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Effects of $CdCl_2$ heat treatment on the morphological and chemical properties of CdTe/CdS thin films solar cells

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ABSTRACT

The morphological and chemical changes of CdTe surface in CdTe/CdS/ITO/glass solar cells, due to $CdCl_2$ solution treatment followed by annealing in air from 340 to 420 °C were studied using SEM and XPS. SEM micrographs showed that the supersaturated $CdCl_2$ samples exhibited recrystallization and a progressive increase in grain sizes upon annealing. The grain sizes of the samples increased up to about 3–4 μm when annealed above 410 °C. XPS spectra for the S *2p*, Cd *3d* and for the Te *3d* were recorded and analyzed for the as-grown structures and for structures annealed at different temperatures with and without $CdCl_2$ treatment. The spectra clearly show that annealing the $CdCl_2$ supersaturated samples removes TeO_3 peaks, while annealing the structures without $CdCl_2$ treatment enhances the TeO_3 peaks. The *I–V* measurements revealed that V_{oc} higher than 680 mV and J_{sc} close to 20 mA/cm^2 were obtained for CdTe/CdS solar cells annealed under optimum conditions of 410 °C for 15 min. The improvement of V_{oc} and J_{sc} after $CdCl_2$ heat treatment can be attributed to dissolving the oxidations at the free surfaces and recrystallizations of CdTe layer.

1. Introduction

CdTe is one of the most promising photovoltaic materials available for use as low cost and high-efficiency thin film solar cells because of its near optimum band gap, high absorption coefficient and manufacturability [1]. The typical structure of CdTe solar cell consists of Au/CdTe/CdS/ITO/glass, in which the hetero-interface limits the performance of solar cell efficiency.

The chemical and morphological properties of CdS and CdTe thin films are strongly influenced by the preparation route. Therefore, a variety of approaches have been used for the synthesis of such materials such as chemical bath deposition (CBD) [2–5], thermal evaporation [3], close-spaced sublimation (CSS) [3], chemical pyrolysis deposition (CPD) [3], and metal organic chemical-vapor deposition (MOCVD) [6–8]. CBD, in particular, has many advantages for the production of photovoltaic devices at moderate temperatures and in controlled conditions, such as excellent uniformity and reproducibility of the film thickness even for a large-scale module.

Irrespective of the growth process, it appears that an annealing in the presence of $CdCl_2$ deposited on the CdS and on the CdTe free surfaces at temperatures around 400 °C is essential to improve the CdT/CdS cell efficiency [4–8]. Interdiffusion and alloy formation were previously investigated using a variety of experimental methods [9–15]. However, the changes in the fundamental material properties induced by $CdCl_2$ annealing treatment, that lead to an improvement in the photovoltaic performance, are far from being understood. In this work we use scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) to study the effect of $CdCl_2$ annealing on the surface morphology and chemical composition of CdTe/CdS heterojunction solar cells fabricated by thermal evaporation and CBD. Current–voltage (*I–V*) measurements were performed in an attempt to understand the correlation between various heat treatment conditions and the performance of the solar cell.

2. Experimental details

The CdS thin films were deposited on ITO substrate by CBD technique using $CdCl_2$, NH_4Cl, $CS(NH_2)_2$ and NH_4OH as starting materials. The deposition bath temperature was fixed at 80 °C. After the deposition, the resulting CdS layer was annealed in air atmosphere at 380 °C for 5 min and its thickness was found to be

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0.15 μm. The CdTe layer was deposited on CdS by thermal vacuum evaporation method using alumina coated tungsten coil basket and a 2.5–3.0 μm thick CdTe film was deposited by 5–10 min evaporation. The substrate temperature was maintained at 390 °C during CdTe evaporation process, and a halogen lamp was used to heat the CdS/ITO/glass substrate.

The CdS/ITO/glass and the CdTe/CdS/ITO/glass structures were soaked in a supersaturated $CdCl_2$ solution for 5 min. After drying at room temperature, the structures were annealed in air at several different temperatures in the 340–420 °C range with varying annealing times.

SEM investigations were carried out at room temperature in order to establish a correlation between the surface morphology of CdTe films and the heat treatment effect as function of anneal temperatures.

