



Revista Mexicana de Física

ISSN: 0035-001X

rmf@ciencias.unam.mx

Sociedad Mexicana de Física A.C.

México

Hernandez Vasquez, C.; Albor Aguilera, M.L.; González Trujillo, M.A.; Flores Márquez, J.M.; Galarza Gutiérrez, U.; Aguilar Hernández, J. R.; Jiménez Olarte, D.

Study of CdTe recrystallization by hydrated-CdCl₂ thermal treatment

Revista Mexicana de Física, vol. 63, núm. 5, septiembre-octubre, 2017, pp. 469-473

Sociedad Mexicana de Física A.C.

Distrito Federal, México

Disponible en: <http://www.redalyc.org/articulo.oa?id=57051630010>

- Cómo citar el artículo
- Número completo
- Más información del artículo
- Página de la revista en redalyc.org

redalyc.org

Sistema de Información Científica

Red de Revistas Científicas de América Latina, el Caribe, España y Portugal

Proyecto académico sin fines de lucro, desarrollado bajo la iniciativa de acceso abierto

Study of CdTe recrystallization by hydrated-CdCl₂ thermal treatment

C. Hernandez Vasquez^a, M.L. Albor Aguilera^a, M.A. González Trujillo^b, J.M. Flores Márquez^c,

U. Galarza Gutiérrez^a, J. R. Aguilar Hernández^a, and D. Jiménez Olarte^d

^a*Instituto Politécnico Nacional-ESFM, Depto. de Física, U.P.A.L.M.,*

Zacatenco, CDMX, 07738, México.

^b*Instituto Politécnico Nacional- ESCOM, Formación Básica, U.P.A.L.M.,*

Zacatenco, CDMX, 07738, México.

^c*Instituto Politécnico Nacional-ESIQIE, Depto. de Ing. en Metalurgia y Materiales, U.P.A.L.M.,*

Zacatenco, CDMX, 07738, México.

^d*Instituto Politécnico Nacional-ESIME, SEPI, U.P.A.L.M.,*

Zacatenco, CDMX, 07738, México.

Received 2 March 2017; accepted 26 July 2017

CdTe thin films solar cells are currently produced using a layer sequence of glass/FTO/CdS/CdTe/metal contact (Cu/Ag), these films are deposited by two different techniques, chemical bath deposition (CBD) and close space vapour transport (CSVt). In order to reach reasonable conversion efficiencies, the device has to be thermally treated in a hydrated-CdCl₂ atmosphere. This study was carried out using X-ray diffraction (XRD), photoluminescence, SEM-EDS, four probe method and SIMS profiling of CdTe. These analyses confirm the presence of hydrated CdCl₂ and CdTe phases on CdTe surface and shown a good recrystallization morphology helping to the carriers mobility along the structure. Using the thermal treatment was possible to reduce the resistivity of CdTe thin film; it is a result to the Cl migration along the CdTe solar cell structure, reducing the defects between CdS and CdTe thin films. A strong CdTe thin film recrystallization was observed by the implementation of a hydrated-CdCl₂ treatment doing to this a good candidate to CdTe solar cells process.

Keywords: CdTe; hydrated-CdCl₂; thermal treatment; recrystallization; CSVt.

PACS: 81.05.Dz; 81.65.Cf; 81.10.Pq

1. Introduction

CdTe is a very promising material for use in thin-films solar cells; its advantages as a solar cell absorber include its high optical absorption coefficient and direct bandgap of around 1.5 eV that is nearly ideal for optimal solar conversion [1]. Now the highest efficiency of CdTe thin film solar cells is 21.5%, achieved by First Solar [2].

Post-deposition processing of polycrystalline CdTe/CdS hetero-junction thin films solar cells with cadmium chloride (CdCl₂) heat-treatment has proved to improve the short circuit current and open circuit voltage of CdTe/CdS thin film solar cell by recrystallization, reorientation and grain enhancement of films for photovoltaic operation [3]. Generally, the CdCl₂ activation can be realized by two methods. The most typical CdCl₂ methods are wet CdCl₂ treatment with a CdCl₂:CH₃OH solution and vapour CdCl₂ treatment. Wet CdCl₂ treatment, which is applied after the deposition of a CdTe absorber layer and prior to the application of a back contact [4].

