Properties of the CdCl$_2$ air-annealed CSS CdTe thin films

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Abstract

Thin 7-9 $\mu$m CdTe films have been deposited on soda lime glass by close-spaced sublimation (CSS). By controlling the CSS temperature-time profile of source and substrate the pinhole-free CdTe films with a good adhesion on roughened glass were prepared. The classical solution-based CdCl$_2$ was applied to enhance the film crystallinity and optoelectronic properties of the CdTe layers. The layers were characterized by X-ray diffraction, Raman and Photoluminescence spectroscopy, scanning microscopy (SEM), energy dispersive X-ray microanalysis and Van der Paw method. CdCl$_2$ heat treatment is a key step in CdTe device processing. However the process leaves a significant amount of chlorine-rich residue on the CdTe surface that decreases performance of the solar cell. Annealing of the CdCl$_2$-treated polycrystalline CdTe improves the optoelectric properties and thus enhances the performance of CdTe/CdS solar cells. A correlation between the structural and optoelectronic properties of CdTe layers and annealing conditions in nitrogen atmosphere at 250, 400 and 450$^\circ$C for 60 min of the CdCl$_2$-treated layers has been found.

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Keywords: CdTe; thin films; CdCl$_2$; N$_2$ annealing; structural properties; optoelectronic properties; solar cell efficiency.
1. Introduction

At the present time the development of high-performance and low-cost solar cells for production of nonconventional energy sources based on the photovoltaic effect is an urgent scientific and technological problem [1]. The CdTe polycrystalline films as an absorber layers are one of the most promising candidates for thin film solar cells due to its direct optical bandgap with energy of about $E_g=1.5 \text{ eV}$ and high absorption coefficient $>5\cdot10^5$/cm [2,3,4]. Therefore, more than 90% of the incident light is absorbed in a few micrometers of the material. In this case, it is possible to fabricate a complete photovoltaic device using only thin film technology. Record conversion efficiency of 17.3% was recently reported by First Solar for polycrystalline CdTe thin-film solar cell modules [5]. However, the theoretical estimations of possible photovoltaic solar energy conversion into electricity for CdTe are of about 29% [6].

Because of its low sublimation temperature, CdTe polycrystalline films can be prepared by several techniques, such as thermal evaporation, electro deposition, sputtering, molecular beam deposition, hot-wall vacuum evaporation, close-spaced sublimation (CSS), etc. [1,7]. The CSS technique is one of the various techniques that have produced encouraging results [1,7,8,9]. During CdTe solar-cell fabrication, after deposition of the absorber layer of CdTe, a standard CdCl$_2$ heat treatment must be carried out in order to improve the cell performance [10,11]. The CdCl$_2$ 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 [12–15]. 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 [13,14]. CdCl$_2$ treatment also dopes CdTe with chlorine. Systematic studies should be carried out to understand the mechanism of CdCl$_2$ treatment on efficiency increase as well as the effect on the CdTe surface modification and micro-structural and electronic properties. The CdCl$_2$ heat treatment, which is usually carried out in the air atmosphere, is a process which leaves a significant amount of chlorine-rich residue and enhances oxidation of the film surface. It was reported that the residual oxide phases and excess substitutional chlorine in CdTe layer increases the series resistance of the cell and decreases the hole concentration, and as a result, decreases the efficiency of solar cell [12–16].

The main objective of the work is to study structural, photoluminescence and electrical properties of the CdCl$_2$ doped CdTe polycrystalline films deposited by CSS in order to understand the nature and chemical composition of CdCl$_2$ heat-treatment products and interaction mechanism with solid CdTe. Also, the influence of annealing under nitrogen atmosphere upon the defect composition and resistivity of the doped with chlorine CdTe thin films.

2. Experimental details

CdTe films with a thickness of 5-7μm were prepared by CSS of 6N purity CdTe powder onto the roughened, degreased in K2Cr2O7 + 10-ml H2O + 100-ml H2SO4solution, at room temperature, rinsed in double-distilled water, dried and thermally etched 2×2 cm$^2$ glass substrates. Source material was heated in the graphite boat by a tungsten coil connected to the main power supply through a temperature controller with K-type thermocouple. The substrate was fixed at a distance of 7mm 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 of 450°C and 500°C were applied for deposition of corresponding samples. The pressure during deposition was below 2·10$^{-3}$Torr. 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 50°C.

