

Effect of “CdCl₂ Treatment” on Properties of CdTe-Based Solar Cells Prepared by Physical Vapor Deposition and Close-Spaced Sublimation Methods

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CdTe is regarded as one of the most promising materials for fabricating CdTe/CdS thin film solar cells with efficiencies up to 16.5%. In this paper we present a comparative analysis of CdTe-based solar cells fabricated by physical vapor deposition (PVD) and close-spaced sublimation (CSS) methods. The structural properties of CdTe base layers and the output parameters of CdS/CdTe solar cells are presented, and the influence of “CdCl₂-treatment” on these properties are discussed. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) analyses were used in the studies. © 2011 The Japan Society of Applied Physics

In spite of large lattice mismatch between cubic CdTe and hexagonal CdS (nearly 9.7%), CdTe/CdS solar cells are characterized by high efficiencies caused by interdiffusion at the junction interface.¹⁾ “CdCl₂ heat treatment” is considered a key step in CdTe/CdS device processing and leads to interdiffusion between CdTe and CdS. It is usually carried out either by depositing a CdCl₂ layer onto the CdTe surface with subsequent annealing in ambient atmosphere or annealing of the structure in CdCl₂ vapor. In the former case, the optimum CdCl₂ thickness varies in a wide range depending on the base layer technology.²⁾ We report the results concerning the effect of CdCl₂ treatment on the output parameters of CdS/CdTe-based solar cells and the crystal structure of the base layers deposited on glass substrates by various ways.

In the first method, CdS and CdTe layers were deposited sequentially by physical vapor deposition (PVD) onto glass substrates covered by transparent 0.5- μ m-thick indium tin oxide (ITO) at the substrate temperatures of 200 and 300 °C, respectively. The thicknesses of the CdS and CdTe layers were 0.35 and 4.0 μ m, respectively. CdCl₂ films were evaporated onto the CdTe surface and the structures were air-annealed in closed box at 430 °C for 25 min. After bromine-methanol etching, the Cu–Au contacts were formed on their surface.

In the second method, CdS films of 80–100 nm thickness and CdTe films of 6–8 μ m thickness were deposited by chemical bath deposition (CBD) and close-spaced sublimation (CSS), respectively, onto borosilicate glass substrates (Corning 7059) with bilayer transparent SnO₂. After NP etching Cu_xTe and HgTe mixture was used to form a back contact. The surface morphology of the CdTe films was studied by Scanning Electron Microscope (SEM; Hitachi S-4000), and X-ray diffraction (XRD) analyses of the films were carried out in a BRUKER D8 ADVANCE diffractometer. Current–voltage (*I*–*V*) parameters of the devices were measured using a 100 mW/cm² solar simulator.

The results of output parameters and diode characteristics of PVD devices are summarized in Table I. The analysis of Table I shows, that an increase in the CdCl₂ thickness up to 0.35 μ m results in the enhancement of device efficiency to $\eta = 10.3\%$, followed by decreases in the diode saturation current density J_0 and series resistance R_s , but a further increase in CdCl₂ thickness leads to an essential decrease in device efficiency and increase in J_0 and R_s . According to refs. 3 and 4, CdCl₂ treatment of the CdTe base layer in the

Table I. Output parameters and diode characteristics of ITO/CdS/CdTe/Cu/Au devices.

	Sample				
	1	2	3	4	5
d_{CdCl_2} (μm)	0	0.06	0.35	0.68	1.2
Output parameters					
V_{oc} (mV)	400	645	773	730	702
J_{sc} (mA/cm ²)	10.7	19.0	20.1	19.0	19.0
FF	0.28	0.58	0.67	0.58	0.41
η (%)	1.2	7.4	10.3	8.0	5.5
Diode characteristics					
R_s ($\Omega\text{-cm}^2$)	28	3.8	2.8	3.5	27.5
R_{sh} ($\Omega\text{-cm}^2$)	230	750	720	705	264
J_0 (A/cm ²)	7.3×10^{-3}	1.5×10^{-6}	8.2×10^{-8}	2.0×10^{-7}	3.0×10^{-7}
Diode factor (A)	7.0	3.8	2.5	3.0	3.8
J_{ph} (mA/cm ²)	11	19.8	20.2	19.3	19.6

presence of oxygen leads to an enhancement in the majority-carrier concentration owing to the generation of Cl_{Te}–V_{Cd} acceptors, which results in the experimentally observed decrease in device series resistance. On the other hand, at a certain chlorine concentration on the grain boundary of CdTe, the recrystallization of the base layer above 400 °C occurs, owing to the presence of a low-temperature eutectic in the CdTe–CdCl₂ system,³⁾ which may result in the diode saturation current density decrease.

It should be noted that, at first glance, the increase in R_s with the CdCl₂ thickness above 0.35 μ m is somewhat strange, however, according to ref. 5, a high concentration of chlorine leads to the generation of electrically active intrinsic point defects in CdTe layers, and instead of the acceptor complexes Cl_{Te}–V_{Cd}, the isoelectronic complexes 2Cl_{Te}–V_{Cd} are formed. The latter results in the decrease in the majority-carrier concentration and therefore the increase in R_s .

The study of the PVD CdTe grain boundary surface by SEM has revealed that CdCl₂ treatment results in the enlargement (5–6 times) of the grain size (Fig. 1).