CdCl₂ treatment has become a standard and critical process in the fabrication of high-efficiency CdTe based photovoltaic devices, considering that CdTe films would have many undesirable characteristics such as small grains, short minority carrier lifetime and high resistivity due to large number of grain boundaries. Regardless of the method used for depositing the CdTe layer. The fact that the CdCl₂ treatment is necessary in polycrystalline CdTe due to the thickness of CdTe thin film decreased after CdCl₂ heat treatment

and the grain size increase [5,6]. However, the exact roles of Cl in enhancing and even limiting CdTe solar cell efficiency are still under debate as many explanations and mechanisms have been proposed. As Ji-Hu Yang [3] found that Cl can either substitute Te atoms to form Cl_{Te} or form interstitial defects. CdCl₂ heat treatment suggests that Cl may have strong interaction with CdTe grain boundaries (GBs).

In this work, hydrated-CdCl₂ heat treatment effects on physical properties of CdTe thin film fabricated using CSVt have been investigated. The morphological analysis of the CdTe films and the influence of the annealing with hydrated-CdCl₂ heat treatment on CdTe surface is investigated using SEM and correlated with EDXS and SIMS techniques, on the other hand the structural characteristics was analysed by XRD and state electronics was studied using photoluminescence at 14 K. Finally, the performance of CdTe solar cells using hydrated-CdCl₂ heat treatment was analysed.

2. Experimental details of fabrication of solar cells

Soda lime glass, SnO₂:F were used as substrates and front contact, CdS thin films were used as window material, the CdS films were grown by 8 min at 76 ± 2°C using CdCl₂ (0.1 M), and SC(NH₂)₂ (0.3 M) as precursor solutions for the Cd and S ion to ion deposition, respectively. NH₄Cl (0.2 M) and NH₄OH(2 M) were used to promote the formation of complex compounds in the chemical bath deposition tech-

nique, the CdS films shown thickness of about 60 nm and 87 % of optical transmittance with band gap value of 2.41 eV [7]. CdTe layers of about 4 μm of thickness were obtained by using O₂, Ar atmosphere, temperatures of 630°C and 530°C for source and substrate blocks respectively under a pressure of 100 mTorr by 3 min in the CSVT (Close Space Vapour Transport) system. After CdTe deposition, a thermal treatment was done, it consists in a muffle heat treatment after a CdCl₂ deposition in a CSVT system, using a controlled Ar atmosphere, temperatures of 350°C and 200°C for source and substrate blocks respectively. In order to recrystallize and reduce the Cd vacancies in the CdTe thin film, finally some samples were cleaned with distilled water in order to remove big CdCl₂ grains and dry with N₂ gas. In this paper CdTe surface morphology after the complete thermal treatment with hydrated-CdCl₂ and FTO/CdS/CdTe/CdCl₂ interfaces is investigated in order to provide more instructions to improve the performance and reproducibility of CdTe solar cells, all the samples developed has the same configuration (FTO/CdS/CdTe).

The structural characteristics of all samples were determined by the X-ray diffraction patterns (XRD), by means of a X'PERT Pro MRD PANalytical X-ray system using the CuK α line. The layer thicknesses were measured with a step profiler (Sloan Dektak II). The morphology associated with the samples was studied by using a scanning electron microscope (SEM) JEOL serie JSM7X. Electric parameters were determined using a 6517B Electrometer/High Resistance Meter. Band gap values of CdTe and CdTe/hydrated-CdCl₂ were obtained by photoluminescence (PL) spectra measurements. To get the PL spectra the samples were mounted on cold finger of cryostat and measurements were made at 14 K using 325 nm He-Cd laser.

Depth profiling were performed by SIMS (secondary ion mass spectroscopy) using an IONTOF 5 spectrometer; the measurements were obtained by using a source of liquid Bi at 30 keV for analysis and Cs beam at 1 keV for sputtering. Considering an incidence beam at 45 nominal degrees. Craters of 400 μm^2 were eroded but 200 μm^2 were considered only in analyses with the objective to exclude crater effects on measurements.

