Effect of CdCl₂ annealing treatment on structural and optoelectronic properties of close spaced sublimation CdTe/CdS thin film solar cells vs deposition conditions

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1. Introduction

Polycrystalline thin-film CdTe has shown considerable promise for terrestrial photovoltaic applications due to its near-optimum bandgap, high absorption coefficient and relative ease of film formation. Thin-film CdTe/CdS cells with efficiencies greater than 10% have been demonstrated using CdTe deposited by a variety of techniques over a wide range of deposition temperatures [1–3]. Record conversion efficiency of 17.3% was recently reported by First Solar for polycrystalline CdTe/CdS solar cell modules [4]. However, the theoretical estimations of possible photovoltaic solar energy conversion into electricity for CdTe are of about 29% [5]. Because of its low sublimation temperature, CdTe polycrystalline films can be prepared by several techniques [6–9]. The closed-space sublimation technique (CSS) is one of the various techniques that have produced encouraging results. During CdTe solar-cell fabrication, after deposition of the absorber layer of CdTe, a standard CdCl₂ heat treatment must be carried out in order to improve the cell performance [10,11]. The CdCl₂ heat treatment has been proved to be a key process step in the fabrication of highly efficient CdTe cells. It was reported to be able to enhance CdTe grain growth, to reduce the defect density in the films, to promote the interdiffusion at the CdTe/CdS junction interface to passivate grain boundaries, and thereby to improve solar-cell efficiency [12–14]. Unfortunately, the effect of grain boundaries and other structural defects on the device properties is not fully understood and the fundamental properties of the CdTe films are not well known. Systematic studies should be carried out to understand the mechanism of CdCl₂ treatment on efficiency increase as well as the effect on the CdTe surface modification and micro-structural and electronic properties.

The main objective of the work is to study the effect of CSS deposition conditions on structural and optoelectronic properties of CdS/CdTe thin films and solar cells.

2. Experimental details

The devices were fabricated in a superstrate configuration by CSS on Corning 7059 glass coated with a 200 nm thick fluorine doped tin oxide layer (FTO). Films of CdS, 150–180 nm thick, were deposited at 400 °C from high-purity CdS powder. CdTe films with a thickness of 3–5 μm were deposited onto CdS layers from 99.999% purity CdTe powder. Source material was heated in the graphite boat by a tungsten coils connected to the main power supply through temperature controller with K-type thermocouple. The substrate was fixed at a distance of 7 mm from the source material, which also was heated by a similar system, while the type K thermocouple was placed above the substrate. The source temperature was kept at 610 °C, while substrate temperatures varied from 250 to 500 °C. The residual pressure during deposition was below 2 × 10⁻⁴ Pa. The deposition time of each film was 5 min, after which the source and substrate heaters were switched off. The chamber was opened after the temperature fell below 30 °C.

After deposition the CdTe/CdS/FTO/glass samples were soaked in a saturated CdCl₂ methanol solution (2.15 g/100 mL methanol), followed by a 30 min heat treatment in air at 420 °C in a two-zone tube furnace.
The heat treated samples were rinsed in deionized water and etched in standard NP (H3PO4:HNO3:H2O) solution to remove the CdCl2 and oxide residues. To finish the cells, the Te/Au bi-layer back contact was deposited by thermal evaporation. Anhydrous, 99.99% CdCl2 was supplied from Alfa Aesar.

The structure of the films was studied with Rigaku Ultima IV diffractometer (Cu Kα radiation, λ = 1.5406 Å, 40 kV at 40 mA; silicon strip detector D/teX Ultra, Rigaku, Japan) in the Bragg–Brentano (θ–2θ) geometry and their morphology was checked by a scanning electron microscope (SEM) Zeiss EVO-MA15 at a 10 kV operating voltage. The crystallite size and lattice parameters were calculated using the PDXL microscope software on the Rigaku system. Solar cells were characterized by current–voltage (I–V) and quantum efficiency (QE) measurements under simulated standard test conditions. I–V curves were measured at room temperature with illumination of 100 mW/cm² using the Oriel class A solar simulator 91159A. The quantum efficiency of the solar cells was measured in the range of 300–1330 nm on a Newport Oriel kit that uses 300 W Xe-lamp, high-resolution monochromator (Cornerstone 260), a digital dual-channel lock-in detector (Merlin), and a calibrated silicon reference detector. The Xe-lamp is a light source to simulate the conventional AM1.5 spectrum for testing of solar cells.