According to the results of the XRD analysis of CdTe, single-phase CdTe films of stable cubic modification were obtained after CdCl₂ treatment. The increase of the CdCl₂ layer thickness from $d = 0.06$ to 0.35 μ m diminishes the lattice parameter of CdTe films. At the same time, the preferential orientation of the grains changes from [111] to [422]. Further increase of the thickness results in the reverse

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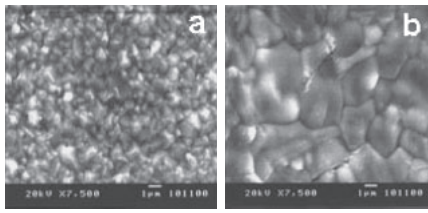


Fig. 1. SEM photomicrograph of CdTe layer deposited by PVD method: (a) before CdCl₂ treatment, (b) after CdCl₂ treatment.

Table II. Effect of CdCl₂ treatment on CdTe base layer crystal structure.

CdCl ₂ layer thickness, d (μm)	0.06	0.35	1.2
Preferential orientation direction	[111]	[422]	[111]
Degree of texture perfection G	1.28	0.58	1.26
Lattice parameter a (\AA)	6.509	6.496	6.506

change of the preferential orientation and lattice parameter growth (Table II).

The lattice parameter of the structurally perfect unstrained CdTe layers is 6,481 \AA .⁶⁾ The two-phase structure, twinning, and high concentration of the stacking faults are typical of CdTe layers textured in the [111] direction.⁷⁾ These structural defects easily form because of an insignificant (about 1%) difference in the formation energies of sphalerite and wurtzite crystal lattices. Thus, the change in the preferential orientation from [111] to [422] at the CdCl₂ thickness of 0.35 μm is evidence of the reduction of the crystal defect concentration.

The improvement of crystal perfection up to 0.35 μm is in good agreement with the concept of the recrystallization mechanism during CdCl₂ treatment. According to ref. 8, CdCl₂ acts as a flux during CdTe recrystallization because the phase diagram for the CdCl₂–CdTe system at 77% CdCl₂ includes a eutectic with a melting temperature of 508 $^{\circ}\text{C}$. The availability of such a low-temperature eutectic leads to the recrystallization of CdTe under the corresponding thermal treatment of the CdCl₂/CdTe heterosystem. It is clear that the process of base layer recrystallization begins with the creation of the nuclei on the grain boundaries near the cadmium telluride and cadmium chloride interface. The growth of the nuclei of random crystal-lattice orientation under near thermodynamic equilibrium conditions results not only in the essential grain growth and decrease in the preferential orientation degree of the CdTe but also in structural perfection within the grains. The latter causes the reduction of the macrodeformations that eventually lead to the experimentally observed approach of the CdTe layer lattice parameter to the theoretical one.⁶⁾

In accordance with the phase diagram for the CdCl₂–CdTe system the cadmium chloride is insoluble in cadmium telluride. As a result of the grain boundary diffusion, chlorine reaches the CdS–CdTe interface, as has been experimentally observed by Terheggen *et al.*⁹⁾ Thus, excess CdCl₂ can lead to the recrystallization of CdTe not only near the CdTe–CdCl₂ interface, but also near the CdTe–CdS interface. The latter can provoke the reorientation effect of CdS on CdTe growth and diminish adhesion between CdTe and CdS, which leads to enhanced macrodeformations in the base layer.

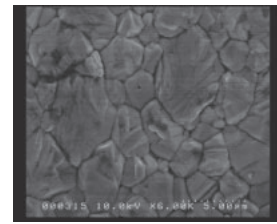


Fig. 2. SEM photomicrograph of CdTe layer deposited by CSS method.

CSS-deposited CdTe thin films crystallized in the cubic sphalerite structure (space group $F43m$) with $a = 6485 \text{\AA}$ and showed a preferential orientation along the [111] direction. CdTe film consists of grains 2–6 μm in size and is dense (Fig. 2). No considerable changes in the structural properties and surface morphology of CdTe films were observed after the CdCl₂ treatment. Both as-grown and CdCl₂-treated CdTe films have a clearly faceted surface morphology and an average grain size of about 3–4 μm .

The difference between the results of CdCl₂-treatment for PVD- and CSS-deposited CdTe films can be explained by the fact that CSS films are deposited at a much higher temperature (620 $^{\circ}\text{C}$ versus 200–300 $^{\circ}\text{C}$) and therefore contain a lower concentration of defects. On the other hand, the large grain size of the films leads to a much lower grain boundary area. Low defect concentration and grain boundary area result in lower lattice strain energy, which is the main factor for the crystallization process.¹⁰⁾ As a result the CSS-deposited CdTe films do not recrystallize at the temperatures and times used in the CdCl₂ treatment.

We prepared a series of glass/n-SnO₂/n-CdS/p-CdTe/back contact CSS device structures for solar cell application. The highest efficiency was obtained with the parameters $V_{oc} = 773 \text{ mV}$, $J_{sc} = 23.92 \text{ mA/cm}^2$, fill factor $FF = 68.7\%$, and total area conversion efficiency of 12.71%.

Thus, the maximum efficiency of CdTe-based solar cells deposited by physical vapor deposition corresponds to the 0.35 μm CdCl₂ thickness CdCl₂ treatment. Unlike the thermally evaporated CdTe films, no considerable changes were observed after CdCl₂ treatment in the structural properties and surface morphology for the CdTe films obtained by the CSS method. The difference between the results of CdCl₂ treatment can be explained by a lower concentration of defects and smaller grain boundary area in CSS-deposited CdTe films, resulting in lower lattice strain energy, which promotes recrystallization and grain growth.

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