NREL/CP-520-25635

Induced Recrystallization of CdTe Thin Films Deposited by Close-Spaced Sublimation

H.R. Moutinho, R.G. Dhere, M.M. Al-Jassim, D.H. Levi and L.L. Kazmerski
National Renewable Energy Laboratory

B. Mayo
Southern University and A&M College
Baton Rouge, LA

Presented at the National Center for Photovoltaics Program Review Meeting
Denver, Colorado
September 8-11, 1998

National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, Colorado 80401-3393
A national laboratory of the U.S. Department of Energy
Managed by Midwest Research Institute
for the U.S. Department of Energy
under contract No. DE-AC36-83CH10093

Work performed under task number PV903201

October 1998

NOTICE

This report was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or any agency thereof.

Available to DOE and DOE contractors from:
Office of Scientific and Technical Information (OSTI)
P.O. Box 62
Oak Ridge, TN 37831
Prices available by calling 423-576-8401

Available to the public from:
National Technical Information Service (NTIS)
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161
703-605-6000 or 800-553-6847
or
DOE Information Bridge
http://www.doe.gov/bridge/home.html

Printed on paper containing at least 50% wastepaper, including 10% postconsumer waste

Induced Recrystallization of CdTe Thin Films Deposited by Close-Spaced Sublimation

H.R. Moutinho,* R.G. Dhere,* M.M. Al-Jassim,* B. Mayo,**
D.H. Levi,* and L.L. Kazmerski*

*National Renewable Energy Laboratory
1617 Cole Blvd.
Golden CO 80401

**Southern University and A&M College
Harding Boulevard
Baton Rouge LA 70813

Abstract. We have deposited CdTe thin films by close-spaced sublimation at two different temperature ranges. The films deposited at the lower temperature partially recrystallized after $CdCl_2$ treatment at 350ºC and completely recrystallized after the same treatment at 400ºC. The films deposited at higher temperature did not recrystallize at these two temperatures. These results confirmed that the mechanisms responsible for changes in physical properties of CdTe films treated with $CdCl_2$ are recrystallization and grain growth, and provided an alternative method to deposit CSS films using lower temperatures.

INTRODUCTION

In a previous publication (1), we studied the changes in the physical properties of close-spaced sublimation (CSS) and physical vapor deposition (PVD) CdTe thin films treated with $CdCl_2$ at 350° and 400°C. The changes observed in the PVD films with the treatment were associated with a recrystallization and grain-growth process. Recrystallization is the process in which a new, better-quality crystalline lattice nucleates and replaces the original one. After the recrystallization process is over, grain growth follows. In contrast to PVD films, CSS films did not show any significant change in physical properties with the treatment, which was attributed to their large-size grains and good quality, and consequent higher resistance to the recrystallization process. In the present work, we tested this assumption by producing two kinds of CSS films at two different temperature ranges. If our hypothesis is correct, we should be able to observe the same phenomenon with the CSS CdTe films deposited at the lower temperatures as we observed with the PVD films.

Furthermore, we also observed in our previous work that, although the initial in-plane compressive stress present in the as-deposited films was eliminated in the PVD films treated at 400°C, because of the recrystallization process, it was not completely eliminated in the CSS films. So, if we produced CSS films at lower temperatures and lower quality (so that they would recrystallize), it was possible that these films would have a better quality than films deposited using standard conditions.

Finally, we studied the evolution of the inhomogeneous stress in films treated at different temperatures to investigate the mechanism responsible for the physical changes during the $CdCl_2$ treatment.

EXPERIMENTAL PROCEDURE

Two sets of CdTe films were deposited on CdS/SnO_2/Glass substrates by close-spaced deposition. The first set was deposited with substrate temperatures from 420° to 474°C and a thickness of 5 μm. The second set was deposited at 620°C and had a thickness of 6.2 μm. For both sets, the chamber was maintained at 16 Torr during deposition with a mixture of oxygen and helium. For simplicity, we will refer to the films deposited at the lower temperatures as LT films and the ones deposited at the higher temperature as HT films.