Elemental analyses were performed by XPS, in which the spectra were recorded with an SSX-100 spectrometer with a monochromatic and focused Al K_α source (E = 1486.6 eV). Most of the core level spectra were recorded with a 600 μm spot diameter and 50 eV pass energy. The corresponding energy resolution is 0.9 eV as measured by the full width at half-maximum of the Au 4*f* core level. The binding energies are referenced with respect to the Fermi level and determined with an estimated accuracy of 650 meV.

Standard *I*–*V* measurements at room temperature were carried out in order to establish a correlation between the $CdCl_2$ thermal treatment of CdTe films and solar cell performance. The metals of Au and In were used for CdTe and ITO layers respectively for ohmic contact formation in the glass/ITO/CdS/CdTe solar cells structure as shown in Fig. 1.

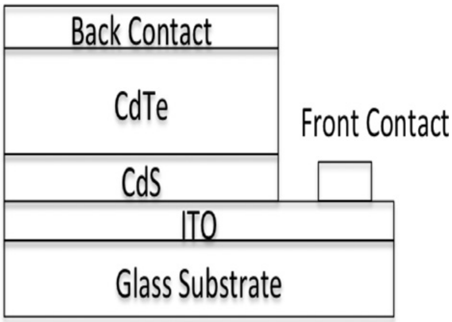

Fig. 1. The configuration of the CdS/CdTe solar cell structure used in the present work.

3. Results and discussion

3.1. Grain size

The surface morphology of the as-grown CdTe and of the $CdCl_2$ treated films annealed for 15 min at 400, 410 and 415 °C temperatures obtained by SEM is presented in Fig. 2. It is seen from the SEM image in Fig. 2(a), that the as-grown CdTe film microstructure has a grain size smaller than 0.5 μm and a roughness of about 10 nm. The SEM micrograph shown in Fig. 2(b) indicates that $CdCl_2$ treatment and annealing at 400 °C did not significantly affect the morphology of the CdTe film, except for softening the sharp features in the film.

The SEM micrograph shown in Fig. 2(c) indicates that CdTe films undergo recrystallization and an increased grain size up to about

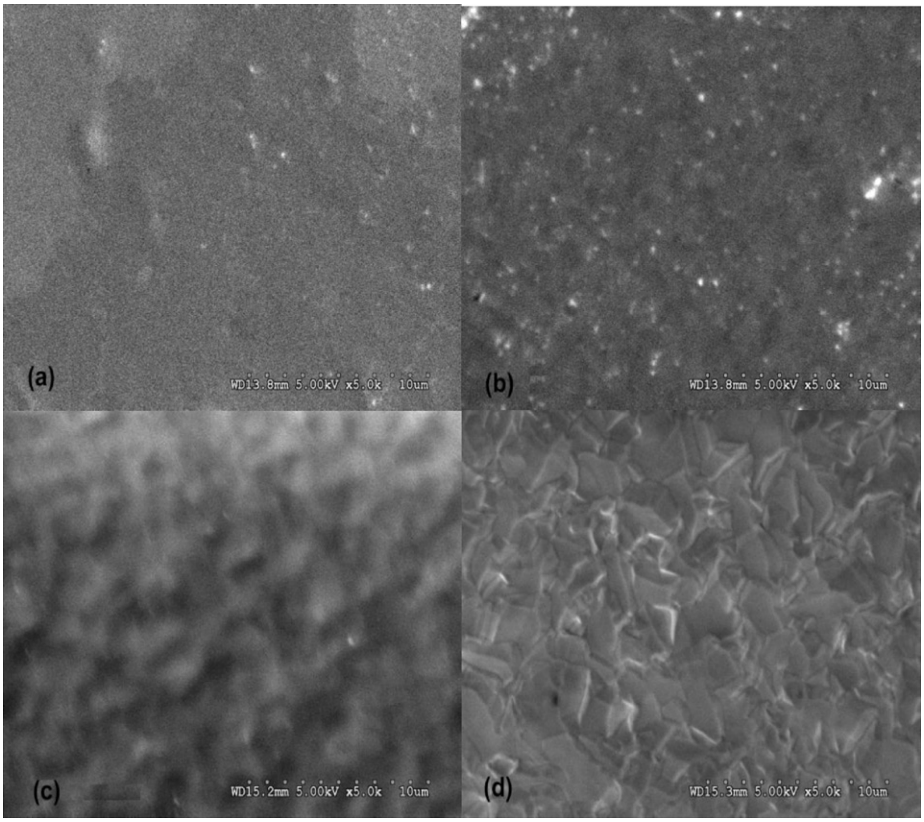

Fig. 2. SEM micrographs of CdTe films as-deposited and after $CdCl_2$ heat treatment: (a) as-grown CdTe grown at 390 °C, (b) annealed at 400 °C for 15 min, (c) annealed at 410 °C for 15 min, and (d) annealed at 415 °C for 15 min.

