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Microtexture of chloride treated CdTe thin films deposited by CSS technique

João Quadros · André L. Pinto · Hélio R. Moutinho · Ramesh G. Dhere · Leila R. Cruz

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Abstract This work investigates the microstructural changes—especially in grain boundary structure and grain orientation distribution—in CdTe thin films deposited by close spaced sublimation at low (LT) and high temperatures (HT) and submitted to a $CdCl_2$ heat treatment. These changes are quantitatively described by microtexture analysis, a spatial distribution of the orientation of the grains. The analysis is performed in a scanning electron microscope by means of identification of the electron backscattered diffraction patterns from individual grains. The texture of each grain, the misorientation between grains, and coincident site lattice boundary maps are obtained. The results show that the $CdCl_2$ treatment did not promote significant microstructural changes in HT-CdTe films, which grow with large and randomly oriented grains, and with a predominance of high-angle boundaries. On the other hand, for LT-CdTe films, this treatment promotes a substantial increase in grain size, a decreasing of preferential orientation, and an increase in the number of CSL and high-angle boundaries. These changes are considered to be a strong evidence for recrystallization.

Introduction

It is well known that the physical properties of polycrystalline materials are affected by their microstructure. In CdTe thin films—a material used for photovoltaic conversion [1]—the microstructural features depend on the deposition process and the $CdCl_2$ activation heat treatment to which these films are submitted for solar cell applications. The $CdCl_2$ heat treatment consists of submitting the CdTe film—the absorber layer of the device—to a heat treatment in the presence of $CdCl_2$. Some of the microstructural changes brought about by this treatment are grain growth and recrystallization [2]. These changes yield a significant improvement in the electro-optical properties of the material, leading to an increase in the cell efficiency. A very simple and low cost technique used to deposit CdTe thin films is close spaced sublimation (CSS). In this technique, films are deposited from a CdTe source separated from the substrate by a distance of a few millimeters [3]. The substrate temperature is an important parameter, affecting the microstructure of the films. Usually, the grain size of films deposited by CSS at low substrate temperatures is smaller than that of films deposited at high temperatures. Also, low temperature films are recrystallized by the $CdCl_2$ heat treatment. The recrystallization process in these films is possible because they are deposited at low substrate temperatures, which leads to the formation of films with smaller grains and more stress than those deposited at high temperatures. The films deposited at high temperatures do not recrystallize and do not show significant microstructural changes after the heat treatment, although their electro-optical properties are significantly improved by the $CdCl_2$ heat treatment [2].

Microstructural properties of CdTe films such as grain size, crystallinity, type of defects, and texture have been extensively investigated in the literature [2–5]. A correlation between these microstructural properties and photovoltaic and electro-optical characteristics has also been established [4, 6]. However, the physical properties of

J. Quadros · A. L. Pinto · L. R. Cruz (✉)
Thin Film Laboratory, Instituto Militar de Engenharia, Rio de Janeiro, Brazil
e-mail: leilacruz@ime.eb.br

H. R. Moutinho · R. G. Dhere
National Renewable Energy Laboratory, Golden, CO, USA

polycrystalline materials are also affected by grain orientation distribution and grain boundary structure. These microstructural features, specifically, have been seldom explored in the CdTe literature, so their quantitative description is the purpose of this work. These features may be quantitatively described by microtexture analysis [7], which consists of obtaining the spatial distribution of grain orientations in the material. The analysis is performed in a scanning electron microscope (SEM) by means of identification of the electron back-scattered diffraction (EBSD) patterns from individual grains. Besides high spatial resolution, the advantage of determining the microtexture using point-to-point measurements is that microstructure features can be directly correlated to their crystallographic orientations. In our previous work [8], the microtexture of untreated CSS-CdTe thin films was for the first time characterized using the EBSD technique; the texture of each grain, the misorientation between grains, and coincident site lattice (CSL) boundary maps were obtained. In the present work, we use this point-to-point analysis to compare the microstructural changes—particularly in grain boundary structure and grain orientation distribution—associated with the $CdCl_2$ heat treatment in CdTe thin films deposited by CSS at low and high temperatures. To our knowledge, it is the first time that changes in grain boundary structure are described for CdTe thin films. Finally, our EBSD results are also compared with studies of this material using other techniques [2, 5].