3. Results and Discussion

Different treatments have been proposed in the direction of promote the CdTe recrystallization, the most common treatments is using CdCl₂ by sublimation or wet technique. How-

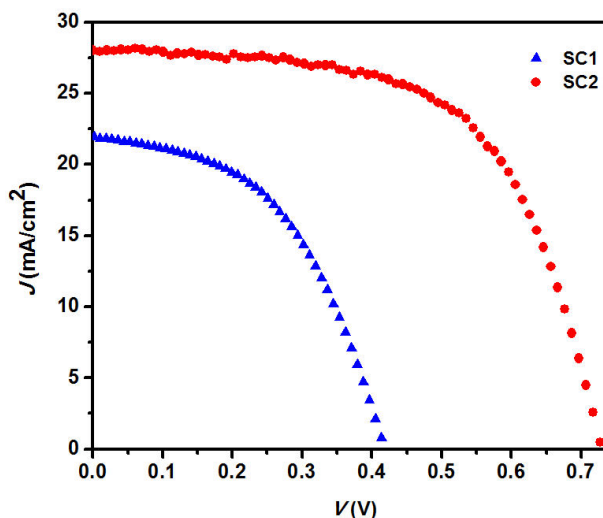


FIGURE 1. J-V curves of solar cells with and without hydrated-CdCl₂ thermal treatment

ever, in this work the treatment was implemented with hydrate-CdCl₂ using the CSVT technique obtaining good response in the CdTe solar cells (see Table I). Two devices SC1 (Solar Cell 1) and SC2 (Solar Cell 2) are presented in the Fig. 1, the first device shows a low efficiency (4.5%) due to the hydrate-CdCl₂ process were not complete, it means there are CdCl₂ salt residues producing a poor back contact for CdTe and then Cu/Au contact was not optimized; the second device presents more efficiency (12%) than the first one, because the hydrate-CdCl₂ heat treatment process was complete. This process remove the CdCl₂ residues produce a better contact Ohmic, generating long CdTe grains and reducing the Cu diffusion from the contact, also the interdiffusion of CdTe and CdS was improve reducing the recombination centers in the heterojunction.

Considering hydrate-CdCl₂ results, four steps of the hydrated-CdCl₂ process was analyzed (see Table I) to understand the thermal treatment behavior.

3.1. Structural properties

X-ray diffraction was done to identify the structure present on each step of the hydrate-CdCl₂ process. Different diffraction patterns related to CdTe and hydrated-CdCl₂ hydrated-CdCl₂ was obtained, the Figs. 2a, 2c show the experimental patterns of TT1 and TT0, the cubic structure was determined for CdTe thin film and an orthorhombic structure for hydrate-CdCl₂ deposition, the peaks identification was done using

TABLE I. Description of each hydrated-CdCl₂ step in the process

Sample	Description
TT0	CdTe as grown
TT1	CdTe + hydrated CdCl ₂ deposition in the CSVT system
TT2	CdTe + hydrated CdCl ₂ deposition + heat treatment in air
TT3	CdTe + hydrated CdCl ₂ deposition + heat treatment in air + cleaned with distilled water

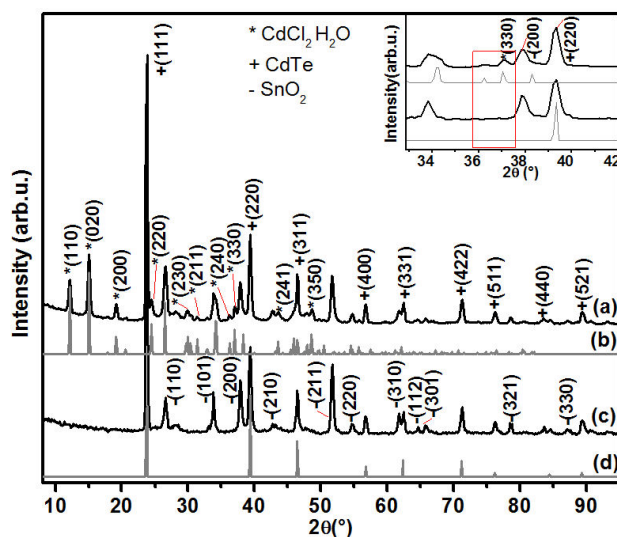


FIGURE 2. XRD of structures (a) CdTe/TT_{CdCl₂} (TT1), (b) hydrated-CdCl₂ modelling, (c) CdTe (TT0) and (d) CdTe modelling.

