Effects of different CdCl₂ annealing methods on the performance of CdS/CdTe polycrystalline thin film solar cells

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In this paper, the effects of different CdCl₂ annealing methods, including vapor annealing and dip-coating annealing, on the performance of CdS/CdTe polycrystalline thin-film solar cells are studied. After annealing, the samples are lightly etched with 1% bromine in methanol to remove surface oxides. Both annealing methods give CdTe polycrystalline thin films with good crystallinity and complete structure. For solar cells containing the annealed CdTe films, cell efficiency first increases and then decreases as the concentration of CdCl₂ solution used for dip-coating annealing increases, and the optimized CdCl₂ concentration is 12%. The uniformity of the performance of all cells is analyzed by calculating the relative standard deviation for each parameter. The uniformity of cell performance can be improved dramatically by dip-coating annealing instead of vapor annealing. Most notably, an appropriate concentration of CdCl₂ (12%) acts as a protective layer that is conducive to realizing uniform high-performance CdS/CdTe solar cells. According to the location of depletion regions, the CdTe films treated by dip-coating annealing show a relatively low doping concentration, except for the sample treated with a CdCl₂ concentration of 6%, which is consistent with the changes of short-circuit current density of the cells. It is believed that these results can be applied to the large-scale production of CdTe polycrystalline thin-film solar cells.

dip-coating, annealing, CdTe thin film, solar cells

1   Introduction

CdTe solar cells have attracted considerable interest because of advantages such as low cost and simple preparation. CdTe is a semiconductor with a direct band gap of 1.5 eV, and has a high absorption coefficient [1, 2]. Currently, the highest conversion efficiency obtained for a CdTe solar cell exceeds 20% and the module efficiency is more than 16% [3]. Considerable work has been performed to further reduce the cost and improve the efficiency of solar cells [4–6]. Annealing is an important step in the fabrication of cells,

and has received wide attention. The performance of cells can be improved by annealing [7–9]. The annealing time, temperature, dopant and atmosphere all affect film properties, and thereby the performance of devices [10–12]. By selecting appropriate annealing conditions, the properties of CdTe thin films, such as grain growth and grain boundary passivation, can be optimized. In laboratory-based cell fabrication, CdTe thin films of high quality are typically annealed in gaseous CdCl₂ atmosphere in a process called vapor annealing, which is similar to the close-spaced sublimation (CSS) method [13]. However, this process may not be suitable for industrial production. Once the cell area increases, the non-uniformity of the film obtained by this method will increase, which will affect performance.

Therefore, we decided to investigate the dip-coating annealing method where $CdCl_2$ solution is pre-coated on the surface of the CdTe film as an alternative to vapor annealing. We changed the concentration of $CdCl_2$ solution to optimize the properties of the film and also analyzed the influence of different annealing methods on the performance of cells. In our previous study, we found that residual $CdCl_2$ crystals remained on the surface of CdTe film after annealing. In addition, an oxide layer will form on the surface after annealing in air. This makes it difficult to directly observe the morphology and structure of the films after dip-coating annealing. In this work, to remove the residual $CdCl_2$ crystals and oxide on the CdTe surface, we lightly etch the CdTe films with 1% bromine in methanol, which is compatible with the device fabrication process. CdS/CdTe solar cells containing these etched CdTe films are prepared and their performance characterized by current density-voltage (*J-V*) and capacitance-voltage (*C-V*) measurements.

2   Experiments

CdTe thin-film samples were deposited by the CSS method according to ref. [14]. Quartz glass with a thickness of 3.5 μm was used as the substrate. Annealing was carried out in a quartz furnace at 380°C for 30 min under an atmosphere of N_2 and O_2 (4:1). Figure 1 outlines the two annealing methods, which differ in the manner of transport and amount of $CdCl_2$ dopant on the CdTe surface. Vapor annealing (Figure 1(a)) is similar to the CSS method. In contrast, dip-coating annealing (Figure 1(b)) involves dipping a CdTe film into an aqueous solution of $CdCl_2$ to coat $CdCl_2$ onto its surface before annealing.
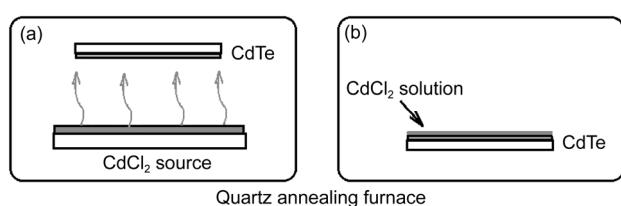
Table 1 lists the different concentrations (weight percent) of $CdCl_2$ solutions used for dip-coating annealing. To study the properties of the CdTe films after annealing, the films were etched with 1% bromine in methanol for 2 s.