The CdTe films received several drops of a saturated $CdCl_2$/methanol solution on the surface and were treated in a Lindberg tube furnace at temperatures ranging from 340° to 400°C.

The surface morphology of the films was studied using atomic force microscopy (AFM), their crystalline structure was analyzed using X-ray diffraction (XRD), and the photoluminescence lifetime of the minority carriers was measured using time-resolved photoluminescence (TRPL).

RESULTS

The morphology of the untreated LT and HT films is shown in Fig. 1. As expected, because of the difference in deposition temperature, the grain size of the HT films is much larger than the one for the LT films. After the treatment at 350°C, we observed small grains on the surface of the LT films and no significant changes in the HT films. The small grains are attributed to the recrystallization process and are assumed to be new grains that have nucleated during the heat treatment. After the treatment at 400°C, there was significant grain growth in the LT films and no significant growth in the HT films. Nevertheless, some small particles were observed in the latter, and may be due to the recrystallization process that had just started in these films. The grain size of the films for different treatments is presented in Table 1.

The evolution of the texture on the LT and HT films is also shown in Table 1. The texture coefficient σ, shown in this table, is related to the preferential orientation of the films (2). For the number of peaks used in the analysis, a value of 2.8 means a completely oriented film, whereas a value of 0 means a randomly oriented film. The as-deposited LT films exhibited strong (111) texture, probably because the (111) surface is the one with lower energy for CdTe films. In contrast, the as-deposited HT films were almost randomly oriented, probably because of the larger entropy during growth, which favors the nucleation of islands with different orientations (3). The LT films treated at 350°C still had strong (111) texture, but small peaks were observed for

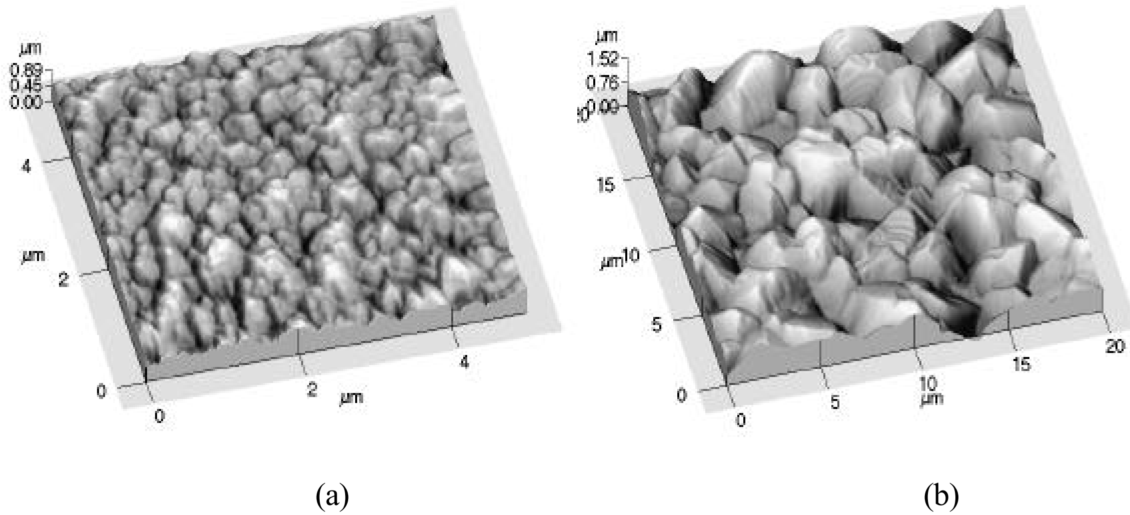

FIGURE 1. AFM images of untreated CdTe films. (a) Low-temperature deposition. (b) High-temperature deposition.

the other crystalline planes. This is reflected in a small decrease in the value of σ. After the treatment at 400°C, the LT films became almost randomly oriented. In contrast, there was not a significant change in the texture of the HT films with the treatment.

