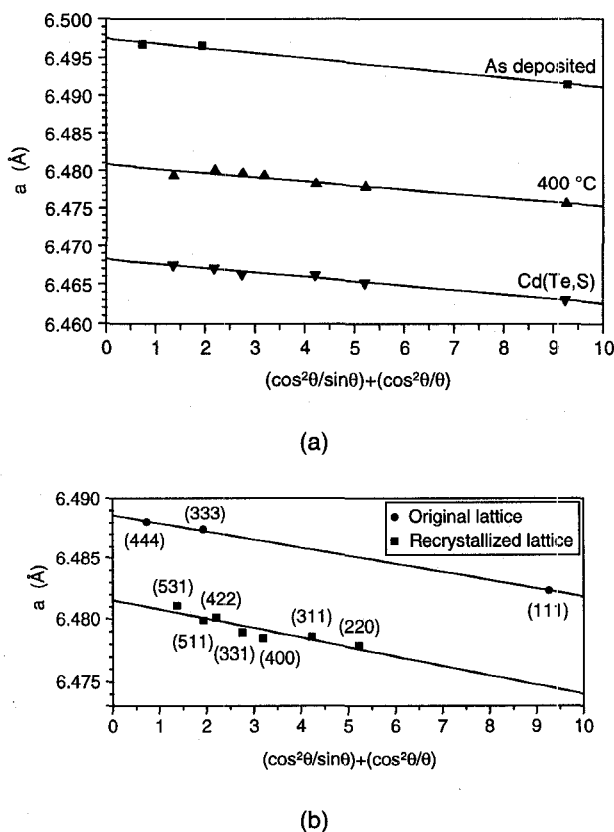


Fig. 3 - Lattice parameter for PVD CdTe samples deposited on CdS. (a) Untreated, and treated at 400°C; (b) Treated at 350°C.

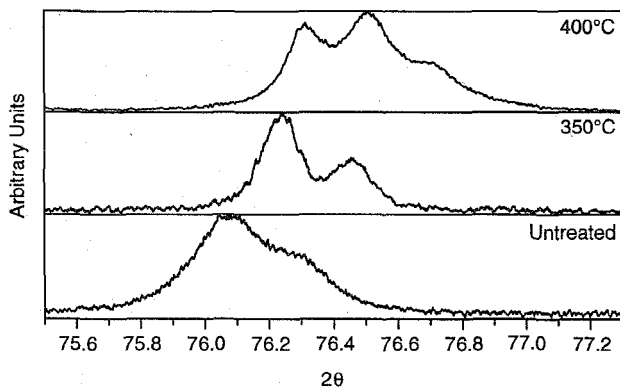


Fig. 4 - Diffraction patterns for the (333)/(511) peak for CdTe samples deposited on CdS.

the latter treatment there was some residual in-plane stress, indicated by a value of lattice parameter equal to 6.490 Å. Also, only one lattice parameter was found for the sample treated at 350°C. The difference between these results and the ones obtained with PVD samples is explained by the fact that CSS samples are grown at a much higher temperature and probably present a lower concentration of defects. Furthermore, the large grain size of these samples results in a much lower grain boundary area. These two factors translate to smaller lattice-strain energy, which is the driving force for recrystallization. For this reason, CSS samples do not recrystallize at the usual temperatures and times used in the CdCl<sub>2</sub> treatment. We believe that the observed improvements in the structural properties of these samples are exclusively due to recovery.

It has been observed that structural changes in CdTe thin films after heat treatment occur only when CdCl<sub>2</sub> is present [13]. As we have demonstrated, these changes occur due to recrystallization and subsequent grain growth. Recrystallization is a function of lattice-strain energy, and time and temperature of treatment. Since for treatment with and without CdCl<sub>2</sub> time and temperature are the same, we conclude that the effect of CdCl<sub>2</sub> in the treatment is to increase the initial strain energy of the material so that recrystallization can occur. The way we propose this to happen is through diffusion of Cl atoms into the films, mainly through grain boundaries, and the consequent increase in defect concentration.

Although no major changes in the structural properties of CSS CdTe samples were noticed after the CdCl<sub>2</sub> treatment, a significant increase in the minority-carrier lifetime was observed. The same effect was observed in PVD CdTe samples. Untreated films had PL lifetimes close to the system response. These values increased more than an order of magnitude after the CdCl<sub>2</sub> treatment at 400°C, approaching 800 ps for both PVD and CSS samples. We attributed this improvement to the elimination of deep defect levels inside the bandgap as a result of the CdCl<sub>2</sub> treatment. More details of electro-optical measurements will be published elsewhere.

## CONCLUSIONS

The effects of the CdCl<sub>2</sub> heat treatment on the structural properties of CdTe films is to promote recrystallization and grain growth, and to reduce stress. Nevertheless, for the recrystallization process to take place, it is necessary that there is enough lattice-strain energy in the film. For this reason, while some films recrystallize during the CdCl<sub>2</sub> treatment (e.g., PVD-grown films), others do not (e.g., CSS-grown films). All films investigated in this work showed significant improvement in minority-carrier lifetimes after being treated with CdCl<sub>2</sub>, mainly at 400°C, which shows the importance of this treatment even in samples with initial high-crystalline quality.

## ACKNOWLEDGEMENTS

The authors would like to thank Dr. R. Birkmire and Dr. P. Meyers for the PVD and CSS CdTe samples, respectively. This work was performed, in part, under U.S. Department of Energy contract No. DE-AC36-83CH10093 with the National Renewable Energy Laboratory.

## REFERENCES

- [1] J. Britt and C. Ferekides, *Appl. Phys. Lett.* **62**(22) (1993) 2851.
- [2] H.M. Al-Allak, A.W. Brinkman, H. Richter and D. Bonnet, *J. Crystal Growth* **159** (1996) 910.
- [3] Y.Y. Loginov, K. Durose, H.M. Al-Allak, S.A. Galloway, S. Oktik, A.W. Brinkman, H. Richter and D. Bonnet, *J. Crystal Growth* **161** (1996) 159.
- [4] W.N. Shafarman, R.W. Birkmire, D.A. Fardig, B.E. McCandless, A. Mondal, J.E. Phillips and R.D. Varrin Jr., *Solar Cells* **30** (1991) 61.
- [5] R.G. Dhere, D.S. Albin, D.H. Rose, S.E. Asher, K.M. Jones, M.M. Al-Jassim, H.R. Moutinho and P. Sheldon, *MRS Symp. Proc.* **426** (MRS, Pittsburgh, 1996) p. 361.
- [6] R.K. Ahrenkiel, *Semiconductors and Semimetals Vol. 39* (Academic Press, San Diego, 1993) p. 67.
- [7] A. Taylor and H. Sinclair, *Proc. Phys. Soc.* **57** (The Physical Society, London, 1945) p. 126.
- [8] J.B. Nelson and D.P. Riley, *Ibid.*, p. 160.
- [9] B. Qi, D. Kim, D.L. Williamson and J.U. Trefny, *J. Electrochem. Soc.* **143**(2) (1996) 517.
- [10] D.G. Jensen, B.E. McCandless and R.W. Birkmire, *Proc. 25<sup>th</sup> IEEE PVSC* (IEEE, New York, 1996) 773.
- [11] H.P. Klug and L.E. Alexander, *X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials* (John Wiley and Sons, New York, 1974) p. 562.
- [12] C. Barrett and T.B. Massalski, *Structure of Metals* (Pergamon Press, Oxford, 1980) p. 449.
- [13] S.A. Ringel, A.W. Smith, M.H. MacDougall and A. Rohatgi, *J. Appl. Phys.* **70**(2) (1991) 881.