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Recrystallization of PVD CdTe Thin Films Induced by $CdCl_2$ Treatment – A Comparison Between Vapor and Solution Processes

Preprint

H.R. Moutinho, R.G. Dhere, M.J. Romero, C.S. Jiang, B. To, and M.M. Al-Jassim
National Renewable Energy Laboratory

Presented at the 33rd IEEE Photovoltaic Specialists Conference
San Diego, California
May 11–16, 2008

Conference Paper
NREL/CP-520-42512
May 2008

NREL is operated by Midwest Research Institute • Battelle Contract No. DE-AC36-99-GO10337

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RECRYSTALLIZATION OF PVD CdTe THIN FILMS INDUCED BY $CdCl_2$ TREATMENT – A COMPARISON BETWEEN VAPOR AND SOLUTION PROCESSES

H.R. Moutinho, R.G. Dhere, M.J. Romero, C.-S. Jiang, B. To, and M.M. Al-Jassim
National Renewable Energy Laboratory, 1617 Cole Blvd., Golden, CO 80127, USA

ABSTRACT

The untreated physical-vapor-deposited CdTe films had small grains, with <111> texture, and a large concentration of deep levels. For $CdCl_2$ treatments at moderate temperature/time, there was partial recrystallization, and a moderate decrease in the concentration of deep levels. For the optimal treatment conditions, there was complete recrystallization and grain growth, and further decrease in stress. Electron backscatter diffraction showed that these films had a mixture of small and large grains, many larger than 30 μm. The larger grains had <111> orientation, whereas the smaller grains were randomly oriented, which provided insight on the grain-growth mechanism after recrystallization. There was a significant increase in the cathodoluminescence signal, indicating a decrease in the concentration of deep levels. When performed at the same conditions, the $CdCl_2$ vapor treatment is more effective in the recrystallization and grain-growth processes than the solution $CdCl_2$ treatment. All the films had a large concentration of twin boundaries.

INTRODUCTION

It is well known that heat treatment with $CdCl_2$ is a major step in preparing high-quality CdTe/CdS solar cells [1,2]. This treatment may or may not induce recrystallization of the CdTe films, depending on the initial stress state of the material, and the type and conditions of the treatment [3]. However, even in films that do not recrystallize, this treatment is important, because it decreases the density of deep levels inside the bandgap and changes the defect structure, resulting in better devices [4]. We have deposited close-spaced sublimation (CSS) CdTe films for many years that do not show significant structural changes after $CdCl_2$ treatment, because they have a relatively low initial stress state and large grains. Recently, we began depositing CdTe films by physical vapor deposition (PVD), at much lower temperatures, which readily recrystallize after $CdCl_2$ treatment. In this work, we study the effects of the $CdCl_2$ treatment performed by two different methods—vapor and solution—at different times and temperatures, to determine the best treatment parameters and the advantages of one method over the other.

One of the main analytical techniques used in this study is electron backscatter diffraction (EBSD) [5,6]. Although this technique was developed a few decades ago, it has gained more attention only recently, with the development of fast personal computers and appropriate software. In EBSD, the electron beam of a scanning electron microscope (SEM) is used to generate diffracted electrons, which are collected by a detector placed close to the sample surface. Because of the small area of the electron beam, this technique gives information on the crystalline orientation of the sample with nanometer resolution, providing orientation maps of the surface, where grains with different orientations can be distinguished, as well as defects, such as twin boundaries. The samples were also analyzed by cathodoluminescence (CL), to study changes in the concentration of deep levels inside the bandgap with the different stages of recrystallization; X-ray diffraction (XRD), to accurately determine lattice parameter; and scanning electron microscopy (SEM) and atomic force microscopy (AFM), to determine surface topography and roughness.

EXPERIMENTAL PROCEDURE

The PVD CdTe films were grown at 325°C on glass/SnO_2/CdS substrate, forming a solar-cell structure. The $CdCl_2$ treatment was performed using two methods: vapor and solution. The vapor treatment was performed in vacuum, by maintaining a constant vapor pressure of $CdCl_2$ over the surface of the film, in a mixture of oxygen and helium. The solution treatment consisted of applying a few drops of saturated $CdCl_2$ solution on the sample surface, then heating it in air. The samples were treated at 350°, 400°, or 420°C, for 5 or 30 min.