Solar cells with the structure fluorine-doped tin oxide (FTO)/CdS/CdTe/Au without any back contact layer were fabricated to examine the performance of the CdTe films. A 100-nm-thick CdS window layer was deposited on commercial soda lime glass substrates coated with FTO by chemical bath deposition. CdTe was deposited on CdS by CSS under the same conditions as mentioned above. Following CdTe deposition, the CdTe films were annealed by the methods described above. After etching with bromine in methanol, Au electrodes were deposited by electron-beam evaporation. To reliably determine the effects of different annealing methods on cell performance, we prepared six cells with an area of 0.07 cm^2 for each set of annealing conditions.

3   Results and discussion

3.1   Film characteristics

Figure 2(a) shows X-ray diffraction (XRD) patterns of the CdTe films annealed by different methods. The XRD patterns clearly indicate that all of the samples have the same structure. Peaks from the oxides of Cd and Te such as CdO and TeO_x are not observed after etching. Each sample exhibits five strong diffraction peaks corresponding to the (111), (220), (311), (400) and (331) planes of CdTe, and the preferred orientation is (111). Obviously, the different annealing methods do not have a marked effect on the structure of the CdTe samples. Furthermore, the concentration of the solution used for dip-coating annealing has little effect on the structure of the CdTe films.

To study the influence of annealing conditions on the grain size in the films, the average grain size in each sample was calculated using the Scherrer equation:

$$D = \frac{K\lambda}{\beta\cos\theta},$$

where θ is the Bragg angle, λ (1.54056 Å) is the wavelength of Cu K_α radiation, D is the average grain size and K is the shape factor. Figure 2(b) reveals that the grain size changes slightly from 55 to 70 nm depending on the annealing method, indicating that the different annealing methods have little effect on the grain size in the CdTe films. Grain

Figure 1   (a) Schematic diagram of vapor annealing, where a $CdCl_2$ source is placed directly on a quartz plate and gaseous $CdCl_2$ is transported from the source to the CdTe surface at 380°C. The distance between source and CdTe is 2 mm. (b) Schematic diagram of dip-coating annealing, where $CdCl_2$ solution is uniformly coated on the CdTe surface before annealing.

Table 1   Concentrations of $CdCl_2$ solutions used in dip-coating annealing[a]

Sample	1-1	1-2	1-3	1-4	1-5	1-6
Concentration (wt%)	Vapor annealing	3	6	12	24	Oversaturated solution
N_D (cm^{-3})	3.8×10^{13}	2.6×10^{13}	4.1×10^{13}	3.5×10^{13}	3.4×10^{13}	3.2×10^{13}

a) Sample 1-1 was annealed by vapor annealing and the others by dip-coating annealing. N_D is doping concentration.
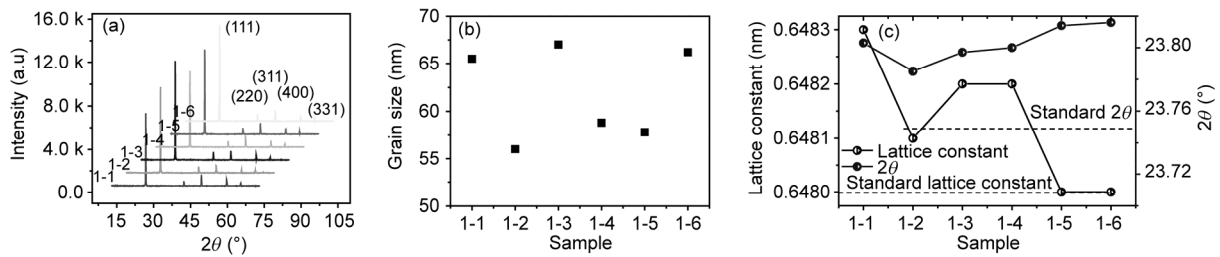
Figure 2   (a) XRD patterns of CdTe films annealed by different methods. Changes of (b) grain size calculated by Scherrer equation, and (c) lattice constant and 2 θ of the (111) peak. The standard lattice constant and 2θ are shown in (c) as dashed lines.