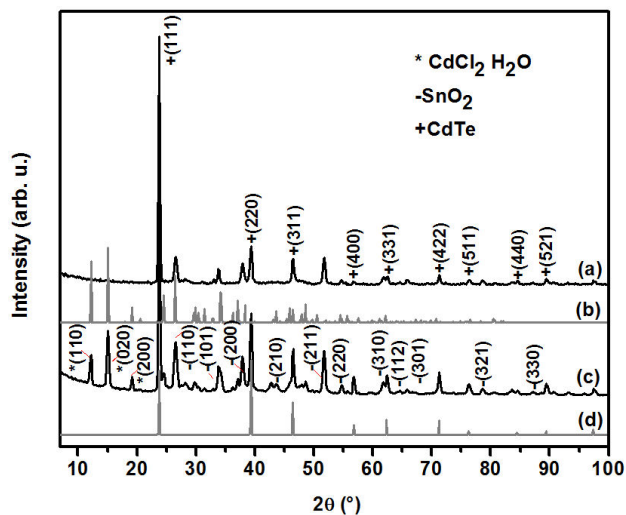


FIGURE 3. XRD of structures (a) CdTe/TT_{CdCl₂}/TT_{air}/H₂O (TT3), (b) hydrated-CdCl₂ modelling, (c) CdTe/TT_{CdCl₂} (TT1), and (d) CdTe modelling.

using PDF # 15-0770 and PDF # 27-0073 respectively. Each peak from hydrate-CdCl₂ modelling match with the experimental pattern (see inset in Fig. 2), it indicates that the thermal process increases the Cd atoms in the CdTe structure.

In the same way a pattern of TT3 was obtained in order to review any changes that could be present on the sample when it is submitted under a heat treatment in air and cleaned with distilled water, thus, the Fig. 3a shows how the principal hydrated-CdCl₂ peaks was diminished. Is possible that the peaks were eliminated or the percentage present in the sample is less than 5%, if it is the case, we know that X-ray diffraction cannot detect a signal from the compound. In the pattern, the plane (111) reveals that recrystallization occurs when grains belonging to another plane nucleate and grow to reach high fractions of volume and consequently modify the

TABLE II. Elemental concentrations in the studied hydrated-CdCl₂ treatment.

Sample	[Cd] (at.%)	[Te](at.%)	[Cl] (at.%)
TT0	47	53	
TT1	50	44	6
TT2	49	48	3
TT3	48	50	2

preferential orientation. Doing a quick calculus, we can conclude that the lattice parameter values did not change with the thermal treatment ($a = 6.497 \text{ \AA}$); respect of FWHM related with the (111) plane values of 0.37° and 0.35° for as deposited CdTe and CdTe (TT3) respectively. Due to the last results the CdTe recrystallization were associated by the intensity variation related with the (111), (220) and (311) planes.

3.2. Morphological properties

Figure 4a shows a common CdTe morphology growth by CSVT, the samples have a big density of grain boundaries on different faces directions. Considering this observation is necessary implement a treatment in favor of reduce boundaries and increase the carriers flow through the metal contact. As mentioned in the introduction, many works has been developed trying to improve this junction (semiconductor/metal), in this case is possible to see in the Fig. 4b the hydrated-CdCl₂ morphology on CdTe surface creating a hydrated-CdCl₂ shell, however, this cover allows to see the CdTe boundaries, after hydrated-CdCl₂ deposition the sample was heat treatment on air reducing the hydrated-CdCl₂ density, therefore, is appreciated a change in the CdTe grains due to the defects on the CdTe surface was reduced and as we could see in X-ray diffraction the CdTe planes are oriented in the (111) direction. Additionally a density of CdCl₂ flakes appear on the CdTe surface (see Fig. 4c), this morphology could reduce the current because the boundaries act like recombination centers. In this way a cleaned process was developed using distilled water, and how the Fig. 4d shows the hydrated-CdCl₂ flakes density was reduced, obtaining a CdTe recrystallization on (111) direction.