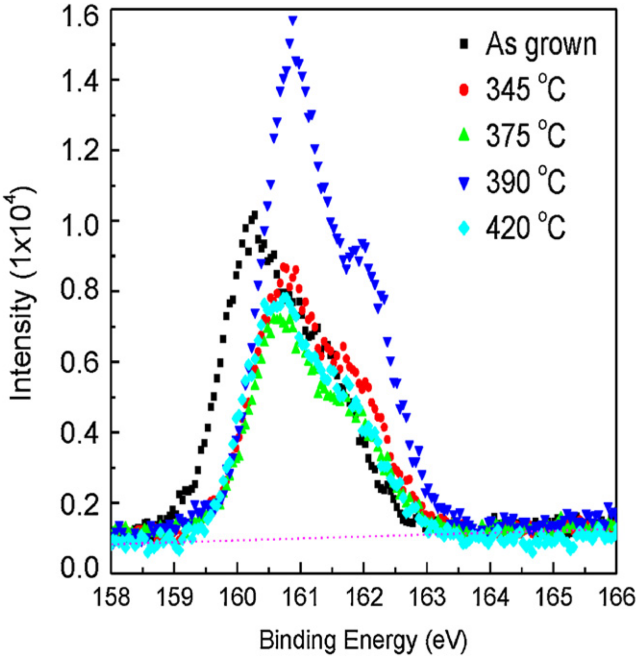

Fig. 3. Linear background XPS spectra of the S *2p* core-level for the as-grown and for the $CdCl_2$ treated CdS films annealed at 345, 375, 390 and 420 °C temperatures.

3–4 μm after $CdCl_2$ treatment and annealing at 410 °C. A marked difference of the surface morphology was observed when the CdTe films were annealed at 415 °C for 15 min after $CdCl_2$ treatment as shown in the SEM image in Fig. 2(d). The microstructure showed a large distribution of grain sizes, ranging from 1 to over 5 μm and a roughness of about 15–20 nm, indicating that the recrystallization process was complete.

3.2. XPS spectra

To determine the effect of $CdCl_2$ heat treatment on the chemical composition at the CdTe and CdS surface, XPS measurements have been performed on the as-grown, and on the annealed samples with and without $CdCl_2$ treatment. The Cd 3*d*, Te 3*d*, and S 2*p* core levels were recorded and analyzed for the CdTe and CdS layers. In order to determine the exact positions of Cd 3*d* and Te 3*d* peaks, they were fit using Winspec program [16]. Nonlinear Shirley-type background was subtracted from the spectra before the fit, and peaks were fitted with mixed singlets (Gaussian–Lorentzian) peaks.

3.2.1. Analysis of the CdS layer

Fig. 3 shows the S 2*p* core-level of the background corrected XPS spectra for the as-grown and for the $CdCl_2$ treated CdS film annealed at 345, 375, 390 and 420 °C temperatures. For the as grown film, the S $2p_{3/2}$ and S $2p_{1/2}$ peaks are observed at 160.2 and 161.4 eV binding energies in excellent agreement with the literature data on CdS [17,18]. Annealing the $CdCl_2$ treated CdS film, shifts the S 2*p* peaks to higher binding energies and reduces their full width at half maxima (FWHMs). The spectra indicate that annealing at 390 °C produces the maximum peak intensity and shifts the binding energy of these peaks to 161.2 and 162.4 eV while annealing at all other temperatures produced little binding energy and intensity change. The Cd atoms of $CdCl_2$ combine preferentially with the S atoms and thus substitute for the oxide atoms at the CdS surface. These phenomena clearly indicate that $CdCl_2$ effectively dissociates the oxide layer at the surface of CdS film. This behavior is similar to the phenomenon of the Cd 3*d* core-level spectra shown in Fig. 4. Fig. 4 shows Cd 3*d* core-level XPS spectra for the as-grown and for the $CdCl_2$ treated CdS films annealed at 345, 375, 390 and 420 °C temperatures. The binding energies of the as grown Cd $3d_{5/2}$ and the Cd $3d_{3/2}$ obtained from fittings are 403.9 and 410.8 eV, respectively. The difference in the binding energies between the Cd 3*d* and CdO peaks is 0.9 eV [19]. Annealing the $CdCl_2$ treated CdS film slightly shifts the Cd 3*d* peaks to higher binding energies and reduces their FWHMs. Cd 3*d* peaks width reduction as the annealing temperature is increased indicate a change in the chemical environment for Cd atoms from Cd in a mixed CdS and CdO state to Cd in CdS state, in agreement with the results of reference [20]. These phenomena clearly indicate that annealing the $CdCl_2$ treated CdS film at 390 °C temperature is most effective in dissociating the oxide layer at the surface of CdS film. Furthermore, it is seen in reference [20] that the Cd $M_5N_{45}N_{45}$ Auger peak is only slightly shifted and deformed by the presence of oxide. Therefore, from Cd 3*d* and Auger peaks one could only qualitatively determine that some form of Cd oxide is on the surface of the CdS films but could not quantitatively determine the amount of Cd oxide.