For EBSD analysis, some CdTe films received one or more of the following treatments: mechanical polishing with 0.05-μm alumina suspension, ion-beam milling with Ar, and etching with a bromine-methanol solution for few seconds.

The samples were analyzed by SEM, using a FEI FIB NanoSEM 200 SEM; EBSD, using an HKL Technology EBSD system, with Nordlys detectors and electronics, mounted in the NanoSEM 200 SEM; CL, using a spectrum imaging system with a cryostage, installed in a JEOL 5800 SEM; AFM, using a Veeco Metrology Dimension 3100 SPM with Nanoscope V controller; and XRD, using a Scintag S1 diffractometer, with Bragg-Brentano configuration.

RESULTS AND DISCUSSION

Surface Morphology

The untreated samples had grain sizes smaller than 1 μm. Treatment with solution $CdCl_2$ at 350°C for 5 and 30 minutes did not affect the morphology significantly, except

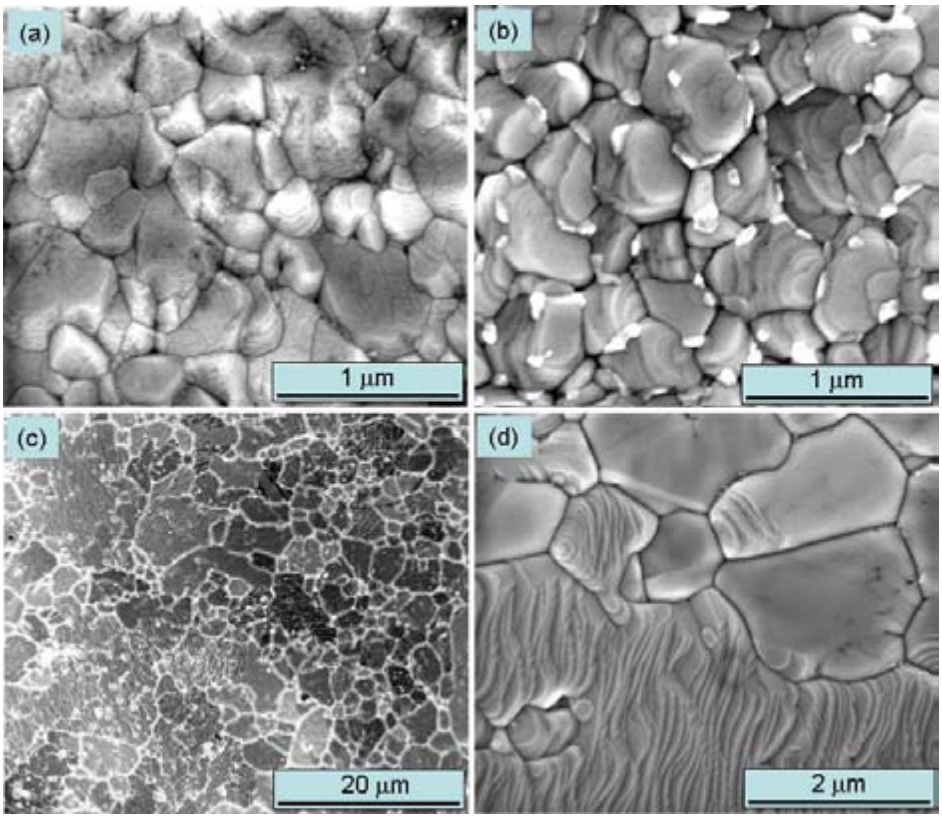

Fig. 1. SEM micrographs of CdTe films treated under different conditions: (a) solution 350°C/5 min; (b) vapor 350°C/5 min; (c) vapor 420°C/5 min; (d) vapor 400°C/5 min.

for softening the sharp features in the film. However, the same treatment conditions for vapor $CdCl_2$ resulted in small grains appearing mostly at grain boundaries, with the sample treated for 30 minutes showing a higher concentration of these grains, which, in general, were also larger and more elongated. These small grains have been observed before [3,4] and clearly indicate ongoing recrystallization, as discussed in the next section. The small grains were also observed on the sample treated by solution $CdCl_2$ at 400°C for 5 minutes. These results are the first indication that the vapor treatment, which keeps an infinite source of $CdCl_2$ on the CdTe surface during the treatment, is more efficient in the recrystallization process than the solution process, which uses a finite amount of $CdCl_2$.