An elemental analysis was done by using EDS, the Table II shows the atomic percentage of Cd, Te and Cl elements present in the different steps of the treatment. In TT0 the Te percentage is more than Cd, this result does not correspond with different authors due to it mentions that CdTe growth by sublimation technique create a rich Cd region, however, for this work the thermal treatment help to create a Te rich region on CdTe surface (TT3 step), Cl signal on the surface decreases considering each step of the process.

3.3. Electrical properties

The hydrated-CdCl₂ process was analyzed from electrical point of view to understand what is the behavior of this pro-

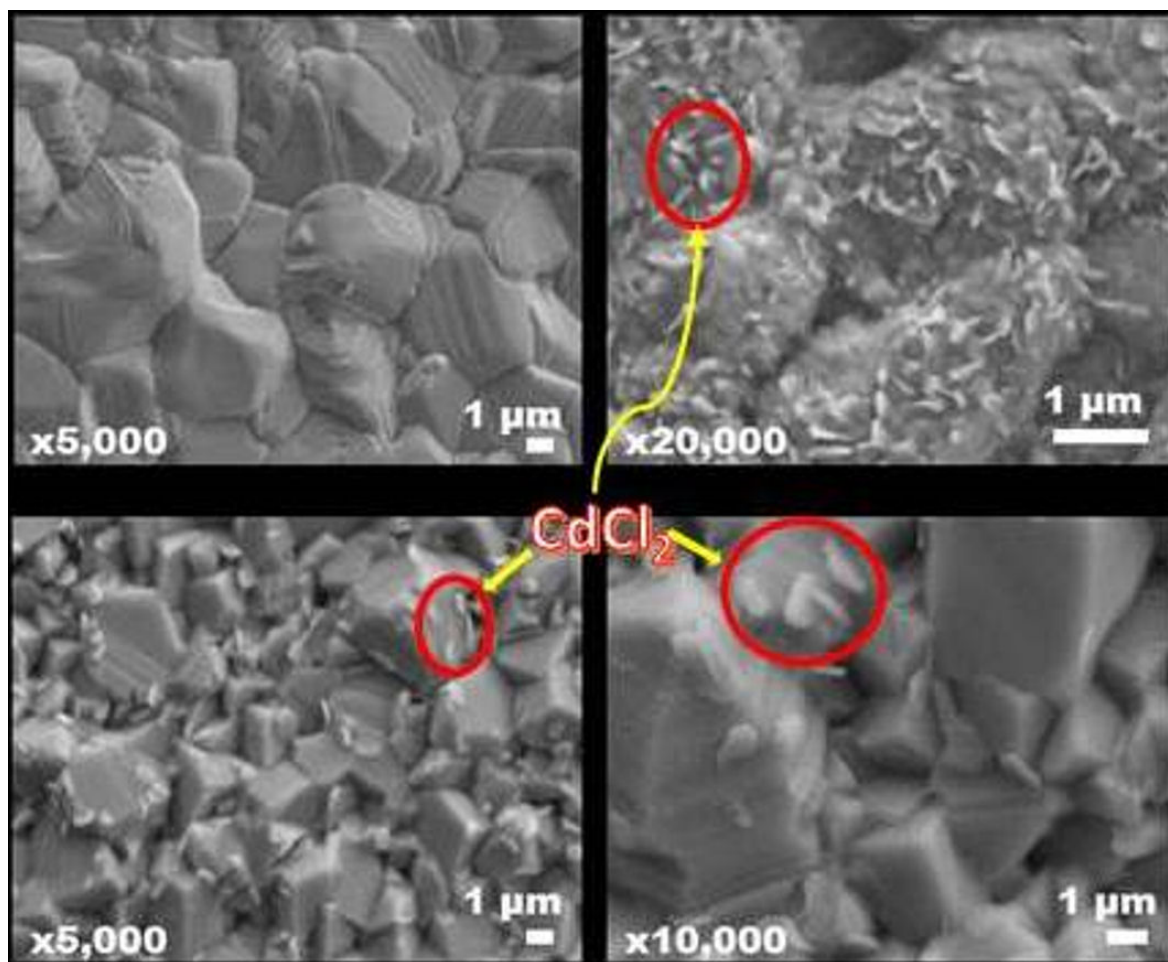


FIGURE 4. SEM images at 5 eV; (a) TT1, (b) TT2, (c) TT3 and (d) TT4

cess on the CdTe surface. Is important to notice that CdTe thin films has a high resistivity (around $3.3 \times 10^5 \Omega\text{cm}$), and implementing the process on TT1 step we could obtain a resistivity of $7 \Omega\text{cm}$ however this result is only for hydrated- CdCl_2 because as we can see in the Fig. 4b the morphology only correspond with hydrated- CdCl_2 and this is the reason of this value, finally the resistivity of CdTe+ hydrated- CdCl_2 