TABLE 1. Grain size, degree of preferential orientation (σ), and photoluminescence lifetime for CSS CdTe films deposited and treated at different temperatures.

T_{dep} (ºC)	Treatment	Grain Size (µm)	σ	PL lifetime (ps)
420-474	As deposited	0.36	2.8	14
	340ºC	0.36	2.8	33
	350ºC	≅0.36	2.5	94
	400ºC	1.6	0.5	442
620	As deposited	2.7	0.5	118
	350ºC	2.6	0.6	103
	400ºC	2.7	0.5	735

The lattice parameter, ***a***, for the films is calculated in Fig. 2, using a method developed by Taylor (4) and Nelson (5). The as-deposited LT films had a lattice parameter larger than the one for a powder CdTe sample (6.481 Å), indicating the presence of in-plane compressive stress (6). The LT film treated at 350°C had two values of ***a***; the larger one was obtained from the (111) planes and was attributed to the original lattice, whereas the smaller one was obtained from all other planes and was attributed to the recrystallized lattice. After the treatment at 400°C, the LT films

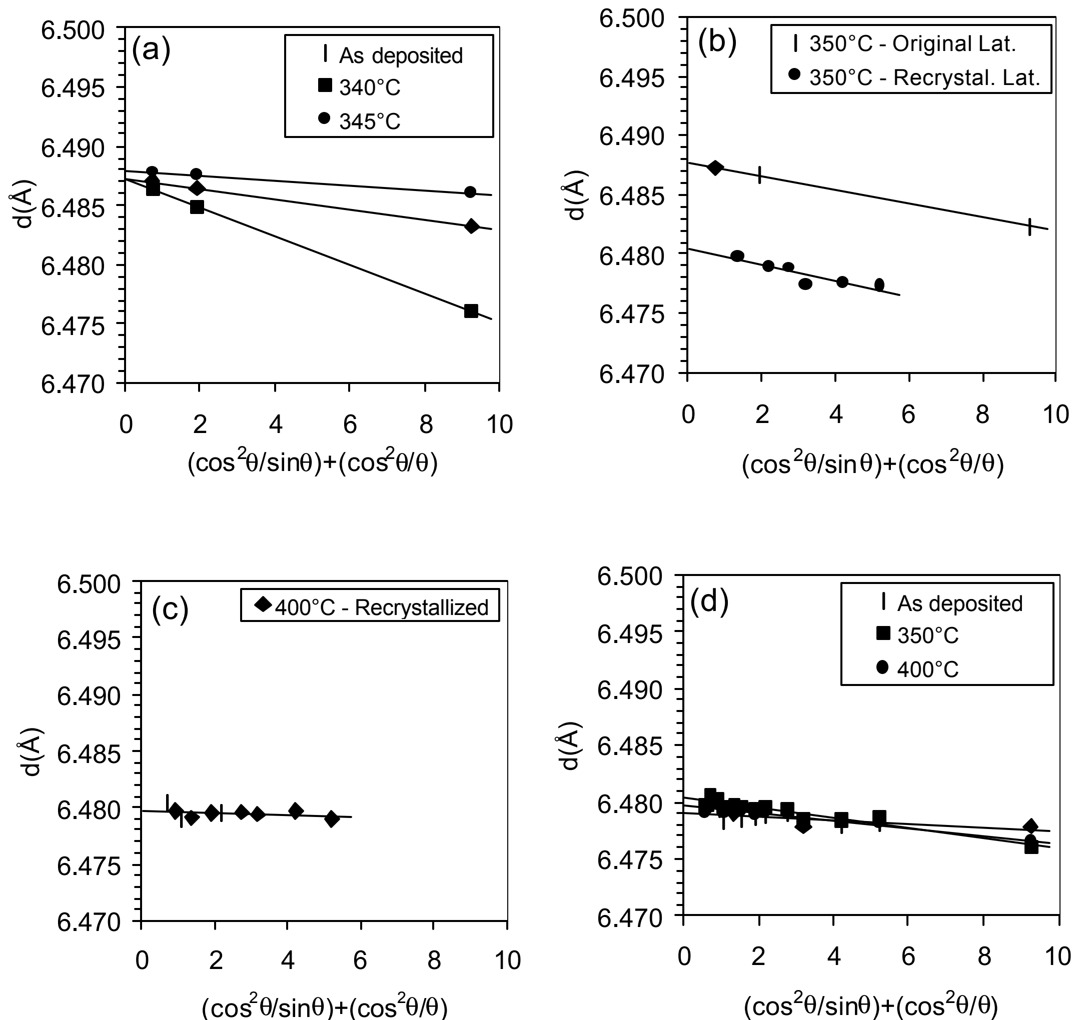

FIGURE 2. Lattice parameter of CSS CdTe thin films before and after $CdCl_2$ treatment. (a)(b)(c) LT films. (d) HT films.

had only one lattice parameter, because of the end of the recrystallization process. In contrast, the untreated HT films had a value of ***a*** close to the one for a powder sample, indicating that they did not have significant in-plane stress. Furthermore, there were no significant changes after the $CdCl_2$ treatment at 350° and 400°C.

Finally, to have information on the inhomogeneous stress in the films, we studied the evolution of the (444) diffraction peak with the $CdCl_2$ treatment. To study the stress in the early stages of the recrystallization process, we treated LT films at 340° and 345°C. The shape and position of the peak for the untreated and treated at 340°, 345° and 350°C LT films were very similar, indicating that both in-plane (position of the peak) and inhomogeneous (width of the peak) stress did not change.

After the treatment at 400°C, there was a clear decrease in both stresses. In the case of the HT films, there was no significant change in this peak with the $CdCl_2$ treatment. The values of PL lifetime for the LT and HT films are reported in Table 1.

DISCUSSION

The results obtained from the AFM images support our previous results. The small particles observed on the LT films treated at 350°C are similar to the ones noticed on PVD films also treated at 350°C. These are new CdTe grains and indicate that these films are being recrystallized. The results are also similar for PVD and LT films treated at 400°C, with significant grain growth, indicating that the films were completely recrystallized. As we would expect, the HT films, deposited at higher temperatures, did not show any sign of recrystallization after the treatment at 350°C. The small grains observed after the treatment at 400°C also support the recrystallization theory, because one would expect that a film with larger grains and lower density of defects would recrystallize at a higher temperature.