There was a striking difference on the surface morphology of the CdTe films after the vapor treatment at 400° and 420°C. The recrystallization process was complete and there was grain growth. The microstructure showed a large variation of grain sizes, from 1 μm to over 30 μm. These films had the largest grains sizes observed for CdTe produced in our laboratory, using any growth method. Yet, they were extremely smooth when compared to CSS CdTe films. As-deposited CSS CdTe films have grain sizes of a few micrometers and roughness of about 290 nm. The untreated PVD CdTe films have a roughness of about 13 nm, and the roughest films, produced after $CdCl_2$ vapor treatment at 420°C for 30 minutes, have a roughness of about 29 nm. This feature is very important for EBSD analysis, as discussed in the next section. The topographies of different CdTe films are shown in Fig. 1. As observed in Fig. 1(d), the grain morphology was not uniform. We observed three types of topographies in most recrystallized films: grains with a smooth surface [top of Fig. 1(d)], grains with terraces at an angle with the surface normal [bottom of Fig. 1(d)], and grains with terraces parallel to the film surface. Also, there were some grains with more than one topography. It was noticed that the small grains had a smooth surface, whereas the large grains had terraces. This characteristic was compared with EBSD data and will be discussed later. There were no major differences on the topography and grain size between films treated in vapor at 400° and 420°C, and for 5 and 30 minutes.

For the solution-treated samples, we observed that recrystallization occurred for higher temperature/time values. For instance, the sample treated at 400°C for 5 minutes was still in the early stages of the recrystallization process. The sample treated at 400°C for 30 minutes and the samples treated at 420°C were completely recrystallized. However, the grain size was much smaller than in equivalent vapor-treated samples—in general, not

larger than 5 μm. Also, although grains with terraces were observed, they were present in a smaller scale. This was another indication that the solution treatment is much less effective in the recrystallization process than the vapor treatment.

Crystalline Structure

The XRD analyses corroborated the interpretation of the SEM and AFM results, as inferred from Table I. The untreated sample had <111> texture and a larger lattice parameter than a powder sample (6.481 Å), indicating a compressed homogeneous stress on the horizontal plane. This stress may be caused by differences in the thermal expansion coefficients between CdTe and the underneath layers. After moderate $CdCl_2$ treatment, two lattice parameters are observed in the analysis (see Fig. 2 for an example): the largest corresponds to the original <111>-oriented lattice, for which the homogeneous stress has been partially released (decrease in lattice parameter), and the smaller is for the new recrystallized lattice [small grains observed in Fig. 1(b)]. This new material is randomly oriented and has a lattice parameter similar to a powder sample. For higher treatment temperature/time values, there is only one value of lattice parameter—close to 6.481 Å—and the samples are randomly oriented, indicating that the recrystallization process is complete. For these samples, there is also a reduction in the inhomogeneous stress, characterized by a decrease in the full width at half maximum of the diffraction peaks.

From Table I, we observe the slower degree of recrystallization for the solution-treated samples. For instance, the sample treated at 350°C for 5 minutes does not show any sign of ongoing recrystallization, whereas the one treated at 400°C for 5 minutes is not completely recrystallized yet. This is equivalent to what was observed in the SEM and AFM analyses.

For the untreated samples, there were no Kikuchi patterns, and, consequently, no EBSD signal coming from

Table I. Lattice parameter for CdTe films before and after treatment with vapor (V) or solution (S) $CdCl_2$.

Sample	Lattice Parameter 1 (Å) (111) Texture	Lattice Parameter 2 (Å) No Texture
Untreated	6.489	-
V350°C/5 min	6.484	6.482
V400°C/5 min	-	6.480
V420°C/5 min	-	6.480
V350°C/30 min	6.483	6.481
V400°C/30 min	-	6.480
V420°C/30 min	-	6.481
S350°C/5 min	6.491	-
S400°C/5 min	6.486	6.483
S420°C/5 min	-	6.480
S350°C/30 min	6.485	6.481
S400°C/30 min	-	6.480
S420°C/30 min	-	6.480

