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Study of CdTe recrystallization by hydrated-$CdCl_2$ thermal treatment

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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-$CdCl_2$ 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 $CdCl_2$ 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-$CdCl_2$ treatment doing to this a good candidate to CdTe solar cells process.

Keywords: CdTe; hydrated-$CdCl_2$; thermal treatment; recrystallization; CSVT.

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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 ($CdCl_2$) 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 $CdCl_2$ activation can be realized by two methods. The most typical $CdCl_2$ methods are wet $CdCl_2$ treatment with a $CdCl_2$:CH_3OH solution and vapour $CdCl_2$ treatment. Wet $CdCl_2$ treatment, which is applied after the deposition of a CdTe absorber layer and prior to the application of a back contact [4].

$CdCl_2$ 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 $CdCl_2$ treatment is necessary in polycrystalline CdTe due to the thickness of CdTe thin film decreased after $CdCl_2$ 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. $CdCl_2$ heat treatment suggests that Cl may have strong interaction with CdTe grain boundaries (GBs).

In this work, hydrated-$CdCl_2$ 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-$CdCl_2$ 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-$CdCl_2$ heat treatment was analysed.

2. Experimental details of fabrication of solar cells

Soda lime glass, SnO_2: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 $76 \pm 2°C$ using $CdCl_2$ (0.1 M), and $SC(NH_2)_2$ (0.3 M) as precursor solutions for the Cd and S ion to ion deposition, respectively. NH_4Cl (0.2 M) and NH_4OH(2 M) were used to promote the formation of complex compounds in the chemical bath deposition technique, 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 mm of thickness were obtained by using O, 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 $CdCl_2$ 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 $CdCl_2$ grains and dry with N gas. In this paper CdTe surface morphology after the complete thermal treatment with hydrated-$CdCl_2$ and FTO/CdS/CdTe/$CdCl_2$ 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 CuKα 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-$CdCl_2$ 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 $CdCl_2$ by sublimation or wet technique. However, in this work the treatment was implemented with hydrate-$CdCl_2$ 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-$CdCl_2$ process were not complete, it means there are $CdCl_2$ salt residues producing a pour 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-$CdCl_2$ heat treatment process was complete. This process remove the $CdCl_2$ 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.

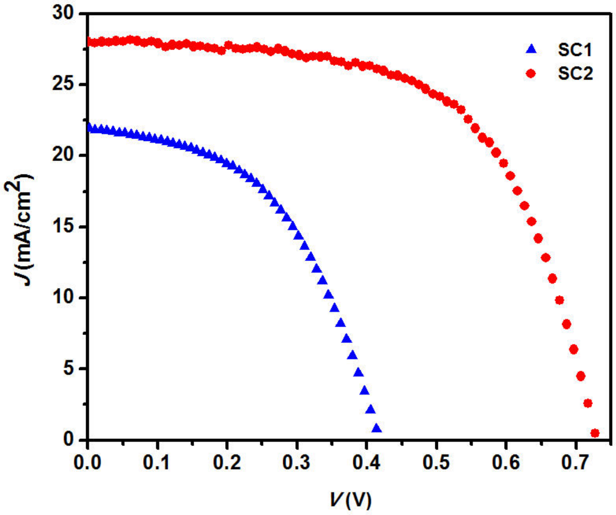

FIGURE 1. J-V curves of solar cells with and without hydrated-$CdCl_2$ thermal treatment

Considering hydrate-$CdCl_2$ results, four steps of the hydrated-$CdCl_2$ 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-$CdCl_2$ process. Different diffraction patterns related to CdTe and hydrated-$CdCl_2$ hydrated-$CdCl_2$ 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-$CdCl_2$ deposition, the peaks identification was done using

TABLE I. Description of each hydrated-$CdCl_2$ 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

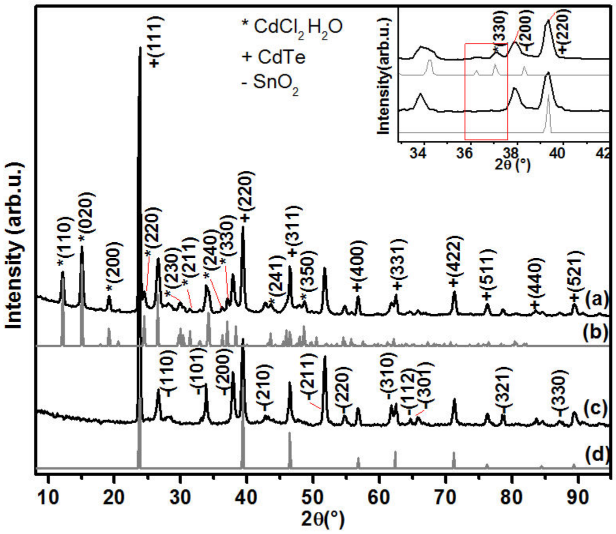

FIGURE 2. XRD of structures (a) CdTe/TT_{CdCl2} (TT1), (b) hydrated-CdCl$_2$ modelling, (c) CdTe (TT0) and (d) CdTe modelling.