doesn't change significantly ($\rho = 1.3 \times 10^5 \Omega\text{cm}$), however the temperature used on each step modifies the morphology of CdTe allowing a good response due to the grain boundaries was diminished and CdTe recrystallize.

3.4. Optical properties

Two principal luminescence bands were observed in the four steps of treatment as shown in Fig. 5. The one present in the range 1.56 eV - 1.58 eV results from donor or acceptor bound excitons. However this shift of the peaks could be produce by O_{Te} acceptors [9] or V_{Cd} complex based acceptors participating in a donor-acceptor pair (DAP) recombination. A further band at 1.44 eV is characteristic of a further complex DAP emission often seen in CdTe. There were some important differences between the spectra of the

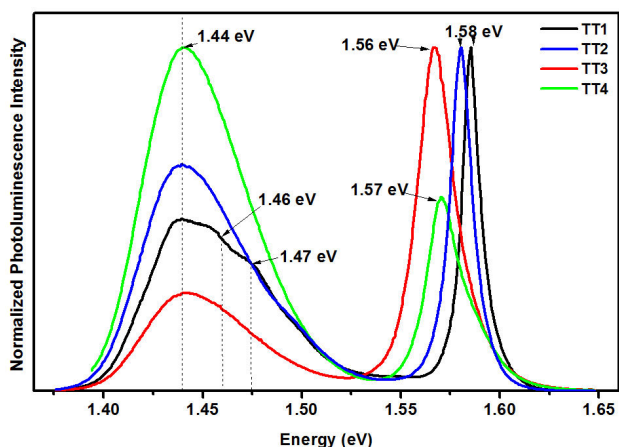


FIGURE 5. Normalized photoluminescence spectra at 14 K (a) TT0, (b) TT1, (c) TT2 and (d) TT3.

samples. The hydrated- CdCl_2 treatment causes a general increase in luminescent intensity indicating either an increase in the concentration of the active centers or a decrease in the non-radiative recombination sites. Considering the CdTe and CdTe treated with hydrated- CdCl_2 samples the 1.44 eV band