The XRD results agreed well with the ones from AFM. The small peaks on the XRD pattern for the LT films treated at 350°C were due to the new recrystallized lattice that was formed during the treatment. Because there was not a unique reference plane, as in the case of the film nucleation, for the recrystallization process, the new grains were randomly oriented. And because these films still had strong (111) texture, we can conclude that the recrystallization process was in the early stages. The small grains, observed in AFM images of these films, were responsible for the peaks with orientation other than [111]. These grains also contributed to the (111)-type peaks, but their contribution was too small to be noticed. The almost complete loss of preferential orientation for the LT films treated at 400°C occurred because the recrystallization process was finished, and the original lattice — the one completely oriented — was entirely consumed. The lack of any preferential orientation for the HT films makes it impossible to infer any information on recrystallization from their XRD patterns.

The two lattice parameters found for the LT film treated at 350°C confirm the existence of two lattices: the original and the recrystallized. It is important to notice that the larger lattice parameter (showing the existence of in-plane compressive stress) was obtained from the (111)-type reflections — both characteristics of the as-deposited LT films. The lower value of $\boldsymbol{a}$ was obtained from all the other reflections, and it reveals a lattice with basically no in-plane stress, as would be expected from the recrystallized lattice. Indeed, as mentioned before, the (111)-type peaks also have a component from the recrystallized lattice; but, at this stage, it is too small to be detected, because the recrystallization process is just starting. The existence of only one lattice parameter, with a value close to the one for a powder sample, for the LT films after treatment at 400°C confirms that the recrystallization process was complete. The values of the lattice parameter for the HT samples were all very close

to the one for a powder sample, indicating that there was no significant homogeneous compressive stress, even for the untreated films.