3. Results and discussion

3.1. SEM and X-ray diffraction studies

SEM investigation of the CdTe films deposited on CdS/FTO/glass at the different growth conditions shows that the shape and size of grains of the polycrystalline films greatly depend on the substrate temperature during deposition. The grain size was found to increase with the substrate temperature. The cross-sectional images of the CdTe films deposited on CdS/FTO/glass at the different growth conditions, before and after CdCl2 heat treatment are shown in Fig. 1. It can be observed from Fig. 1(a) that the films deposited at the lowest substrate temperatures $T_s \leq 300 °C$ exhibit a faceted and highly dispersed structure with average grain size about $d \leq 0.8 \mu m$. The orientation of crystallites is uniaxial. The increase of the substrate temperature, leads to an increase in grain size up to $d \approx 2 \mu m$ at $T_s = 350 °C$ and consequently a decrease in porosity. Further increase of the substrate temperature $T_s \geq 400 °C$, results in an increase in grain size up to $4 \mu m$. Besides increasing the grain size, the increase in the substrate temperature decreases the density of voids and films had a close-packed morphology. Moreover, as can be clearly seen from SEM images the change of the thin film growth mechanism occurred at 300 and 350 °C. In this case, the films have a columnar-like structure with a clear growth texture. The columnar-like structure was most pronounced in the film obtained at 350 °C. The diameter of the columns strongly depends on the growth conditions (substrate temperature—$T_s$, evaporator temperature—$T_e$, $\Delta T = T_e - T_s$). These changes observed in growth mechanism might be induced by particular specific thermodynamic parameters during the CSS deposition and nucleation processes [15,16]. The films obtained at the growth conditions close to the thermodynamic equilibrium ($T_e = 450 - 500 °C$) have practically a monoblock structure along the layers thickness, without porosity or voids, indicating high packing density of the films. It should be mentioned that these results (SEM) are in good correlation with published results obtained at comparable temperature regimes by Luschitz et al. [17] as well as Kosyak et al. [18]. Thus, for CSS CdTe films prepared at different substrate temperatures, Luschitz et al. found three different growth regimes where in the first regime (up to 320 °C) the grains grow as columnar extended grains, in the second regime (above 370 °C) the grains are considerably larger and have lost the columnar morphology, and in the high temperature growth regime the grains seem to be rather compact and dense, implying film quality. The same author highlights that the films formed at the transition regime (340 °C) seem to expose very promising film morphology. Kosyak et al. got SEM images which show a highly dispersed structure for films obtained at $T_s \leq 200 °C$ and columnar-type growing for $T_s \geq 350 °C$. It is reasonable to say that an

![Fig. 1](image-url) SEM surface morphology and cross-sectional microstructure of CdTe/CdS thin films deposited at different substrate temperatures, (a) before and (b) after CdCl2 heat treatment.
overview of the results that were achieved by both author as well our results describe the same pattern of three different growth regimes in which the changes in structure and morphology to electrical properties of solar cells have been produced from the different films. It should be noted that the formed structure and growth regimes depend also on the CdTe deposition, configuration and geometrical parameters of CSS system; therefore this might to be an important aspect which can explain the difference between the results.