size is mainly affected by annealing temperature and time [15]. The position of the (111) diffraction peak for different samples is depicted in Figure 2(c). The peak position changes slightly with the concentration of CdCl$_2$ solution used for dip-coating annealing. We also calculated the lattice constant for the films, as shown in Figure 2(c). Compared with the standard value of 0.648 nm for CdTe, the samples exhibit lattice distortion, and the biggest change is 0.07% for the vapor-annealed 1-1 sample. Lattice distortion is a defect that damages the integrity of the crystal lattice and increases film stress, thus affecting cell performance [16]. After slight etching, the lattice distortion in sample 1-3, 1-4 and 1-1 shows the same trend. These results indicate that the different annealing methods have the same effects on the structural properties of CdTe films.

3.2   Device performance

3.2.1   J-V characteristics

J-V curves of the highest efficiency cells measured under an AM1.5 spectrum at 100 mW/cm^2 are presented in Figure 3(a). The shape of the *J-V* curves depends only slightly on the annealing method, indicating that similar performance can be obtained for both annealing methods. This is because this source in both annealing methods is CdCl$_2$, which will stay on the surface of CdTe. The two annealing methods result in similar hole density in the CdTe layer and comparable impurity profiles for Cl and O, which are important p-type dopants for CdTe [17–19].

Figure 3(b) summarizes the efficiencies of all 36 cells. The cells containing vapor-annealed films exhibited a highest efficiency of 9.02%, shunt resistance (R_{sh}) of 6464 Ω, series resistance (R_s) of 155 Ω, fill factor (FF) of 53.35%, short-circuit current density (J_{sc}) of 23.1 mA/cm^2 and open-circuit voltage (V_{oc}) of 731 mV. For the solar cells containing films treated by dip-coating annealing, those prepared under 1-4 conditions possessed a highest efficiency of 9.32% with R_{sh} of 5871 Ω, R_s of 141 Ω, FF of 54.56%, J_{sc} of 23.9 mA/cm^2 and V_{oc} of 716 mV. The *J-V* curves of these two types of cells almost overlap, as shown in Figure 3(a). These results indicate that we can achieve similar performance for solar cells prepared with vapor or dip-coating annealing. According to the average performance relative to

the 1-1 cells (Figure 3(c)), the cell efficiency first increases and then decreases as the concentration of the CdCl$_2$ solution used for dip-coating annealing increases. FF and J_{sc} also show the same tendency, while R_s exhibits the opposite behavior. FF depends on R_{sh} and R_s. R_{sh} arises from leakage of current through the cell, around the edges of the cell and between contacts of different polarity. R_s is derived from the resistance of the cell materials to current flow and resistive contacts. Figure 3(b) reveals that the range of cell conversion efficiencies depends on annealing conditions. This range is closely related to the uniformity of cells, which can be analyzed by the relative standard deviation (RSD) as follows:

$$RSD = \sigma / \overline{x} = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(x_i - \overline{x})^2} / \overline{x},$$