After the deposition of CdTe layers, the samples were soaked in a saturated CdCl$_2$ solutions for 3-4 hours, followed by a 30 min heat treatment in air at 400±5°C and etched in NP (H$_3$PO$_4$:HNO$_3$:H$_2$O) to remove the oxide residues. Heat treatments of the samples were carried out in a two-zone tube furnace. The CdTe-treated layers were annealed in nitrogen atmosphere at 250, 400 and 450°C for 60 min.

The structure of the films was studied by XRD using Rigaku X-ray diffractometer with Cu Ka$_1$/40kV/40mA radiation source ($\lambda=1.54056$ Å) and their microstructure was checked with scanning electron microscope (SEM). The X-ray diffraction (XRD) analysis was performed using Rigaku software PDXL. Photoluminescence and Raman measurements were performed at room temperature with high resolution micro-Raman spectrometer.
Horiba JobinYvon HR800, equipped with multichannel CCD detection system in backscattering configuration. The incident Nd-YAG laser light with \( \lambda = 532 \) nm and spot size of 10 µm in diameter, was used for excitation. The resistivity measurements were performed by Van der Paw method using indium electrodes.

3. Experimental results and discussions

In Fig.1 for all as deposited samples, the XRD spectra showed a strong preferentially (111) texture orientation together with the low intensity peaks, which correspond to the diffraction from the (220), (311), (400), (331), (422), and (511) planes of the cubic phase, respectively. The as-deposited CdTe at substrate temperature of 450°C exhibits a strong (111) preferred orientation, however the intensities of the (220), (311),...(511) peaks are slightly lower than the intensity of the (111) peak. With increase in the substrate temperature the preference for the (111) orientation is decreased, as is shown for as-deposited layer grown at 500°C, but the intensities of the (220) and (311) are up to 40% of the (111) intensity (higher as compared with sample grown at 450°C). This suggests that at higher substrate temperatures is ensured better growth of a dense structure, thus the films grow both in a perpendicular, as well as in lateral directions.

In both cases, at moderate and higher substrate temperature, after CdCl₂ treatment, air annealing at 400°C and NP(H₃PO₄:HNO₃:H₂O) etching (Fig.1. b) the loss in the preferentially (111) texture orientation is slightly enhanced, while the intensities of the (220) and (311) peaks are increased significantly. This observation is in good accordance with some reports about decrease of the (111) peaks after the CdCl₂ treatment and air annealing, which depends on the annealing temperature and the amount of CdCl₂[17,18]. This may be an indication of change in stoichiometry and a certain degree of randomization in the film texture with annealing depending on the character of the substrates used. It is known that the crystallographic rearrangements are related to the stress in the films and to application of annealing at 400°C and on the CdCl₂ sintering flux. The creation of new grains as a result of a disintegration of some large grains is due to the relaxation of the excessive strains in the lattice. The coalescence of small grains into bigger ones is caused by the CdCl₂ annealing process [24]. In order to study the stress in CdTe films, the XRD measurements were analysed using Rigaku software PDXL. The (111) peak positions for both as deposited films and the films annealed at 400°C are at \( 2\theta = 23.73° \) and \( 23.74° \), respectively corresponding to lattice parameter values of 6.49 Å and 6.48Å, therefore the as-deposited layers have a slightly higher lattice constant compared to the recrystallized layers. 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[18, 21].

One main observation in Fig. 1 is that when coated and soaked with a CdCl₂ layer, the CdTe film showed a set of peaks corresponding to different phases of CdCl₂, CdCl₂·H₂O, CdTeO₃, Cd₂(OH)₃Cl, however after CdCl₂ heat treatment in air at 400°C and etching, the CdTe film showed a much stronger oxidation, as can be seen by the comparative XRD intensity shown in Fig. 1(d, e). The main oxides formed were CdTeO₃, TeO₂, CdO and Te₂O₅. The dominant oxides were CdTeO₃ and TeO₂. The changes of the peak intensities and the emergence of these phases agrees well with those observed in other published works [19,20,18]. From the analysis of XRD spectra we can see that for both substrate temperatures, after coating and soaking with CdCl₂ the films were not oxidized, or the amount of oxides formed was not large enough to be detected by using XRD scattering technique. After CdCl₂ heat treatment in air at 400°C, the diffraction pattern indicates the presence of much more intensive oxide peaks. Supposedly oxides may be formed around and above a temperature of 400°C at the CdTe surface.
Fig. 1 (a) and (b) X-ray diffraction of CdTe films obtained at two different substrate temperatures, before and after annealing in presence of CdCl₂; (d) Detailed X-ray diffraction peaks of the CdTe film after soaking in CdCl₂ solution; (e) and (f) After CdCl₂ heat treatment in air at 400°C and etching in NP (HNO₃ + H₃PO₄ + H₂O) solution.

