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Close spaced sublimation deposition of CdTe layers with process gas oxygen for thin film solar cells

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ABSTRACT

Close spaced sublimation (CSS) is one of the leading technologies for deposition of the absorber layer in CdTe solar cells. For large scale production CSS is a dynamic process where the substrates are moved above the crucible at a close distance. In this study oxygen as a process gas is injected during dynamic CSS deposition. Solar cells are prepared from these layers by $CdCl_2$ activation, copper doping and back contact deposition. The samples are investigated using current voltage measurement, quantum efficiency, scanning electron microscopy of cross sections and deep level transient spectroscopy.

The results show that the precise introduction of oxygen can improve the solar cell efficiency. The reasons for this effect are discussed in this study.

1. Introduction

With the recent efficiency as high as 22.1%, the CdTe solar technology has proved again to be one of the most promising absorber materials for thin film solar cells; further research activities in CdTe-based photovoltaics thus remain highly attractive [1]. The typical CdTe solar cell structure (TCO/CdS/CdTe/Metal) includes transparent conducting oxides (TCO), CdS/CdTe layers and metal as back contact layer. The quality of the CdS/CdTe junction formation and carrier collection is mainly dependent on the deposition technique and deposition parameters of these layers. Polycrystalline CdS and CdTe films can be deposited by a variety of different techniques such as sputtering [2], chemical bath deposition [3], physical vapor deposition [4] and close spaced sublimation (CSS) [5–8]. To meet the key demands for mass production, e.g. high efficiency, high throughput and low production costs, however, the CSS technology appears particularly suited [6,9]. Apart from the CdS/CdTe deposition, the process sequence for the preparation of CdTe based solar cells includes an activation step, comprising chlorine based compounds and annealing at ca. 400 °C [10–14]. The activation step essentially causes recrystallization of the CdTe layer [12,15], sulfur diffusion or S/Te inter-diffusion at the CdS/CdTe interface [16,17], doping of CdS/CdTe-material and optimizes carrier collection [18]. Many researchers have reported the properties of CdTe layers deposited by CSS and the influence of the $CdCl_2$ activation process on electrical and morphological properties [19]. A detailed investigation on substrate temperature dependent CdTe growth morphologies has been reported by Jaegermann et al. under low pressure conditions without introducing any process gas during the film growth [20,21]. Additionally, the influence of process gas (O_2) on the CdS and CdTe layer properties has been reported by many researchers [5,22,23]. In this work, we compare the properties of CSS-CdTe layers deposited with and without O_2 during the growth and the influence of different $CdCl_2$ activation temperatures on solar cell device performance. A detailed investigation of different O_2 partial pressures on CdTe growth properties will be published elsewhere.

2. Experimental

The CdTe thin film solar cells were manufactured in superstrate configuration on commercially available fluorine-doped tin oxide (FTO) glass substrate which includes tin oxide as a buffer layer. The CdS and CdTe layers were deposited by CSS technique on 100×100 mm^2 substrates by using the in-line pilot equipment “CATE” [24]. The CdS and CdTe substrate temperatures during the deposition were in the range of 500–510 °C. The CdS deposition parameters were optimized to have 80 (±10) nm layer thickness. The CdS layers and the reference CdTe layers were deposited without introducing any process gas in the

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chamber. The CdTe layers were also deposited by introducing 20 sccm and 250 sccm of O_2 in the chamber and the corresponding chamber pressures were 0.43 Pa and 7.5 Pa, respectively. The CdTe layer thickness was ~4.5 μm. The TCO/CdS/CdTe layer stack was heat treated after applying the saturated methanolic $CdCl_2$ solution (ca. 1% at 20 °C) on the CdTe layer surface – the so-called activation process. The samples were activated at three different oven set temperatures for 25 min: 400, 430 and 440 °C. The standard Cu doped back contact procedure was applied to dope the CdTe layer and to induce an ohmic or pseudo ohmic semiconductor-metal back contact. An optimized Mo layer was deposited on the CdTe surface to serve as a low resistance metal back contact layer. For comparison of the results, the back contact formation process was kept constant. Using the laser scribing technique (532 nm), 24 dot cells (1 cm^2) were defined on 100×100 mm^2 sized substrates.

The cross-sections of the layer stacks were produced by an ion beam preparation technique (Cross Section Polisher, SM-0910, Jeol). High resolution field emission scanning electron microscopy (FE-SEM, SU 8000, Hitachi) was used to make cross-sectional images. The electron beam induced current (EBIC) measurements were made by connecting front (FTO) and back contact (Mo-metal) layers through a high sensitivity amplifier [25].

The characterization of the solar cells was performed by measuring current voltage (I-V) curves under the simulated AM 1.5 G illumination. The deep-level transient spectroscopy (DLTS) measurements were performed in the temperature range of 80 K to 300 K, using a commercial DLTS system (Sula Technologies) coupled with a temperature controller (Lakeshore model 335). While the pulse width was fixed at 100 ms, a range of rate windows from 2773 Hz (0.36 ms) to 18 Hz (55.4 ms) was used to analyze the DLTS signals.