After CdCl₂ treatment, the film surface consisted of rounded grains with penetrating boundaries. A subsequent CdCl₂ heat treatment further increased the grain size, resulting in planar surface morphology and lateral grain size of ~5 μm, suggesting dramatic reduction of the grain boundary density. The cross-sectional images of the CdCl₂ treated film deposited at 250 °C (Fig. 1(b)) show that the film has high inner porosity and density of voids, with large grain size (larger as compared to the film deposited at 250 °C). Furthermore, the cross-sectional images of the films grown at 300 and 350 °C and treated in CdCl₂ changed dramatically (Fig. 1, b). Thus, the columnar-like structure disappears for films deposited at 300–350 °C after CdCl₂ treatment; nevertheless a 1 μm thick surface layer has large porosity. A subsequent CdCl₂ heat treatment of the films grown at substrate temperature $T_s \geq 400$ °C promoted formation of a block structure with extra-large grain size without pores and voids, implying good crystalline quality of the films.

X-ray diffraction patterns (XRD) of the CdTe films deposited at the different growth conditions, before and after CdCl₂ heat treatment, are presented in Fig. 2 (a, b). X-ray diffractograms show the peaks from (111), (220), (311), (400), (331), (422), and (511) planes of the cubic phase. It is observed that the films obtained at the substrate temperatures 250, 300 and 350 °C exhibits a strong (111) preferred orientation of the crystallites along (111) plane parallel to the substrate. With an increase in the substrate temperature the preference for the (111) orientation is decreased, as is shown for films deposited at 400 °C, as the intensities of the (220) and (311) peaks are up to 40% of the (111) intensity (much higher as compared with films grown at low temperatures).

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**Fig. 2.** XRD patterns of CdTe/CdS thin films deposited at the different substrate temperatures $T_s$, (a)—before and (b)—after CdCl₂ heat treatment. (c). High resolution (511) XRD profiles of CdTe/CdS thin films deposited at substrate temperatures 250 and 450 °C, before and after CdCl₂ heat treatment.
Furthermore, the intensities of (220) and (311) peaks strongly increase when the substrate temperature increases ($T_s > 400\,^\circ\text{C}$). This suggests that higher substrate temperature ensures better growth of a dense structure; thus the films grow both in a perpendicular, as well as in lateral directions. In both cases, at lower and higher substrate temperatures, after CdCl$_2$ treatment, air annealing at 420 °C and NP etching solution (Fig. 2, b) the preferential (111) orientation is decreased as the intensities of the (220) and (311) peaks are increased significantly. This observation is in good accordance with results reported in [19,20] about the decrease of the (111) peaks after the CdCl$_2$ treatment and air annealing, which depends on the annealing temperature and the amount of CdCl$_2$. After CdCl$_2$ heat treatment of the samples grown at 250 and 300 °C the intensities of the (220) and (311) peaks are slightly lower than the intensity of the (111) peak. However, for the CdCl$_2$ treated films grown at $T_s > 350\,^\circ\text{C}$, the intensity of the (111) peak is lower than that of the (220) peak, implying that the films are not (111) textured and has a predominance of the (220) orientation. These variations of the intensity of Bragg peaks suggest that CdCl$_2$ heat treatment, as a process with formation of liquid flux and to hier the rules of liquid phase recrystallization, change dramatically atomic arrangement and hence a certain degree of randomization in the CdTe film texture. The CdCl$_2$ treatment recrystalizes the CdTe layers in such a way that some of the smaller grains coalesce into bigger ones while some of the bigger grains divide into smaller ones and reorient themselves, which gives an entirely different microstructure [21]. The film deposited at the lowest substrate temperature exhibits a highly dispersed structure with smaller grains which are more active and have higher solubility in the melted flux, contributing to stronger mass transport. The process is characteristic for the sintering in the presence of liquid phase [22]. We consider that the structural changes in the CdCl$_2$ heat treatment process are very complex and we assume that this includes all the main steps of recrystallization, grain growth and sintering. The prevalence of one or another step depends on the proportion between solid and liquid flux phases. Due to high solubility of CdS and CdTe in CdCl$_2$ flux, in the first step of the process the main mechanism of grain growth is accomplished by recrystallization. Considering that annealing is carried out in air, due to evaporation of CdCl$_2$ the volume of liquid phase decreases which leads to the sintering of the grains and creation of good contact between them.