Experimental procedure

CdTe thin films were grown at the National Renewable Energy Laboratory (NREL). The films were deposited by CSS onto glass/SnO_2/CdS substrates heated at low temperature (LT)—450 °C—and high temperature (HT)—620 °C [6]. After deposition, the films were submitted to the heat treatment in the presence of $CdCl_2$ vapor [5, 6]. The films deposited at 450 °C (LT films) were treated at 420 and 440 °C for 5 min. The films deposited at 620 °C (HT films) were treated at 400 and 410 °C for 5 min; at higher temperatures, the film peeled from the substrate. Morphology evaluation was performed in a Dimension 3100 Atomic Force Microscope (AFM) from Digital Instruments. Microtexture analyses were carried out at Instituto Militar de Engenharia, in a W-filament JEOL JSM-5800LV SEM, equipped with EBSD system and Orientation Imaging Microscopy (OIM) data collection software from TexSEM Laboratories. The system collects and identifies the EBSD patterns (also known as Kikuchi patterns) generated when the electron beam hits the sample surface, thus providing the orientation of a great number of domains illuminated by the electron beam. The crystallographic orientations of these domains are stored in a file together with the point co-ordinates, the pattern quality and the confidence index. The pattern quality is an index associated with each pattern and may be used to construct quality maps of the scanned area. This is possible because the quality of EBSD patterns is affected by the presence of defects—such as dislocations, precipitates—and internal stress. The confidence index is a parameter associated with the identification of the pattern. Besides the local texture and the spatial distribution of orientations, the misorientation between grains, the grain size distribution, the statistics of special grain boundaries—such as CSL boundaries—and pole figures can be obtained. Further details of this technique may be found elsewhere [7]. Prior to scanning the sample it is very important to prepare the film surface in order to remove contaminants from the region within the penetration depth of the backscattered electrons, which is roughly 20 nm [7]. For this purpose, the surface of the samples was etched in a 88:1:35 phosphoric acid:nitric acid:water solution. Small droplets of this solution were kept on the CdTe surface for 2–5 s. Immediately after, the samples were rinsed in DI water and blown with dry air. When this attack was not effective to show good quality EBSD patterns that was repeated. Some samples—particularly the HT films—were prepared by milling the surface with 5 keV argon ions, at a grazing angle of 1°, for 8 min, using an ion polishing system, model 691, from GATAN. The purpose of this procedure, besides removing any contamination, was to smooth the faceted surface, since the generation of good quality EBSD patterns depends on the surface flatness [8]. The samples thus prepared were positioned at 70° tilt in order to perform the EBSD analysis. The scanned areas were approximately $(15 \times 30)\ \mu m^2$, with a step size of 0.5 μm. For grain size analysis, the cut-off angle used was 15° and the minimum grain size accepted was 3 pixels with orientation difference less than 15°.

Results and discussion

Figure 1 shows the surface morphology of LT-CdTe and HT-CdTe films, before and after $CdCl_2$ heat treatment. The surface of the as-deposited LT film is composed by tiny grains, but the treatment promotes a very abrupt increase in the grain size (note that Fig. 1a and b are at different scales). We observed that this increase depends on the temperature of the treatment. The morphology of HT samples is notably different from the LT samples. The surface of the as-deposited HT film is composed by large and faceted grains, whose size is roughly 2.5 μm. Furthermore, the treatment does not introduce significant variations either in grain size or morphology of this sam-