The surface morphology of the as-deposited, heat-treated and CdCl₂-treated samples is shown in Fig. 2. SEM investigation of two kinds of CdTe samples deposited at a substrate temperature of 450 and 500°C (a, c) shows that the films have a columnar-like structure with clear growth texture, without cracks or pinholes, implying the quality of the films. The cross-sectional images for both kinds of growing at 450 and 500°C after CdCl₂ heat treatment are shown in fig. 2 (b, d). The diameter of columnar-like crystallites strongly depends on the growth condition (substrate temperature -Tₛ, evaporator temperature -Tₑ, ΔT = Tₑ - Tₛ). Grain size of grow samples depends on grain size of the substrate inversely proportional. The columnar-like structure was most pronounced in the films obtained at the growth conditions near the thermodynamic equilibrium (Tₛ=500°C, ΔT=100°C). In this case, the film has practically a monoblok structure along the layer thickness, and the grain size is about of 4-5 μm. After the CdCl₂ heat treatment (b,d), the overall surface morphology of the CdTe films did not change significantly, however some definite trend in terms of the changes in the shape and size of the CdTe grains were observed. The CdCl₂ treatment as a process with formation of a liquid flux, re-crystallizes the CdTe layers in such a way that some of the small grains coalesce into bigger toghether while some of the bigger grains divide into smaller ones and reorient themselves, which gives an entirely different microstructure. Smaller grains 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. The SEM images support the XRD results.
Fig. 2 (a, c) SEM surface morphology and cross-sectional microstructure of CdTe films deposited at temperatures of 450 and 500°C respectively, without a CdCl₂ heat treatment; (b, d) SEM surface morphology and cross-sectional microstructure of CdTe films, after CdCl₂ heat treatment and etching.
Effects of the heat treatment steps on the morphology of CdTe film also were investigated by the more sensitive Raman scattering. Fig. 3 (a) and (b) show the surface Raman scatterings of CdTe layers (1) as-deposited on the heated substrate at 450 and 500°C, (2) treated with CdCl₂, (3) treated with CdCl₂ and annealed in air at 400°C for 30 min and (4) etched in NP(HNO₃ + H₃PO₄ + H₂O) solution respectively. The as-deposited films at both substrate temperatures of 400 and 500°C have a relatively stronger peaks at 125, 141 and 167 cm⁻¹ which according to some authors [O. R. Ochoa et. al.], correspond to the scattering of Te, Te/CdTe and CdTe LO (Longitudinal optical mode) respectively. LO and TO Raman peaks of bulk CdTe are found at 169 and 141 cm⁻¹ [28]. The Te detected by the sensitive Raman scattering exists as precipitates in CdTe, which were formed by aggregation of the Te₂ molecules during the CdTe film deposition. Te precipitates exist as nanocrystallites in a random distribution in CdTe and they have at least two orders of magnitude larger scattering cross-section compared to that of CdTe [16, 22, 27]. So the high Raman intensity of Te compared to that of CdTe shown in Fig. 3 does not mean a comparable material content for Te and CdTe in the films.

Raman scattering of the CdCl₂ treated CdTe films (curves 2 and 3) showed a stronger CdCl₂ Raman peaks at 220 and 231 cm⁻¹ together with slightly lower intensity peaks of Te and CdTe, implying that the layers were dip-coated with a CdCl₂ saturated solution.

After CdCl₂ heat treatment and etching (curves 4), the intensity of the Te Raman peak at 125 slightly increased, higher as compared to the as-deposited layer, however the LO/CdTe Raman peak positions and linewidths show no definite trend in terms of the CdCl₂ heat treatment. Increases in the intensity of the mode observed for Te at 125 cm⁻¹ suggests that NP etch creates Te excess on the CdTe surface and therefore is detected by Raman.