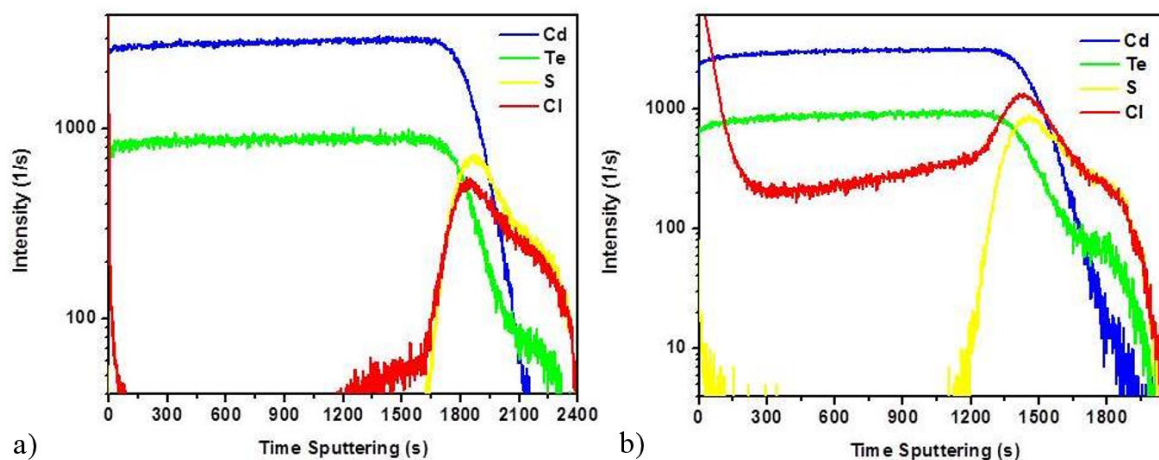


FIGURE 6. Normalized depth profile of (a) SC1 and (b) SC2 photovoltaic devices.

is most intense in the bulk of the CdTe layer after complete treatment, this result origin that DAP luminescence is known to be complicated and possible assignments such as (V_{Cd}) as the acceptor and Cl_{Te} as the donor are speculative. Also analysing the PL spectra from CdTe as grown, is possible to identify three bands 1.44, 1.46, 1.47 (eV), who are related to Te deficiency, O presence and donor-acceptor recombination due to Cl_{Te} respectively. However, in order to review this last SIMS measurement was done.

A solar cell structure (SC2) was analyzed, four signal of each element present in the solar cell (Cd, Te, S, Cl) are studied in order to see the behavior of Cl into the solar cell. Figure 6a shows the Cl signal in the CdS region, it is present in this part due to the CdS growth considering that involves Cl precursors in addition the front contact also contribute Cl because this film is chemical treated on HCl as part of the process. On another hand, the Fig. 6b shows a different Cl signal behavior, as result of hydrated-CdCl₂ process, the CdTe grains recrystallize on (111) plane and a migration of Cl along CdTe structure was determined. As different authors mention the possible Cl migration in CdTe is assured by SIMS, however, is necessary to do another analysis in the interest of determine in which position is localized.

4. Conclusions

Hydrated-CdCl₂ was implemented by CSVT on CdTe thin films in order to recrystallize the CdTe surface. XRD confirms the recrystallization in the (111) plane, this was observed in the SEM images and some hydrated-CdCl₂ crystals are present on the CdTe surface. The hydrated-CdCl₂ treatment causes a general increase in luminescent intensity indicating either an increase in the concentration of the active centers or a decrease in the non-radiative recombination sites. Cl atoms were detected along the CdTe solar cells structures promoting the formation of different compounds in the junctions of the solar cell. The activation leads to modifications in the electronic properties of every layer and interface in the CdTe solar cell.

Acknowledgments

This work was supported by CeMIE-Sol P25, Instituto Politécnico Nacional, SIP 20170141 and 20170315.

1. Ji-Hui Yang, Wan-Jan Yin, J. Sang Park, W. Metzger, and Su-Huai Wei, *Journal of appl. Phys.* **119** (2016) 1-7.
2. M.A. Green, K. Emery, Y. Hishikawa, W. Warta, and E.D. Dunlop, *Prog. Photovolt: Res. Appl.* **24** (2016) 905-913.
3. Xiaoxu Huo *et al.*, *J Mater Sci: Mater Electron* **24** (2013) 2479-2484.
4. M.J. Kim, J.J. Lee, S.H. Lee, and S.H. Sohn, *Solar Energy Materials & Solar Cells* **109** (2013) 209-214.
5. Ali Nawaz, Zamran Rabeel, and Abbas Shah, *World Applied Sciences Journal* **31** (2014) 1522-12530.
6. H.R. Moutinho *et al.*, *Presented at the 26th IEEE Photovoltaic Specialists Conference* (2013) 1-9.
7. J.M. Flores-Marquez *et al.*, *Thin Solid Films* **582** (2015) 124-127.
8. I.M. Dharmadasa, *Coats.* **4** (2014) 282-307.
9. K. Akimoto, H. Okuyama, M. Ikeda, and Y. Mori, *Appl. Phys. Lett.* **60** (1992) 91