where σ is standard deviation, n is the number of cells prepared using the same annealing conditions (here n is 6), x_i is the value of the measured cell parameter and $\overline{x}$ is the average of the measured cell parameter. Figure 3(d) shows the RSD for each cell parameter under different annealing conditions. The uniformity of cells is markedly improved using dip-coating annealing instead of vapor annealing. For example, the average efficiency (7.7%) of 1-1 cells treated by vapor annealing is higher than that of 1-2 cells (7.4%) treated by dip-coating annealing. However, the RSD of the former and latter are 13.3 and 3.21, respectively. As for FF, the corresponding average FF of 1-1 and 1-2 cells are 48.5% and 48.0%, but their RSDs are 8.8 and 1.8, respectively. Thus, the uniformity of cell performance obtained using dip-coating annealing is better than that of cells treated by vapor annealing. Moreover, the uniformity of 1-3 and 1-4 cells is higher than that of other cells annealed by the dip-coating method. As Ref. 18 and 19 state that in the case of a Te-rich CdTe surface, CdCl$_2$ is expected to react with Te to form CdTe. After annealing, the content of Cl at the interface between CdS and CdTe is therefore an order of magnitude higher than that in the bulk of CdTe. This is because Cl species enhance in-diffusion by a reaction–diffusion mechanism, which indicates that this is the diffusion process in the CdTe. During vapor annealing, Cd on the CdTe surface easily reacts with oxygen to form CdO. Once gaseous CdCl$_2$ reaches the surface of CdTe, a stable
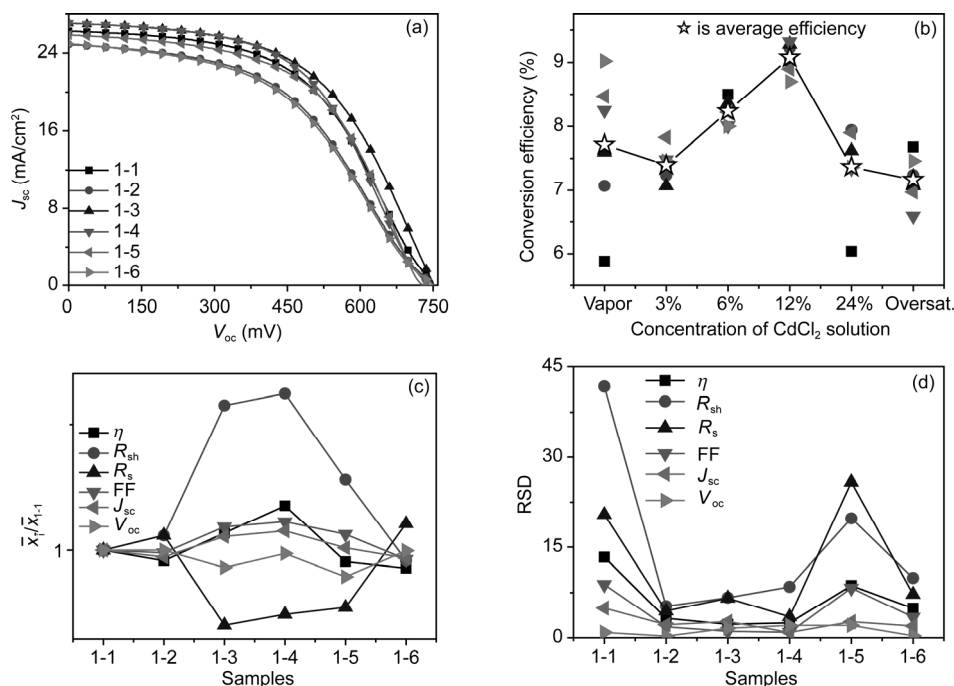
Figure 3 (a) *J-V* curves for the highest-efficiency cells prepared under each set of annealing conditions. (b) Efficiencies of six cells prepared under each set of annealing conditions. (c) Average values of cell parameters relative to that of 1-1 cells $\bar{x}_i/\bar{x}_{1-1}$ and (d) relative standard deviations for cell parameters.

$Cd_3O_2Cl_2$ film can be formed through the reaction of CdO and $CdCl_2$. This partially blocks the in-diffusion of Cl, leading to nonuniform efficiency and corresponding high RSD. When using dip-coating annealing, $CdCl_2$ acts as a protective layer to inhibit the formation of CdO, which then leads to uniform diffusion of Cl. As a result, the uniformity of cell performance is greatly improved. In addition, Cl may be consumed during the annealing process, so CdTe cannot be effectively doped with Cl when CdTe is coated with dilute $CdCl_2$ solution. Alternatively, in the case of a $CdCl_2$ solution of high concentration, R_{sh} may be lowered by lattice distortion. Therefore, only an appropriate $CdCl_2$ concentration of ~12% is useful to improve the uniformity and performance of CdS/CdTe solar cells treated by dip-coating

annealing.