It has been observed previously (7) that CdTe films treated at 400°C for 30 minutes do not show significant changes in their physical properties if $CdCl_2$ is not present during the treatment. Furthermore, the recrystallization process is a function of stress in the film and of treatment temperature/time. Based on these facts, we believe that the effect of $CdCl_2$ is to increase the stress in the films in the early stages of the treatment, triggering the recrystallization process. Nevertheless, this increase in stress was not detected in films treated at 340° and 345°C (at this stage there are still no signs of recrystallization), when comparing the shape and position of the (444) peak. Although these results seem to go against our theory, in reality they support it. In most cases, the diffusion of elements in polycrystalline materials are much faster through grain boundaries (8). In our model, diffusion into the film, during the $CdCl_2$ (probably Cl) treatment, increases the stress at grain boundaries, triggering the recrystallization process in these sites. This agrees with the XRD results, because the XRD signal comes predominantly from the intragranular material, and it is not going to detect an increase in stress at the grain boundaries. Also, it agrees with the fact that, as we have observed previously (1), nucleation always seems to start at grain boundaries.

The PL lifetime results show a significant increase in the quality of the films even if recrystallization is not present (HT films), as has been observed in our previous work. This confirms the importance of the $CdCl_2$ treatment, even for samples that do not recrystallize, and it suggests that the effects of this treatment in the physical and electro-optical properties of the films are not directly connected. The difference in the lifetimes of LT and HT films treated at 400°C is probably due to the difference in grain size. It is possible that if we increase the $CdCl_2$ treatment temperature, it will result in LT films with larger grains and higher values of PL lifetime.

CONCLUSIONS

We were able to induce recrystallization in CdTe thin films deposited by close-spaced sublimation, for the first time, by depositing films at lower substrate temperatures and with smaller grain size and larger concentration of defects. This shows that the main effect of the $CdCl_2$ treatment in the physical properties of CdTe films is to promote recrystallization and subsequent grain growth, independent of deposition method. Furthermore, for these changes to take place, it is necessary that a minimum amount of stress is present in the untreated films, which explains why CSS CdTe films deposited using standard conditions do not recrystallize.

We presented an alternative method to deposit CSS CdTe films using lower substrate temperatures. We believe that, with the optimization of the parameters of the $CdCl_2$ treatment, high-quality films can be produced using these lower temperatures.

ACKNOWLEDGEMENTS

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. H.R. Moutinho, M.M. Al-Jassim, D.H. Levi, P.C. Dippo, and L.L. Kazmerski, J. Vac. Sci. Technol. A **16(3)**, 1251 (1998).
2. K.H. Kim and J.S. Chun, Thin Solid Films **141**, 287 (1986).
3. P. Pirouz, F. Ernst, and T.T. Cheng, Mater. Res. Soc. Symp. Proc. **116**, 57 (1988).
4. A. Taylor and H. Sinclair, Proc. Phys. Soc. **57** (The Physical Society, London, 1945) p. 126.
5. J.B. Nelson and D.P. Riley, Proc. Phys. Soc. **57** (The Physical Society, London, 1945) p. 160.
6. H.P. Klug and L.E. Alexander, X-Ray Diffraction Procedures for Polyfcrystalline and Amorphous Materials (Wiley, New York, 1974) p. 757.
7. S.A. Ringel, A.W. Smith, M.H. MacDougal, and A. Rohatgi, J. Appl. Phys. **70**, 881 (1991).
8. P.G. Shewmon, Diffusion in Solids (J. Williams Book Company, Janks, Oklahoma, 1983) p. 164.