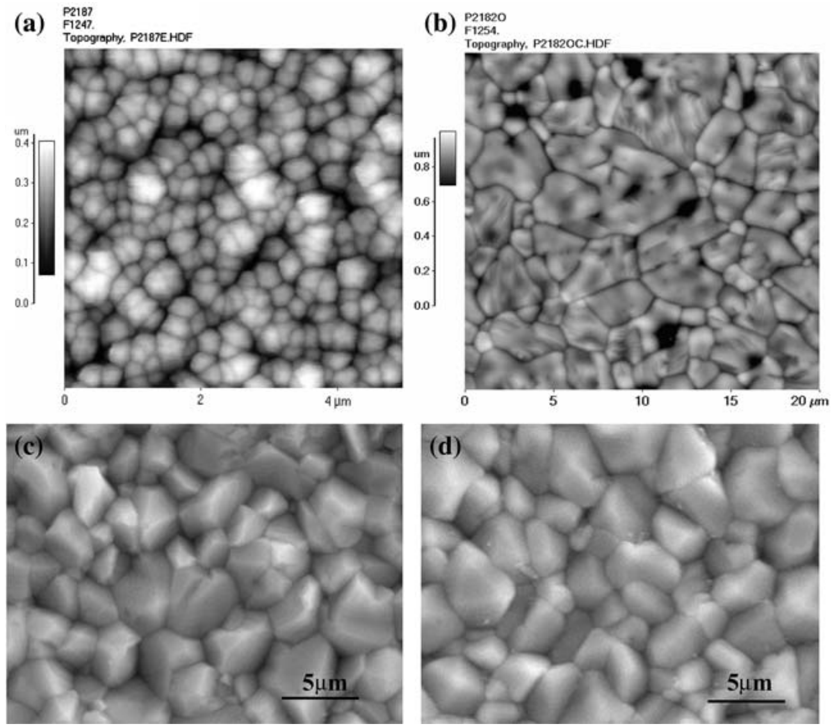

Fig. 1 Morphology of CdTe films: (**a**) LT-CdTe, as-deposited (AFM image); (**b**) LT-CdTe, $CdCl_2$/heat treated at 440 °C (AFM image); (**c**) HT-CdTe, as-deposited (SEM image); (**d**) HT-CdTe, $CdCl_2$/heat treated at 400 °C (SEM image)

ple. These results have already been reported by other investigators [2, 5]; in the particular case of the LT samples investigated in this work, they showed that the $CdCl_2$ heat treatment plays an important role in promoting recrystallization and grain growth.

The grain size in as-deposited LT samples (Fig. 1a), which is roughly 0.3 µm, was a limiting factor to perform EBSD analysis, because our SEM is equipped with a tungsten filament; so, grain or subgrain structures should be larger than 1 µm [9]. These samples were, however, analyzed by X-ray diffraction (XRD) using the Bragg-Brentano geometry. Although the texture components cannot be fully determined from this analysis (because we did not use a texture chamber), it was observed that as-deposited LT films have a strong reflection in the ⟨111⟩ direction. This orientation has also been observed in the literature [2, 5] and has been attributed to the low temperature of the substrate that favors the formation of small grains with orientation associated to the plane (111), since the surface energy of this plane is low compared with other planes of the material.

Figure 2 shows (111) pole figures obtained by EBSD for LT films treated with $CdCl_2$ at 420 and 440 °C. The texture components were identified using the orientation distribution function (ODF). By way of comparison, here are shown just the (111) pole figures for the different processing conditions. It can be observed that the film treated at 420 °C has a (111) preferential orientation. The (111) pole figure shows a strong texture component at the center, with maximum density of 7.99, which means that most