It is known that the crystallographic rearrangements are related to the stress in the films and to application of air annealing at 420 °C in the CdCl$_2$ sintering flux [23,24]. In order to study the stress and intermixing in CdTe films, the XRD measurements were analyzed by Rigaku software PDFXL. Changes in the crystallite size and lattice parameter before and after CdCl$_2$ treatment are listed in Table 1. As given in Table 1, the lattice parameter of the CdTe films increases from 6.482 to 6.486 Å when the substrate temperature of the films increased from 250 °C to 500 °C. The increase in the lattice constant with the increase of substrate temperature may be due to development of internal stress in the film grains which triggers the prolongation [25]. Also, we got an increase in crystallite size from 131 to 936 Å for the change in the substrate temperature from 250 to 500 °C, which was calculated by using XRD diffractograms and Scherrer’s formula. After CdCl$_2$ treatment the crystallite size increases considerably and has a similar value for all samples. It can be seen from Table 1, that the as deposited films grown at different substrate temperatures have a high in-plane lattice constant compared to the recrystallized films. Thus, the lattice parameter of as-deposited films decreases from 6.486 to 6.481 Å for the CdCl$_2$ treated films. A. Romeo, A.N. Tiwari et al., suggested that this effect is due to the fact of the relaxation of the compressive stress which is generated by the lattice and thermal mismatch between the CdTe and the underlying substrate [26]. The lattice parameter may also decrease due to the formation of CdTe$_{x}$S$_{y}$ and CdS$_{1-x}$Te$_x$ alloys in the absorber layer which occurs by interdiffusion between CdS and CdTe during CdCl$_2$ treatment in air [13,27]. The progressive diffusion, which creates a distribution of lattice parameters within the film, can be easily detected with X-ray diffraction line-profile analysis. The analysis of the data presented in Fig. 2(c) proved the changes in the XRD profiles of the CdTe (511) peak for CdCl$_2$ treated films. Therefore, the CdCl$_2$ treatment produced a broad asymmetric peak with a tail extending towards higher angle (lower d-spacing), indicative of significant alloying with CdS. Alloy formation is more pronounced in films deposited at low substrate temperature having small grains and high grain-boundary density. In such films, a high partial pressure or concentration of CdCl$_2$ together with O$_2$ during CdCl$_2$ treatment will result in considerable alloy formation. For samples, deposited at high temperature and having large grains, the absorber layer exhibits a narrow CdTe (511) XRD profile, indicating a negligible degree of alloy formation. The SEM images support the XRD results.

### Table 1

<table>
<thead>
<tr>
<th>$T_s$ (°C)</th>
<th>Cryst. size (Å)</th>
<th>$a_0$ (Å)</th>
<th>$a_0$ (Å)</th>
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<td>As deposited films</td>
<td>After CdCl$_2$ treatment</td>
<td>As deposited films</td>
<td>After CdCl$_2$ treatment</td>
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### Fig. 3