3. Results and discussion

Table 1 shows the I-V parameters of the solar cells prepared with and without O_2 gas input during the CSS-CdTe layer deposition. For the reference sample (SD1), under the given TCO/CdS/CdTe condition, the optimized activation temperature is 400 °C. The reference solar cells produced without any intentional process gas during the CdTe layer growth yields ~13% solar cell efficiency. Introducing 20 sccm of O_2 during the CdTe growth in the chamber yields the same efficiency as the standard cell (Table 1) and increasing the oxygen partial pressure (250 sccm) showed about 1% absolute increase in solar cell efficiency (~14%). The higher activation temperature (430 °C) of the reference cell (SD2) leads to reduction of the solar cell efficiency with considerable loss in open-circuit voltage (V_{oc}) and fill-factor (FF). On the other hand, interestingly, the CdTe layers deposited in O_2 atmosphere do not show such strong V_{oc} and FF loss. Especially, in case of CdTe deposition with the low O_2 partial pressure, the device efficiency increased to 14% (LO2) with 430 °C activation. The slight loss in FF and V_{oc} is compensated by the gain in short-circuit current (J_{sc}). However, for the sample (HO2) prepared with 250 sccm O_2, only about 0.5% improvement was obtained. Fig. 1 shows the SEM cross section of the as-deposited CdTe layers. A strong difference in CdTe morphology and grain size can be seen between the samples. The mean CdTe grain size decreases with respect to the O_2 partial pressure in the chamber. The reference sample (Fig. 1a) has a block-like microstructure with large and compact CdTe grains. The CdTe layer, grown in presence of an O_2 atmosphere, shows a columnar microstructure (Fig. 1b). The CdTe layer deposited with higher O_2 partial pressure has a poor morphology with many pores at the grain boundaries and a rough CdTe surface (Fig. 1c). The CdS morphology and the layer thickness are the same for all the samples before the activation process. As an example, Fig. 2d shows the as-deposited CdS layer morphology (CdTe layer of this sample was deposited with 250 sccm O_2 input).

The activation process does not show any considerable change in CdTe morphology of the reference samples even at higher activation temperature up to 440 °C except a slight increase in CdTe grain size. After the activation process, the CdTe layer morphology and CdTe grain size of the samples appears similar independent of CdTe deposition condition. However, the CdS layer starts to agglomerate at higher activation temperatures above 400 °C causing a direct contact of CdTe layer with TCO layer. The agglomerated CdS layer thickness varies locally in the range of 0 to 200 nm and the lateral grain size up to 250 nm for high activation temperature (440 °C). Therefore, the loss in V_{oc} and FF of the sample SD2 is due to the presence of many defects and therefore increased recombination at the TCO/CdTe junction [26,27]. The formation of CdS agglomeration for the samples grown in an O_2 atmosphere and activated at higher temperature > 400 °C is shown in Fig. 2. The as grown CdS layer (Fig. 2d) shows a dense and compact grain structure. After the activation process at 400 °C (Fig. 2a) some pores within the CdS layer are visible due to grain growth. With increased activation temperature (430 °C and 440 °C, Fig. 2b and c) the CdS agglomerate more and more and the remaining CdS grains become larger. At an activation temperature of 440 °C (Fig. 2c) the TCO/CdTe contact is the predominant contact. At higher activation temperature (430 °C, 440 °C) the amount of remaining CdS is less than before the activation process. That means some CdS has dissolved and diffused into the CdTe layer. However, no strong reduction in V_{oc} and FF is observed for the CdTe samples deposited in O_2 atmosphere. Presumably, the higher amount of grain boundaries of the CdTe layers, grown in an O_2 atmosphere supports the dissolution of the CdS and the diffusion of sulfur into the CdTe [28]. The higher amount of grain boundaries presumably increases also the amount of chlorine in the CdTe layer after the activation process. Thus, the sulfur diffusion in CdTe:O might lead to different interface states in comparison to the pure TCO/CdTe. In addition, the presence of excess oxygen during the CdTe growth could have also improved CdTe carrier mobility and life time thereby might help to retain the V_{oc} of the device [5].

In Fig. 3 the SEM and corresponding electron beam induced current (EBIC) images of samples grown without and in an O_2 atmosphere and activated at 400 °C are shown. The EBIC image of the sample with no O_2 (Fig. 3c) shows a strong difference in brightness between the inner grains and nearby areas of the grain boundaries. A higher EBIC and therefore lower recombination of electron hole pairs occurs in the nearby area of the grain boundaries. The sample grown in an O_2 atmosphere shows a more uniform EBIC image (Fig. 3d). Furthermore the CdTe layer has an equiaxed grain structure (Fig. 3b). While the activation process, there is a strong recrystallization of the CdTe layer, from the columnar

Table 1
Comparison of the solar cell parameters prepared with different O_2 partial pressure during CSS-CdTe deposition and different activation temperatures.

Sample name	O_2 during CSS-CdTe (sccm)	CdTe chamber pressure (Pa)	$CdCl_2$ activation (°C)	FF (%)	J_{sc} (mA)	V_{oc} (mV)	Efficiency (%)
SD1-(reference)	Nil	0.1	400	70.1	22.4	832	13.1
LO1	20	0.43	400	68.2	23.4	822	13.2
HO1	250	7.5	400	73.7	23.1	836	14.2
SD2	Nil	0.1	430	61.7	24.6	754	11.4
LO2	20	0.43	430	67.5	25.4	817	14
HO2	250	7.5	430	65.6	25.5	811	13.6
HO3	250	7.5	440	63.3	27	787	13.4