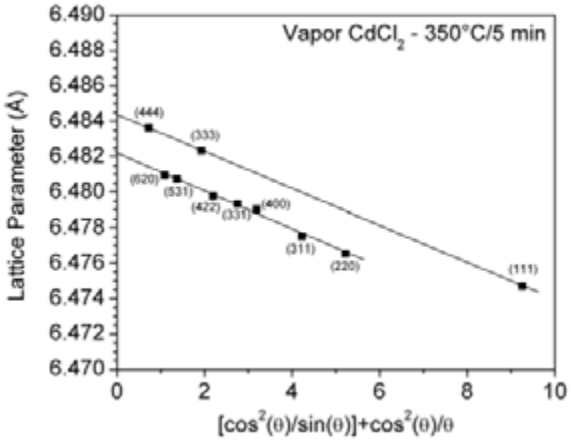

Fig. 2. Lattice parameter determination for a CdTe film after vapor $CdCl_2$ treatment.

grain-boundary regions. In general, this is caused by topographic features that prevent diffracted electrons from reaching the detector. This effect has been observed before, in CSS CdTe samples, and a solution for the problem is to flatten the sample surface. In the past, we successfully used the following methods for this purpose [7]: ion-beam milling; or mechanical polishing followed by light ion-beam milling or etching in bromine methanol solution. We applied these methods to several samples, but the EBSD results did not change significantly. This was not surprising, because these samples had a roughness about one order of magnitude less than CSS samples, and it was unlikely that surface features were the problem. Another possibility is that regions around grain boundaries have very poor crystallinity, and do not generate Kikuchi patterns. An example of typical EBSD data from these films is shown in Fig. 3(a). The images in Fig. 3 are formed by a combination of band contrast, which is a measure of the intensity of the Kikuchi patterns and is related to crystallinity quality, grain boundaries (black lines), coincidental site lattice (CSL) boundaries (red lines), and inverse pole-figure coloring. The CSL Σ3 boundaries are twin planes related by a rotation of 60° around the <111> direction between neighboring material. The <111> texture of the untreated films is characterized by the blue coloration of the grains in this representation, and by the central region and the ring on the {111} pole figure inset. Note that there is a spread of several degrees on the <111> preferential orientation. Similar EBSD results were obtained for the partially recrystallized samples concerning the poor signal at grains boundaries and the <111> texture [Fig. 3(c)]. Unfortunately, EBSD did not have enough spatial resolution to detect the randomly oriented small recrystallized grains.

Unlike CSS CdTe films, the PVD recrystallized films, which have good crystallinity and are still reasonably flat, produced excellent EBSD data without any surface preparation, as observed in Figs. 3(b) and 3(d). The problems with regions close to grain boundaries were not observed in these films. Notice that there is still a large