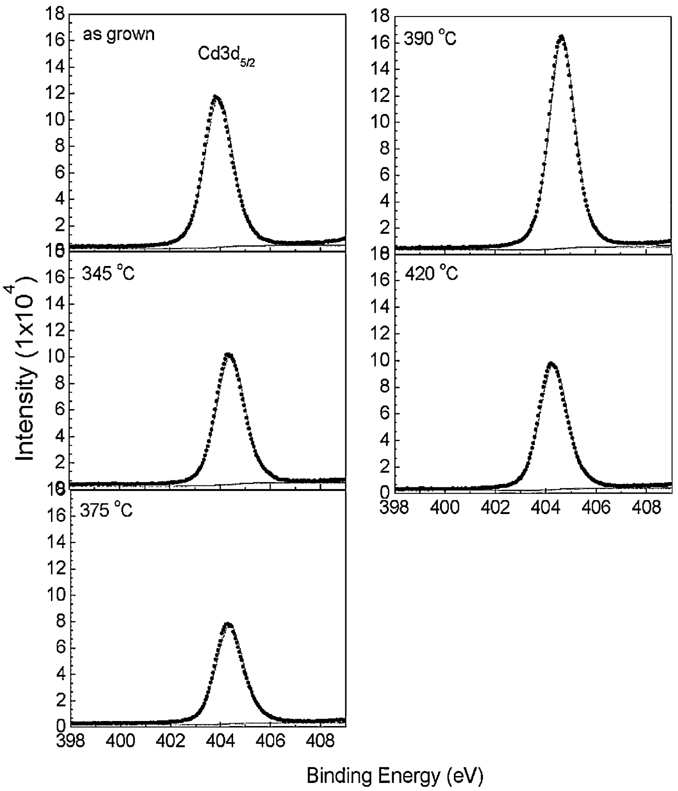

Fig. 4. XPS spectra of the Cd $3d_{5/2}$ core-level for the as grown and for CdS films annealed at 345, 375, 390 and 420 °C temperatures. The peaks were fit with mixed singlets (Gaussian–Lorentzian) peaks. A nonlinear Shirley-type background was subtracted from the spectra before the fit.

3.2.2. Analysis of the CdTe layer

Normalized intensities of Te 3*d* high resolution core-level XPS spectra for the as-grown CdTe films and for CdTe films annealed at 390 °C temperature without and with $CdCl_2$ treatment are shown in Fig. 5. The spectra unambiguously show intensive oxidations in the sample annealed in the absence of $CdCl_2$ treatment, while oxidations almost completely disappeared in the sample annealed in the presence of $CdCl_2$.

Therefore, to further investigate the effect of $CdCl_2$ annealing, we fitted the Te 3d peaks for the as-grown sample and for the $CdCl_2$ treated samples annealed at 345, 390, and 420 °C temperatures. Fig. 6 shows the results for Te $3d_{5/2}$. The binding energies of the Te $3d_{5/2}$ and the Te $3d_{3/2}$ appear at 571.5 and 581.8 eV, respectively,

