Study of CuxTe polycrystalline thin films for CdTe solar cells

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Abstract—CuxTe polycrystalline thin films were prepared by co-evaporation method. The influence of the film characteristic on the CdS/CdTe photovoltaic device performance was investigated. The results show that as-deposited CuxTe thin films are amorphous phase. While after annealing, samples were polycrystalline phases with increasing temperature. Especially, when NCu : NTe was 1 : 1.44 the film showed more evident polycrystalline phase and the crystallization degree increased. Furthermore, Cu and Te elements of the annealed films form ions from XPS analysis. The C-V, I-V characteristics indicate that the CuTe buffer layers eliminate the Roll Over phenomenon. Meanwhile, the back contact properties, such as the diode characteristics (A) of the forward junction and the dark saturation current density (Jsc) have been improved. As a result, the conversion efficiency is improved by 14.5%, from 10.3% to 12.667%.

Keywords-CuxTe; anneal; polycrystalline thin film; co-evaporation; solar cells

I. INTRODUCTION

Polycrystalline CdS/CdTe thin film solar cells are promising candidates for the economical large-scale manufacturing of electricity in the near future. They develop remarkably in recent years' research [1, 2]. One of the main researches is to improve the back contact. Formation of the ohmic contact on the CdTe absorber layer is well known as a critical technical issue because of CdTe's high work function and the difficulty of obtaining high p doping in the back region. The material of the back contact for CdTe has been investigated and applied, such as ZnTe, ZnTe/ZnTe:Cu [3-5]. Copper (Cu) has been found to be an acceptor dopant for CdTe film and is widely used in high-efficiency CdTe solar cells.

However, Cu plays two roles in CdTe device performance. The advantages are that it produces a back contact with low resistivity by forming highly degenerated p+ copper telluride (CuxTe) compounds, and it dopes the bulk CdTe, thus achieving higher carrier concentration. However, Cu can diffuse into the CdTe bulk and CdS film to form carrier traps that impact device performance. Although a number of papers report on Cu-containing back-contacts, a full understanding of Cu effects on CdTe device performance still remains an important topic for the CdTe community. Cu2Te has been widely used as back-contact to CdTe film [6-10]. Many processing parameters have been studied to investigate the effects of Cu, including Cu thickness [7], Cu deposition rate [9], and annealing temperature [10]. It is commonly reported that the use of Cu2Te correlates with good device performance.

In this paper, we obtain the primary back contact layer of CuxTe prepared by co-evaporating to control the Cu concentration. We report on two aspects related to our work on a CuxTe back-contact: (1) property of the CuxTe films, and (2) effects of the CuxTe back-contact on device performance.

II. EXPERIMENTAL

A. Fabrication of the sample

SnO2: F coated glass was used as substrate. CdS and CdTe films were deposited by chemical bath deposition (CBD) and close space sublimation (CSS), respectively. Te and Cu films were deposited by vacuum co-evaporation. The Te (5N) and Cu powder (5N) were put in quartz crucible heated indirectly by tungsten heater and molybdenum heater respectively. Two quartz monitors monitored the deposition rates of Te and Cu on-line. Post-grown annealing was performed in a nitrogen (N2) atmosphere. The back electrode Ni was deposited by electron beam evaporation. Details of fabrications and post treatments were described in Refs. [11].

B. Measurements and analyses

X-ray diffraction (XRD) measurements were made with a DX-2600 system from Dandong Radical apparatus Co. A Scenting PTS diffract meter with a Cu Kα tube operated was used to study the CuxTe structure. Wide-angle 2θ scan from 10° to 90° taken at a 0.06° step was used to identify the phases present.

XPS (X-Ray Photoelectron Spectroscopy) was measured by using XSAM800 from England Krato Co.. The x-ray source is from Al kα (1486 eV).

The current-voltage (I-V) characteristics under of AM1.5 were measured with a XJCM-8 solar cell tester made by Xi’an Jiaotong University. Dark current-voltage (I-V) measurements

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were performed with a 4155C semiconductor characteristic tester made by Agilent Company.