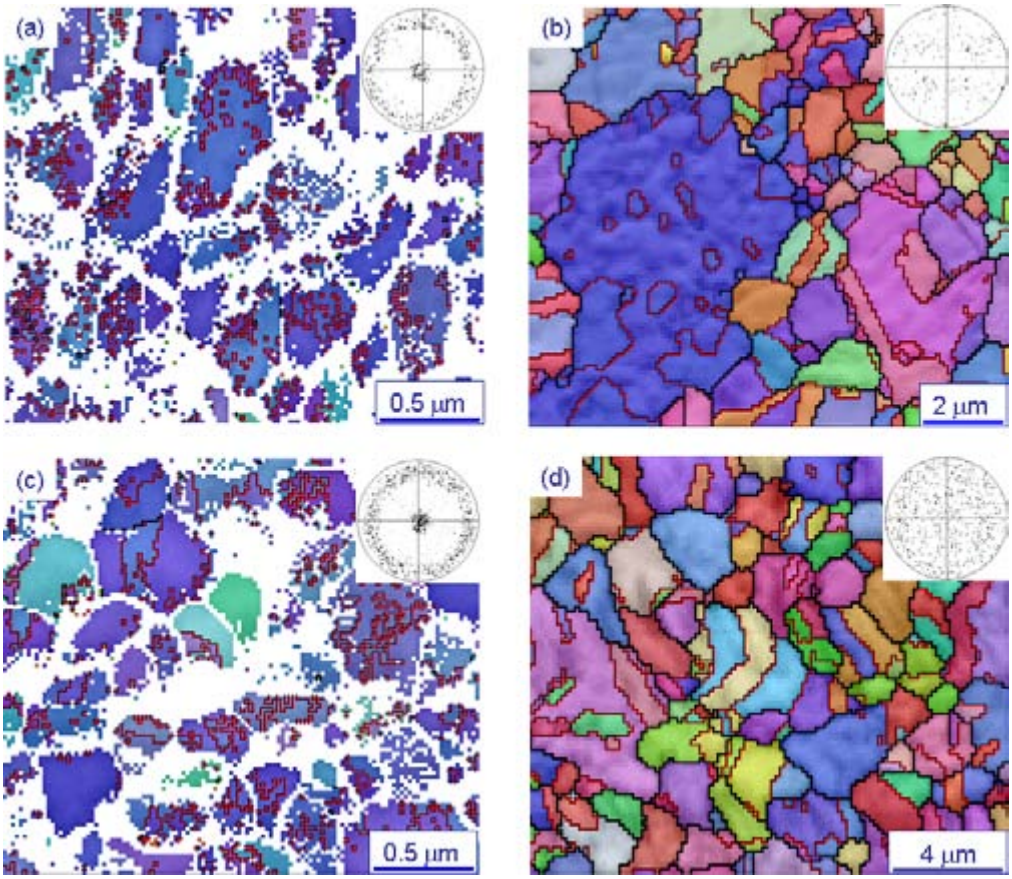

Fig. 3. EBSD data composed of band contrast + grain boundaries (black lines) + CSL Σ3 boundaries (red lines) + inverse pole-figure coloring. Insets: {111} pole figure. (a) untreated CdTe; (b) CdTe after vapor $CdCl_2$ at 400°C for 5 minutes; (c) CdTe after solution $CdCl_2$ at 400°C for 5 minutes; (d) CdTe after solution $CdCl_2$ at 400°C for 30 minutes.

concentration of 60° <111> twin boundaries. These boundaries were found in every sample analyzed in this work, and their density did not change significantly from the untreated to the recrystallized films, which is explained by their low formation energy, as reported in the literature [8]. The loss of preferential orientation is observed in the coloration of the grains and in the homogeneous pole figures. A high-magnification study of vapor-treated samples showed that large grains have <111> orientation [notice the large blue grain in Fig. 3(b)], whereas small grains are randomly oriented. This can be correlated with the differences in topography observed in the SEM and AFM analyses between large and small grains, i.e., in general, small grains are smooth and randomly oriented, whereas large grains have terraces and are <111> oriented. These results indicate that the (111) surface is the lowest-energy surface in CdTe, and that, after recrystallization, the <111>-oriented grains grow at the expense of grains oriented in less-favorable directions. Surface energy may be particularly important in the grain growth process of these films, which have large grain sizes in comparison to their thickness (about 3 μm). These results also indicate that, in the conditions used in this work, the grain growth process was not complete.

As observed in the SEM and AFM analyses, there is no significant difference in the EBSD data for samples treated in vapor at 400° and 420°C, and for 5 and 30 minutes. However, for solution-treated samples, there is a strong difference in the degree of recrystallization between samples treated at 400°C for different times, as observed by comparing Figs. 3(c) and 3(d). Also, the effectiveness of the vapor treatment is clearly demonstrated by comparing Figs. 3(b) and 3(c), which show samples treated by the two methods at the same temperature and time. Finally, notice the large difference in average grain sizes for films treated with vapor and solution $CdCl_2$ [Figs. 3(b) and 3(d)].

Electro-Optical Properties

The untreated CdTe films produced a very weak CL signal, close to the system response of the equipment, indicating a large concentration of deep levels inside the bandgap. This explains the low efficiencies observed in

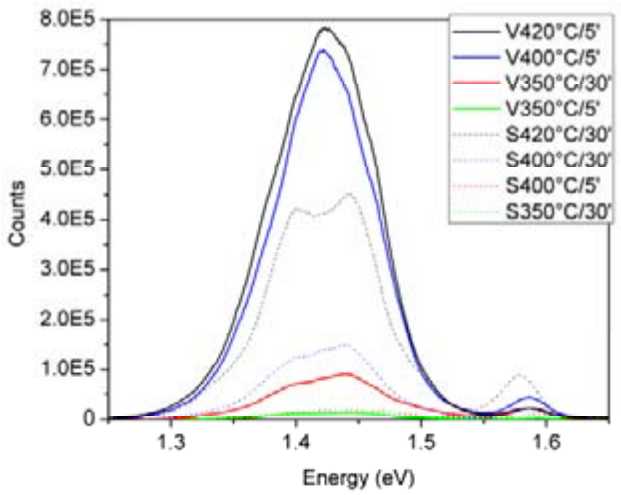

Fig. 4. CL data for CdTe thin films after treatment with vapor and solution $CdCl_2$.

solar cells produced with these films before $CdCl_2$ treatment. The same was observed for the solution treatment at 350°C for 5 minutes, confirming the results from other analyses.