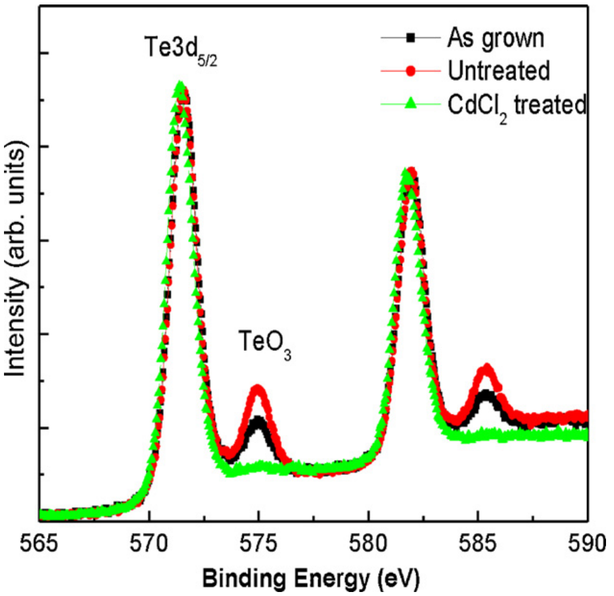

Fig. 5. Normalized XPS spectra of the Te 3*d* core-level for the as-grown and for the untreated and the $CdCl_2$ treated CdTe films annealed at 390 °C temperature.

and correspond to Te—Cd bonds. The two oxide peaks observed at binding energies of 574.9 and 585.2 eV, respectively, correspond to Te—O bonds and are attributed to TeO_3. The chemical shift of the TeO_3 peaks from the Te—Cd peaks is approximately 3.4 eV in good agreement with reference [20].

In Fig. 6, it is also seen that the intensities of the Te $3d_{5/2}$, Te—Cd peaks of the $CdCl_2$ treated sample increase as the annealing temperature is increased from 345 to 420 °C, while those of the TeO_3 peaks decrease dramatically. Quantitatively, considering the area under each of the Te $3d_{5/2}$ peak fits shown in Fig. 6, the relative percentage of the TeO_3 on the surface of the CdTe film can be determined from the ratio of the intensity for the chemically shifted Te $3d_{5/2}$, TeO_3 peak to the total intensity of the Te $3d_{5/2}$ peaks. For the as grown sample and for samples annealed at 345, 390, and 420 °C temperatures, the relative percentages of the TeO_3 peaks are 11%, 18%, 2% and 9% respectively. It is seen that the TeO_3 almost disappear and the CdTe film surface mainly contain Te—Cd bonds for the sample annealed at 390 °C. The Cd atoms of $CdCl_2$ substitute for the oxide atoms at the CdTe surface, as they can combine preferentially with the Te atoms at the CdTe surface. These phenomena clearly indicate that $CdCl_2$ effectively dissociates the oxide layer at the surface of CdTe film when annealed at 390 °C. This behavior is similar to the phenomenon of the Cd 3*d* core-level spectra shown in Fig. 7. Fig. 7 shows Cd $3d_{5/2}$ core-level XPS spectra for the as-grown and for the $CdCl_2$ treated CdTe films annealed at 345, 390 and 420 °C temperatures.

The binding energies of Cd $3d_{5/2}$ and Cd $3d_{3/2}$ obtained from fittings are 405.1 and 412 eV, respectively. Since the difference in binding energies between the Cd 3*d* and CdO peaks is only 0.8 eV [20], these two peaks cannot be resolved. After annealing the $CdCl_2$ treated CdTe film, the FWHMs of the Cd 3*d* peaks decrease and their intensities increase with increasing the annealing temperature. This result suggests that the oxide layer at the CdTe surface is dissociated and replaced by the Cd atoms due to $CdCl_2$ treatment.