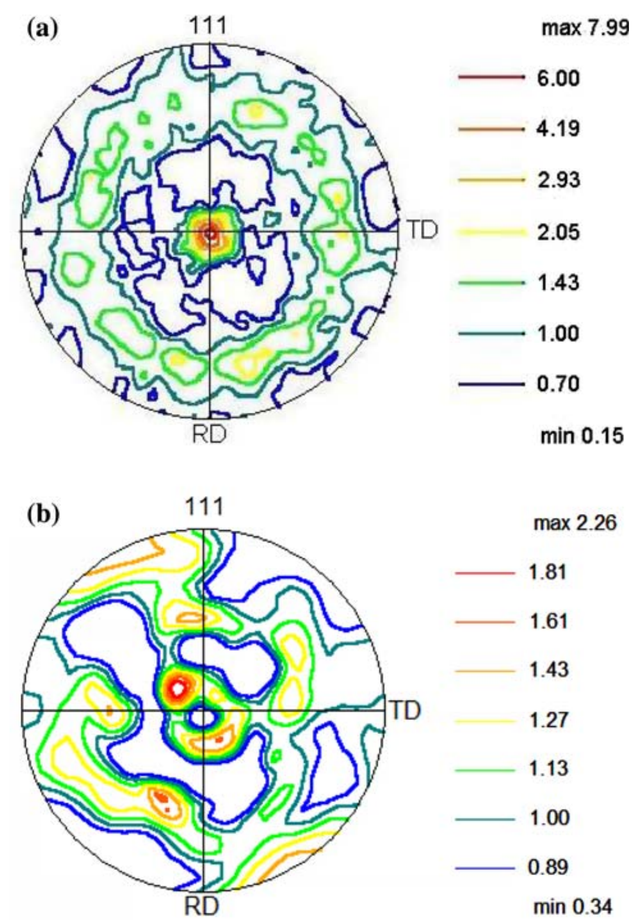

Fig. 2 EBSD pole figures of LT-CdTe films treated with $CdCl_2$ at: (**a**) 420 °C; (**b**) 440 °C

grains have the normal to the (111) plane parallel to the normal direction, thus revealing a strong ⟨111⟩ texture component. Increasing the temperature to 440 °C decreases the texture, as indicated by the distribution of pole densities at Fig. 2b. Moutinho et al. [5] obtained similar results from XRD; the loss of texture was attributed to recrystallization. Recrystallization in this kind of film was demonstrated for the first time by the authors, who observed the nucleation of new CdTe grains randomly oriented in the matrix. Our results corroborate their conclusions, since, according to the experimental data, besides abrupt grain growth, the treatment promotes a reorientation of the grains in new directions, an evidence for recrystallization, as will be discussed later. This reorientation occurs mainly in the ⟨220⟩ and ⟨311⟩ directions, as shown in the pole figures.

Figure 3 shows (111) pole figures obtained by EBSD for as-deposited and $CdCl_2$/heat treated HT-CdTe films. It can be seen that as-deposited film is almost randomly oriented, showing a slight texture in the ⟨220⟩, ⟨311⟩, and ⟨111⟩ directions. The film treated at 400 °C is also almost randomly oriented, the distribution of orientations remaining essentially unchanged after the treatment. This result also corroborates the conclusion of Moutinho et al. [2], that CSS HT-CdTe films grow randomly oriented, for the high substrate temperature increases the probability of nucleation of randomly oriented grains.

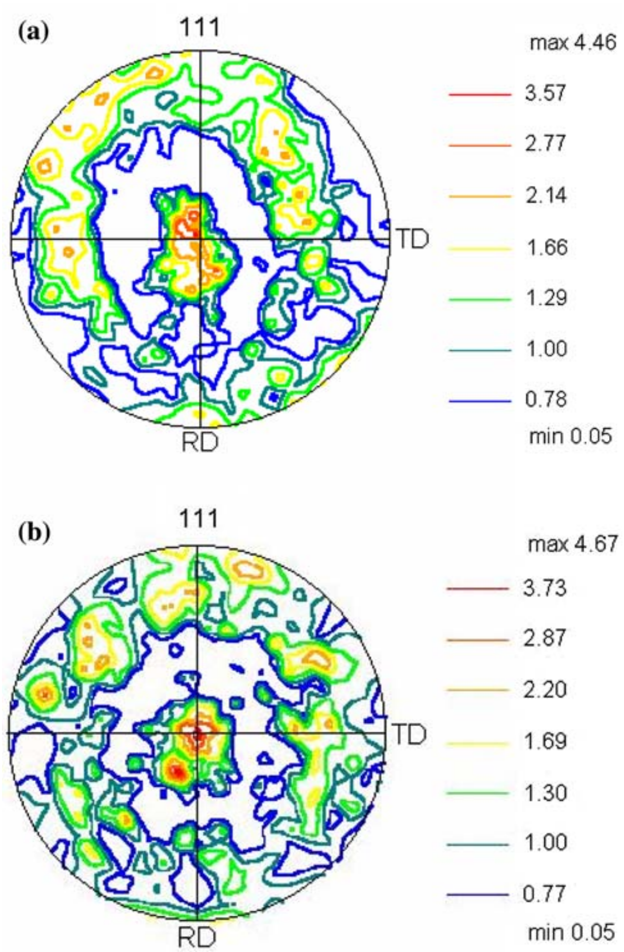

Fig. 3 EBSD pole figures of HT-CdTe films: (**a**) as-deposited; (**b**) $CdCl_2$/heat treated at 400 °C

Typical orientation maps of LT-CdTe films are shown in Fig. 4. Each shade is associated with a crystallographic direction, according to the inverse pole figure shown at the bottom. In the sample treated at 420 °C, most of the grains are arranged so that (111) planes are parallel to the surface of the film. After treatment at 440 °C, there is a reorientation in new directions, as verified before in Fig. 2.