The effect of the CdCl₂ annealing process on the structural properties of CdTe films is to promote recrystallization, which is obvious from the results of XRD and SEM of the sample; as a result the morphology of the CdTe is strongly affected. Moreover, the results of XRD show that the crystallization and morphology of the CdTe is strongly affected not only by the CdCl₂ treatment, but also by the condensation temperature on the substrate.

![Raman spectra of the CdTe films recorded at room temperature for the samples obtained at the substrate temperatures of 450 and 500°C: (1) as-deposited on the heated substrate at 450 and 500°C, (2) treated with CdCl₂, (3) treated with CdCl₂ and annealed in air at 400°C for 30 min and (4) etched in NP(HNO₃ + H₃PO₄ + H₂O) solution respectively.](image-url)
One of the most important effects is that the presence of the CdCl₂ treatment as a process with formation of liquid flux and to hire the rules of liquid phase recrystallization, dopes CdTe with chlorine, but leaves a significant amount of chlorine-rich residue and enhances the film surface oxidation[13-15]. It is known that the low resistance p-type conductivity in CdTe can be attributed to the low concentration of chlorine (10^{16} - 10^{18} at/cm³) in the CdTe lattice [12,29]. The NP(HNO₃:H₃PO₄:H₂O)solution removes flux residue and chlorine from the surface. It is clear, that not before full removal of the residues the concentrations of the chlorine in the telluride lattice can be decreased and regulated. Even in the case of NP(HNO₃:H₃PO₄:H₂O)solution etch removes all detectable traces of chlorine from the surface, solution etch will not be able to remove the traces from the grain-boundaries[12]. Excess substitutional chlorine increases photocconductivity and decreases p-type conductivity of CdTe [13]. Vacuum annealing removes flux residue and decreases the chlorine concentration, implying the changes in the optoelectronic properties[13,14]. Taking into account these and based on the experiments presented above, the following steps have been focused on the investigation of changes in the optoelectronic properties as a result of annealing in nitrogen atmosphere. Figure 4 shows the photoluminescence spectra of CdCl₂ doped CdTe films, annealed at different temperatures under nitrogen atmosphere. The doping information, thermal treatments and resistivity of samples are summarized in table 1. The sheet resistance at room temperature for the as-grown sample is ~10^{11} ohm per sq. while it has been decreased to ~10^{8} ohm per sq. in the CdCl₂-treated samples. In general, as-deposited CdTe films fabricated by various techniques have high electrical resistivity (10^{7} to 10^{9} Ω·cm). Table 1 shows resistivity value versus annealing at different temperatures under nitrogen atmosphere of samples after recrystallization. The optimal annealing temperature at our preparative conditions, where the resistivity has the smallest value, is around 450°C. As can be seen from fig. 4 a) and table 1, after CdCl₂ heat treatment, the samples have an intense 1.5 eV PL band, whereas the resistivity and dark to light resistance ratio K_F have quite high values. This can be explained by the fact that CdCl₂ heat treatment leaves too high chlorine concentration in CdTe lattice, which generates a high concentration of the isoelectronic complexes V_{Cd2ClTe} and Te_i2ClTe[13]. As a result, the resistivity of CdTe increases but not yet photoconductivity is formed. Thus, the higher is the p-type resistivity of the film the stronger is the intensity of the 1.5 eV PL band.