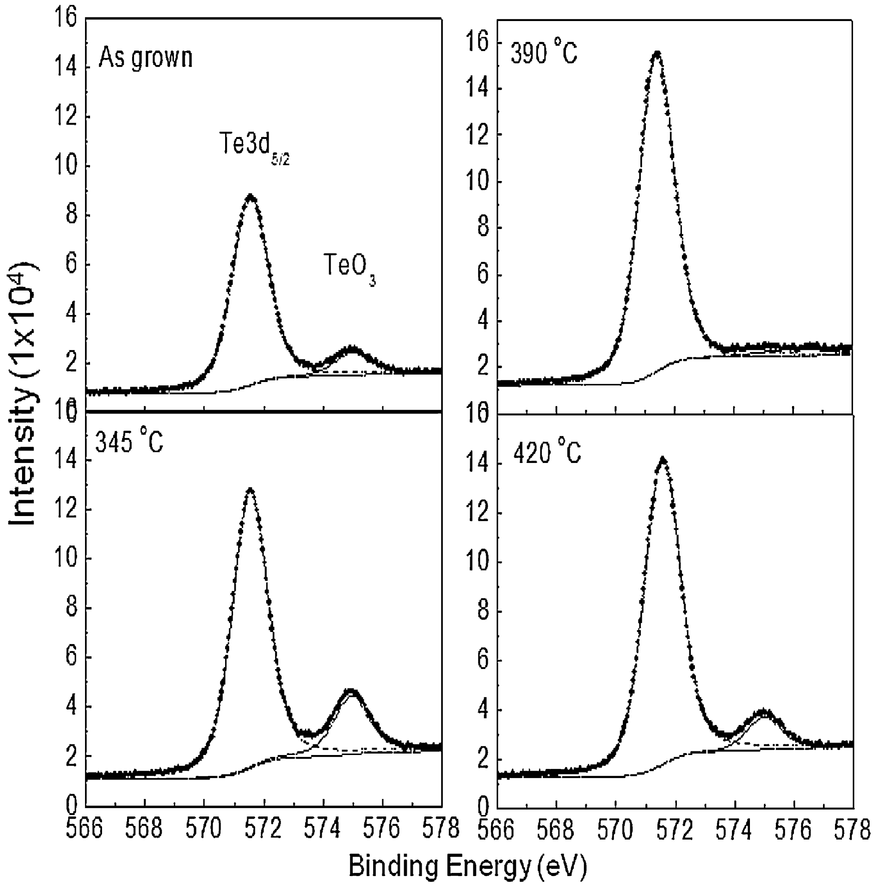

Fig. 6. XPS spectra of the Te $3d_{5/2}$ core-level for the as grown and for the $CdCl_2$ treated CdTe films annealed at 345, 390 and 420 °C temperatures. The peaks were fit with mixed singlets (Gaussian–Lorentzian) peaks. A nonlinear Shirley-type background was subtracted from the spectra before the fit.

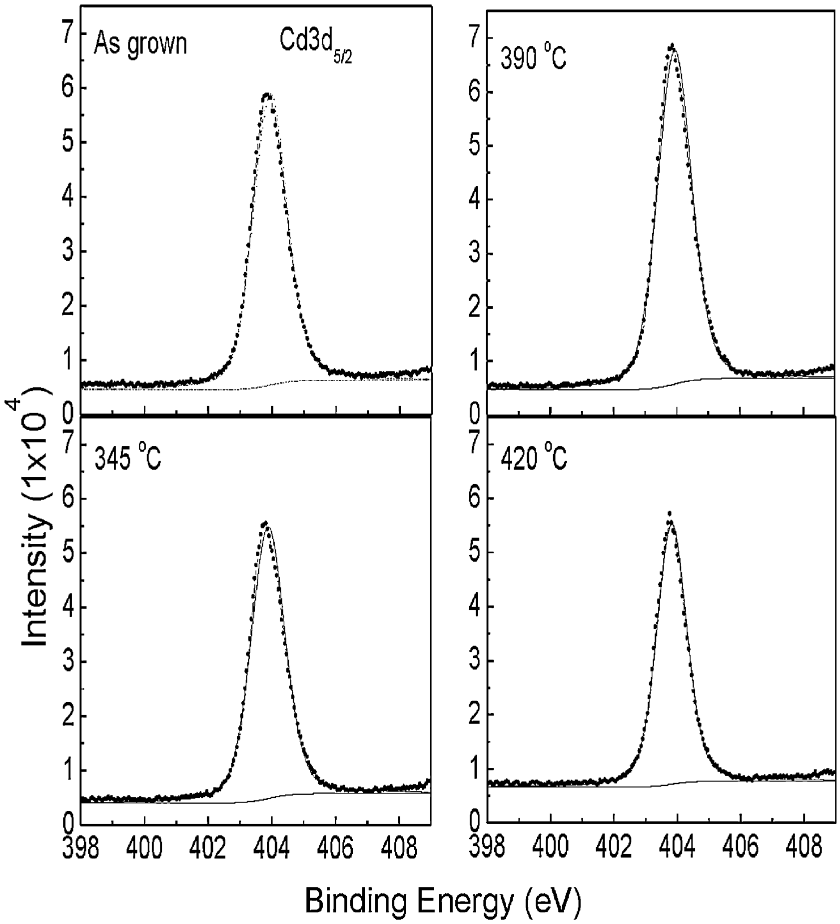

Fig. 7. XPS spectra of the Cd 3*d* core-level for the as grown and for CdTe samples annealed at 345, 375, 390 and 420 °C temperatures. The peaks were fit with mixed singlets (Gaussian–Lorentzian) peaks. A nonlinear Shirley-type background was subtracted from the spectra before the fit.