The histograms in Fig. 5 show the distribution of low (misorientation angle $\leq 15°$) and high-angle (misorientation angle $>15°$) grain boundaries (GB) in LT-CdTe films treated with $CdCl_2$. The distribution shifts towards higher misorientations as the temperature of the treatment increases up to 440 °C. At this temperature, a typical misorientation distribution of a randomly oriented assembly of grains is observed—with a mean of 40° [10]. The results for HT and LT films are summarized in Table 1. For the LT films, it is observed that the amount of high-angle boundaries increases with the temperature of the $CdCl_2$ heat treatment. In HT films, the microstructure is basically composed of high-angle boundaries; the number of these boundaries is not changed by the treatment and is larger than in LT films treated below 440 °C.

Figure 6 shows the distribution of special high-angle GB in LT-CdTe films treated with $CdCl_2$. It can be seen that there is a considerable percentage of CSL boundaries with $\Sigma \leq 29$. CSL, as the name implies, are boundaries between two lattices that have coincident sites, when these lattices are superimposed. This confers an ordered structure to the boundary, which means that neighboring grains fit better than grains separated by random boundaries [7]. The parameter Σ refers to the reciprocal of the ratio of CSL sites to lattice sites, that is, the lower is the sigma value the better is the fit at the boundary [10].

Table 2 compares the percentage of CSL GB in LT and HT-CdTe films. The relative number of CSL boundaries in LT-CdTe films is larger than in HT samples. Moreover, the treatment did not modify the distribution of CSL boundaries in HT films. For the $CdCl_2$/heat treated LT films, it is seen that the amount of CSL boundaries—especially $\Sigma3$ twin boundaries and $\Sigma29$—increases as the temperature of the treatment increases (see also Fig. 6), showing that the $CdCl_2$ heat treatment promotes particular and ordered misorientations between grains.

These results clearly show that the grain boundary structure in CdTe films is highly sensitive to processing parameters, such as the substrate and $CdCl_2$ heat treat-

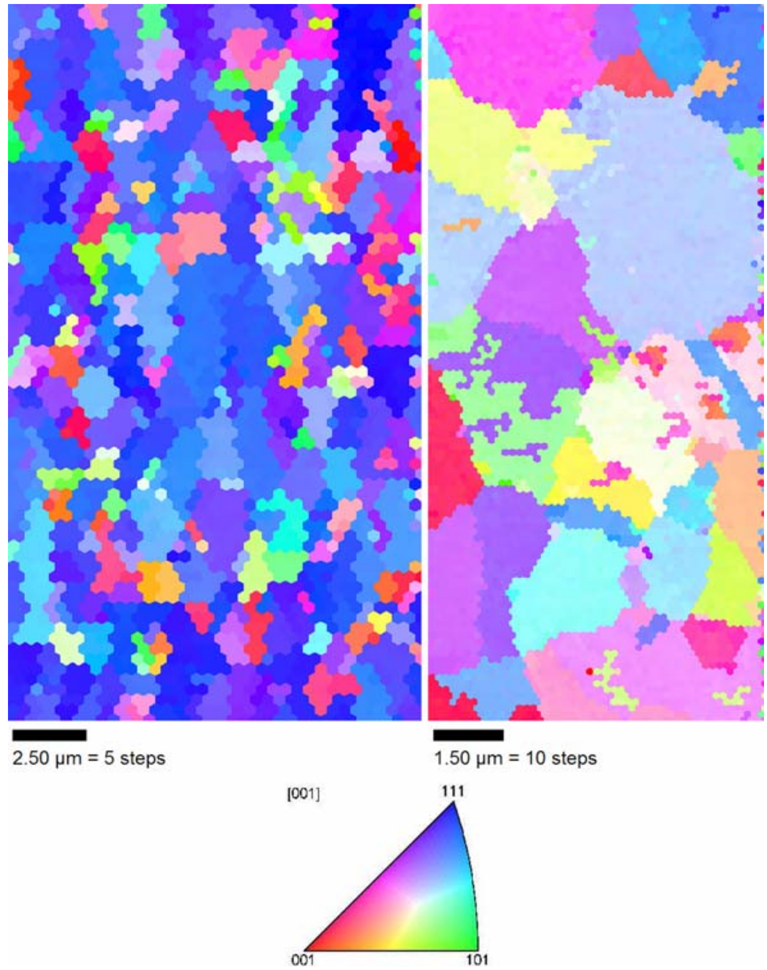

Fig. 4 Orientation maps of LT-CdTe films treated with $CdCl_2$ at: (**a**) 420 °C; (**b**) 440 °C