3.2.2 C-V performance

C-V characteristics of the solar cells were measured in the dark at a frequency of 1 MHz. Because the back contact of the cells may dominate the capacitance response at high forward bias, only data recorded for bias <0.6 V were used. C^{-2}-*V* calculated from *C-V* data is presented in Figure 4(a). These curves possess a narrow linear region with a span of no more than 0.3 V, which indicates that all of the cells behave as steep-sided junctions. The doping concentration (N_D) of the each film was obtained from the magnitude of the slope of C^{-2} versus *V* in the linear region ranging from 0.3 to 0.6 V, and the values are listed in Table 1. N_D varied slightly with annealing conditions and changed in a similar
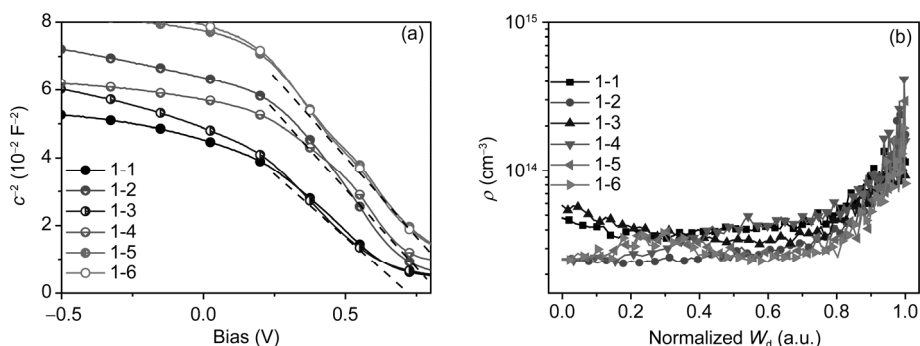

Figure 4 (a) Plots of C^{-2} versus *V* for cells treated under different annealing conditions. N_D was obtained from the magnitude of the slope of C^{-2} against *V* in the linear region of bias voltage from 0.3 to 0.6 V according to the formula: $C=A[\varepsilon_r\varepsilon_0qN_D/2(V_D-V)]^{1/2}$. (b) Plots of doping density ρ versus normalized depletion region width W_d ($W_d=\varepsilon_r\varepsilon_0A/C$). $W_d=0$ is the position near CdS and $W_d=1$ is the position near the back electrode ($V_{bias}>0.6$ V) where the capacitance from the back contact begins to dominate.

manner to J_{sc}, as shown in Figure 3(c).

To analyze the dependence of doping properties on annealing method, doping density ρ-depth profiles for all cells were plotted (Figure 4(b)). All curves show the same shape, which means that the carrier concentration in all films has the same profile. Figure 4(b) indicates that ρ was higher near the back electrode, which is beneficial to reduce the contact barrier between CdTe and the back electrode. The increase in N_D can be attributed to two factors: etching that will make the surface of CdTe Te-rich, and annealing effectively inducing p-type $CdCl_2$ doping. Additionally, N_D fluctuates slightly near the CdS/CdTe interface because a large number of deep states formed. N_D of cells treated by vapor annealing is slightly higher than that of cells treated by dip-coating annealing except for 1-3 cells. This difference is consistent with the change of J_{sc} [18–20].

4   Conclusions

CdTe thin films were annealed by two methods that differed in the manner of transport and the amount of $CdCl_2$ dopant on the surface of CdTe. After annealing by either method, CdTe polycrystalline thin films with good crystallinity and complete structure were obtained. The annealing conditions affected the performance of solar cells containing the annealed CdTe films. For CdTe films treated by dip-coating annealing, a lower concentration (<6%) or higher concentration (>12%) of $CdCl_2$ solution caused the performance of cells to decrease because of their lower *FF* and R_{sh}. Higher cell efficiency was obtained by optimizing dip-coating annealing conditions. The uniformity of performance of cells treated by dip-coating annealing was better than that of cells treated by vapor annealing, especially that of sample 1-3 and 1-4. These results indicate that only an appropriate concentration of $CdCl_2$ is useful to improve the uniformity and performance of CdS/CdTe solar cells. N_D varied slightly with annealing method in a similar manner to J_{sc}. Overall, our results show that uniform, and high-performance solar cells can be achieved by dip-coating annealing using an appropriate concentration of $CdCl_2$ solution.

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