3.3. *I–V measurements*

Fig. 8 shows the *I–V* device characteristics before and after the $CdCl_2$ heat treatment at 410 °C for 15 min. It illustrates the effect of treatment on the solar cells performance. It indicates that the device does not show acceptable rectifying characteristics without $CdCl_2$ treatment. With $CdCl_2$ treatment the *I–V* characteristics of device has a low-resistivity ohmic contact to the CdTe layer. The improvement of V_{oc} and J_{sc} after $CdCl_2$ heat treatment could be explained as follows. With the right annealing temperature, the $CdCl_2$ treatment is necessary to dissolve the oxidations at the free surfaces and the thermal anneal process can improve recrystallization as well as film morphology, which result in a remarkable improvement to the CdS/CdTe solar cell performance.

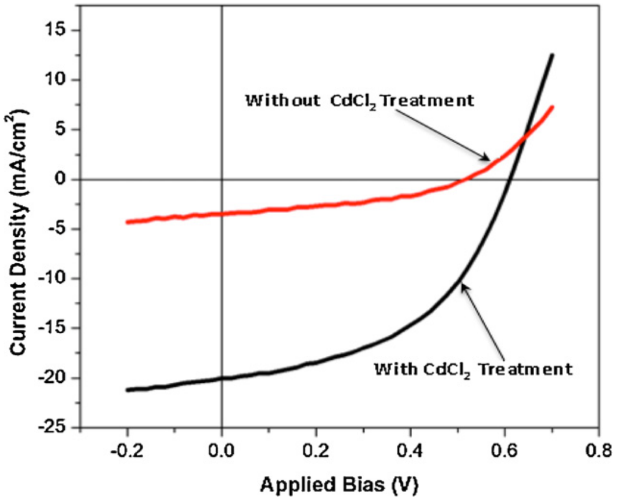

Fig. 8. *I–V* characteristics of a CdS/CdTe without and with $CdCl_2$ heat treatment at 410 °C for 15 min.

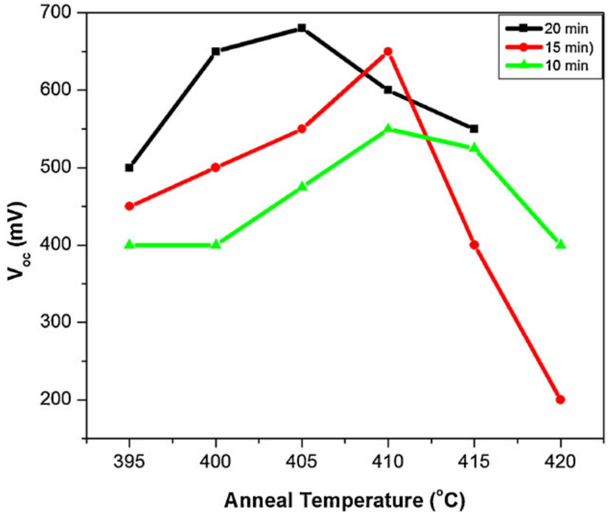

Fig. 9. Variation of V_{oc} as a function of annealing temperature.

Fig. 9 reveals that an open circuit voltage (V_{oc}) goes through a maximum as the annealing temperature changed from 395 to 420 °C and the time from 10 to 20 min. V_{oc} of more than 680 mV and J_{sc} close to 20 mA/cm^2 were achieved for CdS/CdTe solar cells annealed under optimum conditions of 410 °C for 15 min. The reduction of V_{oc} was observed as the anneal temperature is increased from 410 °C to 420 °C.

4. Conclusion

In conclusion, a remarkable improvement to the CdS/CdTe films solar cells performance can be achieved when annealed at an appropriate temperature in the presence of $CdCl_2$ on the free surfaces of CdTe and CdS. From our SEM and *I–V* measurements, the performance of the $CdCl_2$ treated cells is optimized at annealing temperature around 410 °C for 15 min. However, the annealing temperature necessary to almost completely dissolve the oxidations at the CdTe and CdTe free surfaces obtained in our XPS measurements is 390 °C.

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