In Fig. 4, we show several CL curves for CdTe films treated under different conditions, in vapor and solution $CdCl_2$. The large central peak in each spectrum corresponds to donor/acceptor transitions, whereas the small peak, on the right, is related to excitonic transitions. Compared to the untreated film, there is an increase in the signal for samples treated in vapor $CdCl_2$ at 350°C at 5 and 30 min, related to a higher stage of recrystallization, as mentioned previously. For higher treatment temperatures and times, there is a significant increase in the CL intensity because of the complete recrystallization of the CdTe film. These results indicate that the new recrystallized material has a lower concentration of deep levels inside the bandgap, which increases the radiative recombination, and is a direct measure of the improvement in material quality after the $CdCl_2$ treatment. We did not notice a major difference in the CL signal for recrystallized films treated at 400° and 420°C, and 5 and 30 minutes. In reality, the properties of the films are not completely uniform, and the CL signal can vary up to about two times, as the beam is scanned over the surface. Considering the average data, the sample treated with vapor at 400°C for 5 minutes provided the best CL signal. Notice in the graph that samples treated with the solution $CdCl_2$ have smaller CL signals than equivalent samples treated with vapor $CdCl_2$, indicating lower quality; this is in complete agreement with the previous analyses. In some samples, the energy of the exciton peak shifts with the treatment, as observed in Fig. 4. This indicates a change in the band structure of the material. However, additional analyses, considering the inhomogeneity of the films, will be necessary before we can explain these changes.

CONCLUSIONS

The vapor $CdCl_2$ performed at moderate temperatures resulted in partial recrystallization; at higher temperatures, it resulted in recrystallized smooth films with large grains and a relatively low density of deep levels. These low values of roughness (<30 nm) are desirable for preparing back contacts and for cells using a substrate configuration. Although these films were randomly oriented, the large grains, some with grain sizes larger than 30 μm, had a <111> preferential orientation, indicating that the (111) surface has the lowest energy in this material. The solution $CdCl_2$ treatment was not as efficient in the recrystallization process. Although completely recrystallized films could be obtained, the grain size was smaller and the density of deep levels was larger than in films treated in vapor $CdCl_2$ at the same conditions. These results indicate that the vapor $CdCl_2$ treatment is recommended over the solution treatment for the preparation of high-efficiency devices.

A large concentration of 60° <111> twin boundaries was observed in every CdTe film analyzed in this work, even after recrystallization and grain growth, confirming the low energy of these interfaces.

ACKNOWLEDGEMENTS

This work is supported or funded under DOE Contract No. DE-AC36-99GO10337.

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1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
May 2008	Conference Paper	11-16 May 2008

4. TITLE AND SUBTITLE
Recrystallization of PVD CdTe Thin Films Induced by $CdCl_2$ Treatment – A Comparison Between Vapor and Solution Processes: Preprint

5a. CONTRACT NUMBER
DE-AC36-99-GO10337

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
H.R. Moutinho, R.G. Dhere, M.J. Romero, C.S. Jiang, B. To, and M.M. Al-Jassim

5d. PROJECT NUMBER
NREL/CP-520-42512

5e. TASK NUMBER
PVA73201

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
National Renewable Energy Laboratory
1617 Cole Blvd.
Golden, CO 80401-3393

8. PERFORMING ORGANIZATION REPORT NUMBER
NREL/CP-520-42512

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSOR/MONITOR'S ACRONYM(S)
NREL

11. SPONSORING/MONITORING AGENCY REPORT NUMBER

12. DISTRIBUTION AVAILABILITY STATEMENT
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13. SUPPLEMENTARY NOTES

14. ABSTRACT *(Maximum 200 Words)*

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15. SUBJECT TERMS
CdTe; thin films; PV; recrystallization; physical vapor deposition; close-spaced sublimation; electron backscatter diffraction; grain-growth process; ion-beam milling; electro-optical properties;

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