III. RESULTS AND DISCUSSION

A. The performances of CuTe polycrystalline thin films

The XRD patterns of as deposited Cu$_x$Te thin films are shown in Fig1, and the x value increases from the bottom to the top. When the ratio of Cu atom and Te atom in the Cu$_x$Te thin films was lower (N$_{Cu}$:N$_{Te}$ =1), only the peaks corresponding to CuTe with cubic phase structure (noted “A”) and Cu1.4Te with orthorhombic phase structure (noted “B”) were easily observed, which indicated Cu atom and Te atom reacted each other to form different Cu-Te alloys during the film deposited process. An amorphous crystalline cell appearing between 20~30 deg indicated some amorphous crystalline component exists in Cu$_x$Te thin films. That is because there was redundant Te with amorphous structure in the film during the process of forming solid solution of CuTe and Cu1.4Te polycrystalline structure. With the ratio of Cu and Te element increasing, the film presented apparent amorphous structure. When N$_{Cu}$:N$_{Te}$ was 1.44 in Cu$_x$Te thin films, the peak of Cu$_x$Te with hexagonal phase structure took up; N$_{Cu}$:N$_{Te}$ increasing to 1.75, CuTe, Cu$_{1.4}$Te phase disappeared, and very a little Cu$_2$Te phase appeared; N$_{Cu}$:N$_{Te}$ increasing to 2, the Cu$_2$Te diffraction peak became faint, and some similarly to “steamed bread” peaks appeared. These indicated as-deposited Cu$_x$Te thin film presented mainly amorphous crystalline structure.

The Cu$_x$Te phases varied before and after post-annealing. We used the sample with N$_{Cu}$:N$_{Te}$ was 1 or 1.44 to study the change of XRD patterns for the thin films after annealing.

The annealing temperature was found to impact the phase changes of Cu$_x$Te. Fig. 2 shows XRD patterns of six samples. These samples had identical Cu/Te ratio (N$_{Cu}$:N$_{Te}$ =1) and the Cu$_x$Te thickness (100 nm), but different post-treatments: one sample remained “as-deposited” and five samples were annealed at different temperatures of 100°C, 125°C, 150°C, 175°C, and 200°C. Some amorphous crystalline component and CuTe (noted “A”) and Cu1.4Te (noted “B”) polycrystalline phase structure can be observed for the as deposited sample. The relatively intensity ratio of the CuTe (001) peak and Cu1.4Te (002) peak was 0.63. After annealing at 100°C, the major phase was CuTe and Cu1.4Te, and the amorphous crystalline phase disappeared. The relatively intensity ratio of the CuTe (001) peak and Cu1.4Te (002) peak was 1.63. Peak intensity indicated that Cu2Te was the dominant phase of the samples annealed at 100°C. With increasing annealing temperature (from 125°C to 175°C), the Cu1.4Te diffraction peak became fainter and fainter until it disappeared. And eminent CuTe cube phase structure, (001), (002), (003) and (004) diffraction peaks of samples came forth. When annealing temperature was 200°C, the Cu1.4Te (002) diffraction peak at 14.65° appeared again.

A series of XRD patterns of samples is illustrated in Fig3. These samples has the same Cu/Te ratio (N$_{Cu}$:N$_{Te}$=1.44). Films thickness and post-treatments are identical to the samples in Fig2. It can be seen that CuTe and Cu$_{1.4}$Te were the dominant phase and the Cu$_2$Te phase disappeared for the sample at lower annealing temperature. The peak intensity indicated that the content of CuTe was more than that of Cu$_2$Te for the sample annealed at 100°C and 125°C. With increasing annealing temperature, CuTe intensity gradually decreased while Cu$_2$Te increased. When annealed at 150°C, only the dominant peak (Cu$_{1.4}$Te) existed, while CuTe peak became very faint. When the post-annealing temperature increased to 175°C, some Cu$_2$Te phase came again, while CuTe disappeared. When annealed at 200°C, Cu$_{1.4}$Te (003), (006) diffraction peaks were the dominant phases.

In order to explore the character of Cu$_x$Te thin films deeply, we use XPS to analysis chemical information and calculate the atom ratio of Cu and Te. Fig.4 and Fig.5 shows the XPS spectrum of Cu and Te of thin films with N$_{Cu}$:N$_{Te}$=1 or 1.44 annealed at 150°C, respectively. The band energy of Cu and Te elements with the central energy Cu3d3/2, Cu3d3/2, Te3d3/2, Te3d5/2 are 932eV, 952.3eV, 587eV, 577eV, respectively [11]. While Cu3d peaks lay at 932.5eV, and 952.3eV. Chemical displacement increased a little. Te Cu3d peaks lay at 573.643eV, and 583.006eV. Chemical displacement decreased by 4eV. The central energy of Cu
increased for that the cord energy of inside layer of Cu are higher than that of outside layer losing electron. On the contrary, central energy of Te decreased because accepting electrons from Cu made the cord energy decrease. It indicated Cu and Te form compound in annealed CuxTe film with whether NCu:NTe=1 or NCu:NTe=1.44.