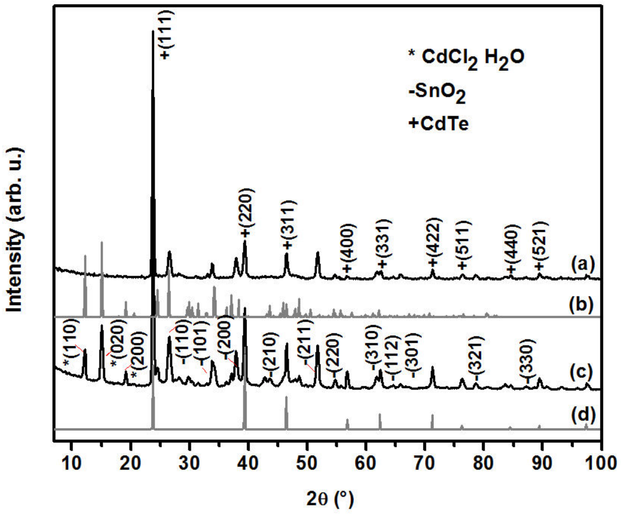

FIGURE 3. XRD of structures (a) CdTe/TT_{CdCl2}/TT_{air}/H_2O (TT3), (b) hydrated-CdCl$_2$ modelling, (c) CdTe/TT_{CdCl2} (TT1), and (d) CdTe modelling.

using PDF # 15-0770 and PDF # 27-0073 respectively. Each peak from hydrate-CdCl$_2$ 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 summited under a heat treatment in air and cleaned with distilled water, thus, the Fig. 3a shows how the principal hydrated-CdCl$_2$ 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 preferential orientation. Doing a quick calculus, we can conclude that the lattice parameter values did not change with the thermal treatment (a = 6.497 Å); 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.

TABLE II. Elemental concentrations in the studied hydrated-CdCl$_2$ treatment.

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

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-CdCl$_2$ morphology on CdTe surface creating a hydrated-CdCl$_2$ shell, however, this cover allows to see the CdTe boundaries, after hydrated-CdCl$_2$ deposition the sample was heat treatment on air reducing the hydrated-CdCl$_2$ 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 CdCl$_2$ 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-CdCl$_2$ 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-CdCl$_2$ process was analyzed from electrical point of view to understand what is the behavior of this pro-