Table 1: Thermal treatment and resistivity values of CdTe samples*

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>T_{substrate} (°C)</th>
<th>d (μm)</th>
<th>Dopant</th>
<th>CdCl₂ thermal treatment Tₚ x t_p (°C x h)</th>
<th>Annealed in Nitrogen atm. T_a x t_a (°C x h)</th>
<th>R_{dark} Ω/□</th>
<th>R_{light} Ω/□</th>
<th>ρ_{dark} (Ω·cm)</th>
<th>K_F</th>
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<tbody>
<tr>
<td>S1</td>
<td>450</td>
<td>7</td>
<td>CdCl₂</td>
<td>400 x 0.5</td>
<td>--</td>
<td>2*10⁴</td>
<td>2*10⁷</td>
<td>1.4*10⁵</td>
<td>10</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>250 x 1</td>
<td>5*10⁸</td>
<td>4*10⁷</td>
<td>3.5*10⁵</td>
<td>12.5</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>400 x 1</td>
<td>7*10⁷</td>
<td>1.5*10⁷</td>
<td>4.9*10⁴</td>
<td>4.6</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>450 x 1</td>
<td>7*10⁷</td>
<td>2*10⁷</td>
<td>7*10⁴</td>
<td>3.5</td>
</tr>
<tr>
<td>S2</td>
<td>500</td>
<td>7</td>
<td>CdCl₂</td>
<td>400 x 0.5</td>
<td>--</td>
<td>2.5*10⁸</td>
<td>3*10⁷</td>
<td>1.7*10⁵</td>
<td>8</td>
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<td>4.9*10⁵</td>
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<td></td>
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<td></td>
<td></td>
<td>400 x 1</td>
<td>3*10⁷</td>
<td>1*10⁷</td>
<td>2.1*10⁴</td>
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<td>1*10⁷</td>
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<td>2</td>
</tr>
</tbody>
</table>

* d is thickness of CdTe films, μm; T_p and t_p are recrystallization temperature and time respectively; T_a and t_a are temperature and time of annealing in nitrogen atmosphere; R_{dark} is dark resistance; R_{light} is light resistance; K_F is dark to light resistance ratio; ρ is resistivity.
At small chlorine concentrations mainly complexes $V_{CdClTe}$ and $TeCl_{Te}$ are formed in CdTe and these complexes are shallow acceptors in CdTe and cause high $p$-type conductivity of CdTe at 300 K [13]. Figure 4 b) shows the photoluminescence spectra of chlorine doped CdTe thin films and annealed under nitrogen atmosphere at temperature of 250°C. It can be observed, that the annealing in nitrogen atmosphere at 250°C slightly decreases the intensity of the 1.5 eV PL band and resistivity of films implying that the process of outdiffusion of chlorine has started. Further annealing under nitrogen atmosphere at higher temperatures of 400 and 450°C show definite trend in terms of the decreasing of 1.5 eV PL band and resistivity values, that one can attribute to more intensive process of outdiffusion of chlorine and generation of more cadmium vacancies due to a higher partial vapor pressure and mobility of cadmium [14]. As a results decreases the concentration of chlorine-based neutral complexes and increases the concentration of A-centers. The main defects which form the 1.5 eV PL band here are substitutional chlorine $Cl_{Te}^+$ (donor) and complex $V_{CdClTe}$ (acceptor). If chlorine concentration is decreased first decreases the concentration of $Cl_{Te}$, and as a result, the intensity of the 1.5 eV PL band and resistivity of films. $Cl_{Te}$ seems to be a main hole trap in doped with chlorine $p$-type CdTe. One order of magnitude conductivity may be correspond to the corresponding increase in the concentration of charge carriers.
4. Conclusions

The effect of the CdCl$_2$ immersion and heating on the structural properties of polycrystalline CdTe films is to promote re-crystallization, which is obvious by the results of XRD and SEM of the samples; as a result the morphology of the CdTe is strongly affected. The crystallization and morphology of the CdTe polycrystalline thin films are strongly affected not only by the CdCl$_2$ treatment but also by the condensation temperature on the substrate.

The experimental results presented by Raman and XRD, showed that the presence of CdCl$_2$ enhanced the film surface oxidation during the annealing process in the air atmosphere. Also, Raman scattering show that Te exists as precipitates in CdTe, and CdCl$_2$ heat treatment enhanced these precipitates in the films.

CdCl$_2$ heat treatment as a process with formation of a liquid flux and to hire the rules of liquid phase recrystallization, which betters the structure and increases conductivity, dopes CdTe with chlorine, but leaves too high chlorine concentration in CdTe. Excess substitutional chlorine increases the resistivity of films and the intensity of the 1.5 eV PL band of CdCl$_2$ doped films.

Annealing in nitrogen atmosphere removes flux residue and decreases the chlorine concentration, also decreases the resistivity of films and the intensity of the 1.5 eV PL band of CdCl$_2$ doped films. One order of magnitude conductivity may be correspond to the corresponding increase in the concentration of charge carriers and we believe it will promote to increase of CdTe solar cell efficiency. The experimental results reported in this study should help understand the mechanism of the key fabrication step, specifically the CdCl$_2$ treatment, on the efficiency increase for a CdTe solar cell.

Acknowledgments

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