ment temperatures. The amount of high-angle GB in LT films treated below 440 °C is lower than in HT films, but after they are treated at 440 °C this amount is about the same as in HT samples. The heat treatment temperature also contributes to increase the number of CSL boundaries in LT films. On the other hand, the heat treatment does not change the grain boundary structure in HT films, which is dominated by high-angle boundaries (96%). Although the number of high-angle boundaries in LT films treated at 440 °C is about the same as in HT samples, an important difference should be pointed out: in LT films, 35% of the boundaries are of the CSL type, while in HT films, most of them are ordinary grain boundaries. The CSL GB found in treated LT films are mostly twin boundaries (Σ3), as shown in Table 2. This fact together with the large increase in grain size and the emergence of new orientations are a strong evidence of recrystallization. As observed in metals, annealing twins are frequently seen in recrystallized grains. Also, in some cases, the formation of twins represents the only means of generating new orientations different from those present before recystallization [10]. In our material, recrystallization is driven by the lattice-strain energy stored in LT films due to the low substrate temperature. In HT films, the high substrate temperature favors the growth of films with large grains and a low density of defects; this leads to the formation of non-deformed crystalline structures and for this reason recrystallization does not occur.

The analysis of GB properties becomes important, since they are very efficient recombination centers, reducing the carrier lifetime. An increase in the density of CSL boundaries represents an important microstructural change that could lead to an increase in both carrier lifetime and solar cell efficiency. Indeed, the fact that the relative number of CSL boundaries in LT films is greater than in HT films may be the reason why carrier lifetime in LT films is larger than in HT films, as reported in the literature [6]. In addition, an investigation carried out by All-Jassim et al. [4] clearly shows that $CdCl_2$ heat treatment in LT samples reduces carrier recombination at grain boundaries, the degree of grain boundary passivation being a function of the treatment temperature. Our results suggest that grain

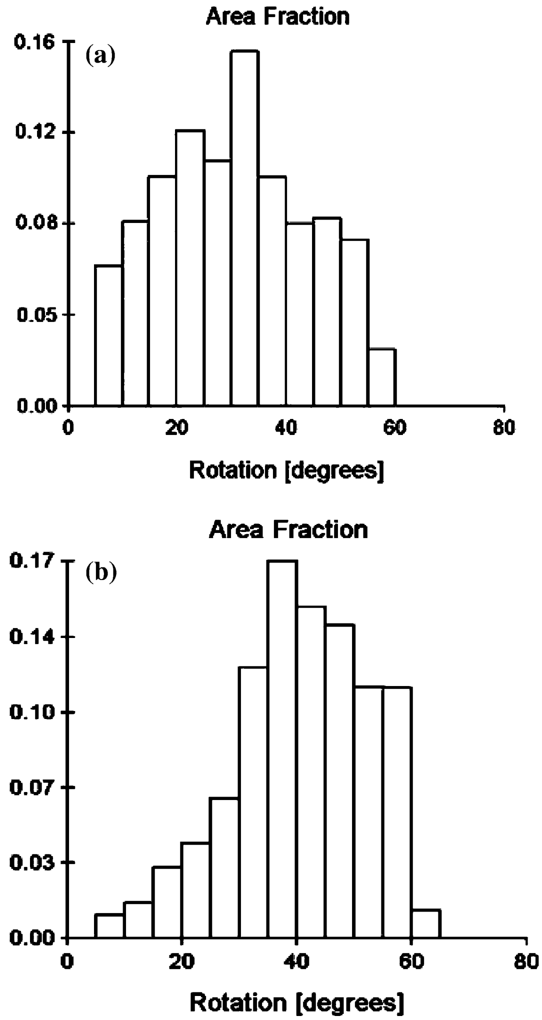

Fig. 5 Distribution of low and high-angle boundaries in LT-CdTe films treated with $CdCl_2$ at: (**a**) 420 °C; (**b**) 440 °C