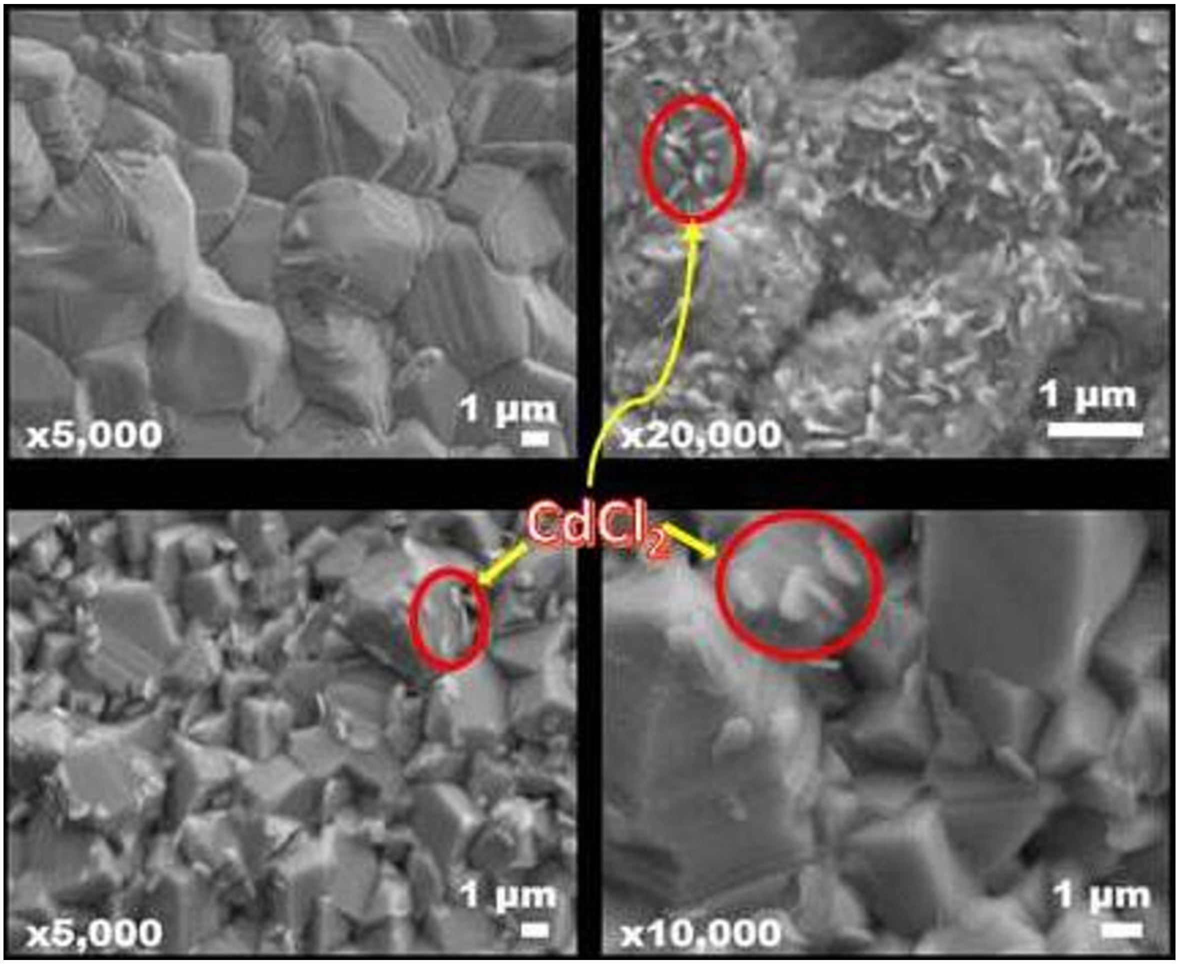

FIGURE 4. SEM images at 5 eV; (a) TT1, (b) TT2, (c) TT3and (d) TT4

cess on the CdTe surface. Is important to notice that CdTe thin films has a high resistivity (around 3.3×10^5 Ωcm), and implementing the process on TT1 step we could obtain a resistivity of 7 Ωcm 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 ($\rho = 1.3 \times 10^5$ Ωcm), 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 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

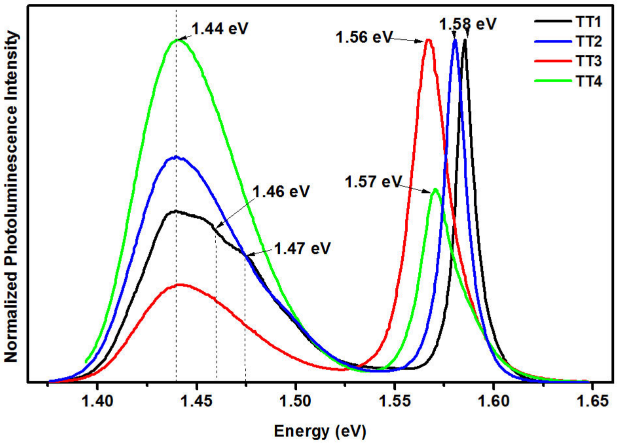

FIGURE 5. Normalized photoluminescence spectra at 14 K (a) TT0, (b) TT1, (c) TT2 and (d) TT3.

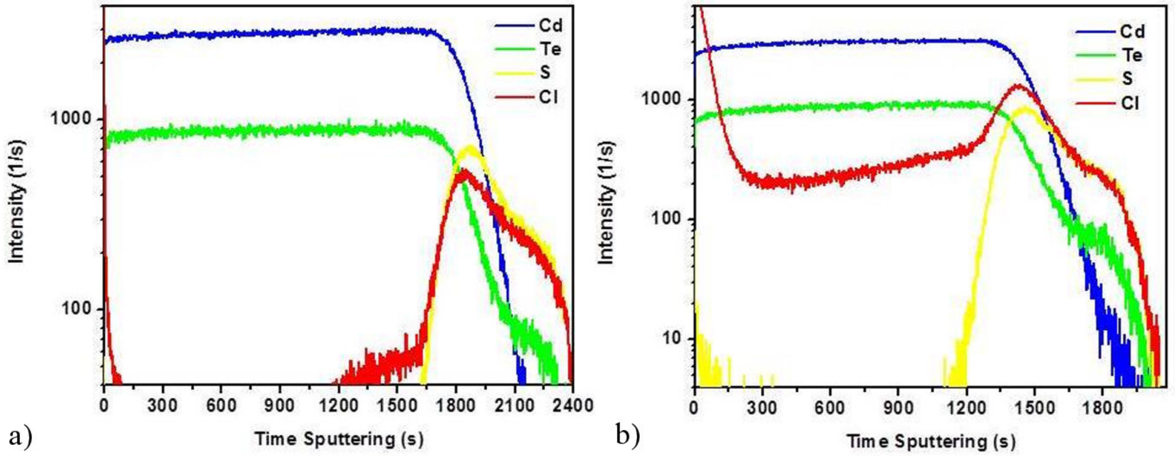

FIGURE 6. Normalized depth profile of (a) SC1 and (b) SC2 photovoltaic devices.

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-CdCl$_2$ 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-CdCl$_2$ 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-CdCl$_2$ crystals are present on the CdTe surface. 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. 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.

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