The atom ratio of Cu and Te is 0.95 and 1.44 from the result by FAT analyzing model, which is consistent with the dates from the quartz monitors.

In our work, we selected 150 °C as the annealing temperature and 1.44 as the atom ratio of Cu and Te for the CuxTe thin films.

\[ J = J_p + J_n \]  

(2)

\( J_p \) is hole current density, and \( J_n \) is electron current density. If without considering \( J_p \), \( J \) will be saturated to \( J_{sd} \) due to reverse junction. So the voltage of reverse junction will attain a saturation value.

\[ V_{dark} = \frac{AKT}{q} \ln \left( \frac{J_{sd}}{J_s} \right) \]  

(3)

This is the Roll Over phenomenon reported in some Ref. [12]. That is to say current will be saturated at higher voltage in addition.

Fig.6 summarizes the dark I-V characteristic curves for CdTe solar cells with or without CuxTe (x=1.44) layer. These samples with Cu$_x$Te were annealed at 150 °C for 30 min in N2 atmosphere It can be seen the dark current density of the device without Cu$_x$Te did not increase in exponential form but go to a saturated value at higher bias voltage (>0.75eV). This is the Roll Over phenomenon analyzed above. On the contrary, the I-V curve of the cells with Cu$_x$Te did not show apparent saturation current characteristic but exponential relation ship. The phenomenon that CdTe/Ni back contact junction causes severe rollover in the J–V curves was also observed in our CdS/CdTe devices, which were developed for the thin-film tandem cell project [13].

\[ \begin{array}{|c|c|}
\hline
\text{sample} & \text{Dark saturation current density } J_0 \ (\text{mA/cm}^2) & \text{diode factor } A \\
\hline
\text{With Cu$_x$Te layer} & 4.9786 \times 10^{-6} & 1.96 \\
\text{Without Cu$_x$Te layer} & 3.35463 \times 10^{-4} & 4.28 \\
\hline
\end{array} \]  

(4)

The J–V parameters of cells are also listed in Table 1. We can summarize the effects of the CuxTe phase on device performance from Fig. 6 and Table 1 as follows: (1) introducing CuxTe layer to between CdTe and back electrode can eliminate “cross-over” feature (2) the dark current and diode ideal factor of the device with CuxTe was less than that without CuxTe. The less dark current is beneficial to promote the short-circuit current density (Jsc). CuxTe layer improves the contact of CdTe and back electrode.

In p-n junction, barrier capacitance satisfies...
\[
C_T = A \frac{\varepsilon_r \varepsilon_0 q N_B}{\sqrt{2(V_n - V)}}
\]  

(4)

A is the area of p-n junction; \(\varepsilon_r\) and \(\varepsilon_0\) are relatively permittivity and permittivity of material in vacuum; q is charge electron quantum; NB is impurity concentration of lightly doping limbic sample; VD is the built-in potential barrier, V is voltage in addition. Then doping concentration satisfies

\[
\frac{d}{dV} \left( \frac{1}{C^2} \right) = \frac{2}{A^2 \varepsilon_r \varepsilon_0 q N_B}
\]

(5)

Fig. 7 shows the C-V curves of CdTe solar cells with and without CuXTe (x=1.4) buffer layers. A reverse junction was obviously formed in the CdTe solar cell without CuXTe buffer layers. Furthermore, its junction capacity decreased, space-charge region narrowed, effective doping concentration decreased to \(1.42 \times 10^{19} \text{cm}^{-3}\). On the contrary, in CdTe solar cell with CuXTe buffer layers, the junction capacity increased, space-charge region broadened. Under zero biasing voltage, effective acceptor concentration was increased to \(1.63 \times 10^{14} \text{cm}^{-3}\), which was 15% more than the former. Cu ion may diffuse into CdTe surface and substitute Cd ion as the acceptor impurity, so the doping concentration increases.

**IV. CONCLUSIONS**

(1) CuXTe thin films as deposited prepared by co-evaporation present amorphous phase, while different annealed samples presented different phase with increasing annealing temperature. Especially, when NCu:NTe was 1:1.44 the film showed more evident polycrystalline phase and the crystallization degree was better. Furthermore, the annealed film formed CuXTe.

(2) CuXTe buffer layer eliminated the Roll Over phenomenon and improved back contact characteristic properties, diode characteristics of the forward junction and dark saturation current density of the CdTe solar cells.

**ACKNOWLEDGMENT**

The authors thank Professor Zhu JM for XRD analysis and the center of analysis and Test of Sichuan University for XPS analysis. This research has been supported by University Doctor Foundation (No.20050610024)

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