Table 1 Distribution of low- and high-angle grain boundaries in LT and HT-CdTe films

Sample	Percentage of GB (%)	
	Low-angle	High-angle
LT film, $CdCl_2$/heat treated—420 °C	14.5	85.5
LT film, $CdCl_2$/heat treated—440 °C	2.5	97.5
HT film, as-deposited	3.5	96.5
HT film, $CdCl_2$/heat treated—400 °C	3.1	96.9
HT film, $CdCl_2$/heat treated—410 °C	4.1	95.9

boundary passivation, frequently mentioned in the literature [4, 11], may be related to the formation of CSL boundaries.

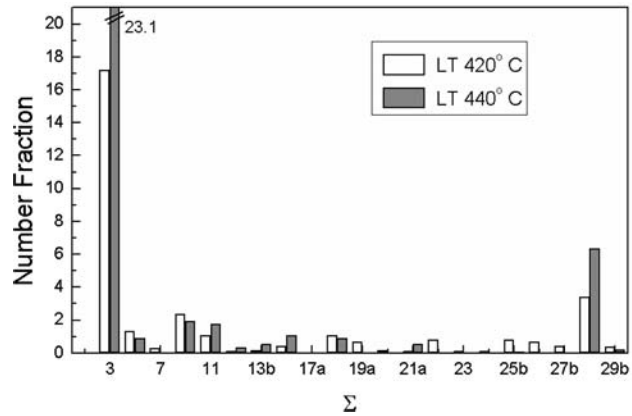

Fig. 6 Distribution of CSL grain boundaries in LT-CdTe films treated with $CdCl_2$

Finally, it is important to emphasize that although $CdCl_2$ heat treatment apparently does not change the grain size, the grain morphology, the grain orientation or the grain boundary structure in HT-CdTe films, the literature [3, 11, 12] is unanimous in acknowledging that the physical properties of HT films are better after the $CdCl_2$ treatment. Our HT-results suggest that these improvements are not due to grain boundary structure modification, as in LT films; instead, it is possible that they are related to intragrain passivation. Further investigations are being carried out to confirm this hypothesis.

Conclusions

The EBSD technique was used to quantitatively describe the microstructural changes in CdTe thin films submitted to the $CdCl_2$ heat treatment. As-deposited LT-CdTe films have small grains and a strong preferential orientation along [111] direction. After $CdCl_2$ heat treatment, a huge increase in grain size, a decreasing of preferential orientation, and an increase in the number of high-angle and CSL boundaries are observed. Such microstructural changes are considered to be a strong evidence for recrystallization. Unlike LT films, as-grown HT-CdTe films have large and randomly oriented grains, and a predominance of ordinary high-angle boundaries. After $CdCl_2$ heat treatment, all these microstructural features remain essentially the same and no evidence of recrystallyzation is seen in these films. The results suggest that, for photovoltaic applications, the grain boundary structure in LT films is better than in HT films. The microtexture description carried out in this work constitutes a preliminary analysis to better understand how $CdCl_2$ heat treatment helps to improve the electro-optical properties of CdTe films.

Table 2 Distribution of CSL grain boundaries in LT and HT-CdTe films

Sample	Percentage of CSL GB (%)								
	Σ3	Σ5	Σ7	Σ9	Σ11	Σ13	Σ27	Σ29	Total
LT film, $CdCl_2$/heat treated—420 °C	17.1	1.3	0.3	2.4	1.1	0.3	1	3.7	27.2
LT film, $CdCl_2$/heat treated—440 °C	23.1	0.9	0	1.9	1.8	0.9	0	6.4	35
HT film, as-deposited	7.5	1.2	1.5	2.3	3.1	0.8	1.5	0.3	18.2
HT film, $CdCl_2$/heat treated—400 °C	9.5	1	1	2.1	4	1.3	1.2	0.4	20.5
HT film, $CdCl_2$/heat treated—410 °C	6.3	1.6	1.7	2.3	3	0.7	1	0.4	17

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