The room temperature photoluminescence spectra of the CdTe/CdS samples obtained at different substrate temperatures, before and after CdCl$_2$ treatment, are shown. For all as deposited samples PL emission band is peaked at 1.49 eV. Moreover, the amplitude of the PL intensities strongly depends on the growth conditions. As it can be seen from Fig. 3, the most intense band corresponds to the films obtained at high temperatures 450 and 500 °C. Therefore, CdTe/CdS films obtained at such growth condition have high crystallinity and revealed in more perfect structure. This result is in good accordance with the data presented above by SEM and XRD. The PL intensity decreased with the smallest grain size in the film. Therefore, the dislocation density for these films is larger than in the case of films grown at high temperature. In addition, PL emission in a polycrystalline system may be significantly influenced by grain boundaries (GBs). One effect of GBs is that the PL bands are broadened by the variety of recombination.
centers that can exist in a polycrystalline film [29]. At low substrate temperature GBs can provide an effective channel for non-radiative recombination. After CdCl₂ treatment the relative PL intensity increases considerably reaching a similar value for all samples (Fig. 3, curve 1). It has been shown that the increase of the PL intensity is strongly affected by CdCl₂ annealing which leaves too high chlorine concentration in CdTe lattice and generates a high concentration of the isoelectronic complexes $V_{\text{Cd}2\text{Cl}}$ and $\text{Te}_{2}\text{Cl}_2$. The main defects which form the 1.49 eV PL band here are substitutional chlorine $\text{Cl}_\text{Te}$ (donor) and complex $V_{\text{Cl}}\text{Cl}_\text{Te}$ (acceptor) [30–32]. It was observed that after CdCl₂ heat treatment the PL spectra for the films grown at smallest temperatures exhibit high intensities (much higher as compared to the as deposited). This result is in a good accordance with the data presented by SEM and XRD where for the films deposited at the lowest temperature having submicrometer initial crystalline size, significant recrystallization mechanism occurs during the CdCl₂ treatment. Thus, the highly dispersed structure with high surface energy is more active for recrystallization by mass transport trough CdCl₂ liquid flux. The process is characteristic for the sintering in the presence of liquid phase. For the samples grown at high temperature a small difference between the PL intensities before and after CdCl₂ treatment occurred. Also, according to the data presented above by X-ray pattern for the films which have a large initial grain size and perfect structure, the recrystallization process occurs through the diffusion mechanism. Thus, for the films obtained at such growth condition the chlorine concentration is much lower than in the films grown at smallest temperature, implying the optoelectronic properties and hence the performance of the devices.

3.3. Quantum efficiency measurements and device results

Quantum efficiency measurements (Fig. 4) showed enhanced response in the blue wavelength region for the cells grown at lowest substrate temperature indicating excessive consumption of CdS during the CdCl₂ annealing process. Such CdS consumption during CdCl₂ annealing process is commonly observed due to CdS–CdTe intermixing [33–35]. XRD measurements confirm that excessive consumption of CdS observed by EQ for cells grown at lowest substrate temperature and treated in CdCl₂ originates from enhanced CdS–CdTe intermixing. The degree of alloying is indicated by simultaneous changes in short wavelength response (due to the change in CdS thickness) and the long wavelength response (due to the formation of lower band gap intermixed $\text{CdS}_\text{x}\text{Te}_{1-x}$). Excessive intermixing can result in direct connections between the absorber and front electrical contact as FTO, giving rise to inferior junction properties, which reduce open-circuit voltage ($V_{\text{oc}}$) and fill factor (FF) [36]. The device results for the structures obtained at different growth conditions are listed in Table 2. It was observed that the photovoltaic properties of the solar cells strongly depend on the growth condition, intermixing and pinholes. The primary influence of the high substrate temperature in combination with CdCl₂ treatment is on the good crystalline quality of both CdTe/CdS on the junction ensuring better photovoltaic parameters and hence the highest efficiency of 11.6%. At this temperature, an ideal balance is obtained between defect annealing and interdiffusion. The CdTe solar cell, which was grown at smallest temperature, exhibited the worst cell performance with an efficiency of only 2.3%, and the poor performance is attributed to the presence of pinholes and excessive intermixing which increased in the CdCl₂ treated case (Fig. 5).

4. Conclusions

In this work we studied the effect of deposition temperature in conjunction with CdCl₂ treatment on structural and optoelectronic properties of CSS CdTe/CdS thin film solar cells. It was shown that an increase of the substrate temperature from 250 to 500 °C leads to the changing of the film growth mechanism. Structural, morphological and PL spectra characterization of the CdTe/CdS structures after CdCl₂ treatment has highlighted progressive recrystallization, grain growth and interdiffusion. Interdiffusion between CdS and CdTe occurs during the CdCl₂ heat treatment, which was more pronounced for the structures obtained at low substrates temperature, yielded in low efficiency cells. The CdTe solar cells deposited at high substrate temperature showed extremely high crystalline quality CdTe/CdS heterojunction and highest efficiency.

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