Solar Energy 136 (2016) 460–469

Contents lists available at ScienceDirect

Solar Energy

journal homepage: www.elsevier.com/locate/solener

The phase segregation in CdTe/CdS heterojunction and its effect on photo current of CdTe thin films solar cell

Bin Lv [a,*], Ligang Ma [b], Yun Li [a], Bo Yan [a], Pinggen Cai [a], Xiaoshan Wu [b]

[a] Center of Optics and Optoelectronics Research, College of Science, Zhejiang University of Technology, Hangzhou 310023, PR China
[b] Center for Photovoltaic Engineering, National Lab of Solid State Microstructures, Department of Physics, Nanjing University, Nanjing 210093, PR China

ARTICLE INFO

Article history:
Received 22 June 2016
Accepted 18 July 2016

Keywords:
Multilayers
Optical materials
Diffusion
Heterostructures

ABSTRACT

The S-Te inter-diffusion in CdTe/CdS heterojunction has been studied by X-ray diffraction, Atomic force microscope and Spectroscopic ellipsometry. For the first time, the phase segregation of $CdTe_yS_x$ compound that is confirmed by X-ray measurement has been taken into account in the analysis of ellipsometry, which promotes the analytical reliability. Benefit from the dielectric constants obtained from the ellipsometric data, the external quantum efficiency of the solar cell has been fitted without any paradoxical assumption used before. Results show that high temperature process such as Close space sublimation leads to significant S-Te inter-diffusion and shallows the junction obviously, but this does not happen in magnetron sputtered device. Tellurium diffusion into CdS can reduce the blue response of solar cell, meanwhile sulfur diffusion into CdTe lowers the band gap of CdTe which increase the quantum efficiency at long wavelength. Finally, the conversion efficiency of solar cell can be improved by suppressing the current leakage near the edge of cell. The fill factor is 54.8% and the efficiency reaches 9.28%.

1. Introduction

CdTe thin film solar cell is one of the photovoltaic technologies capable to compete with the classic crystalline silicon solar cell (Toma et al., 2014), especially for the low production cost levels. High efficiency CdTe solar cells are extensively investigated and the best efficiency of 21.0% has been reported by First Solar (Green et al., 2016). Recently, many kinds of near-filed microscopes (Major et al., 2014; Li et al., 2014; Leite et al., 2014; Major and Durose, 2009) have been used to scan the heterojunction. The depletion region can now be observed directly so that the minority carrier-collection is no longer only an invisible parameter of external quantum efficiency (EQE) expressions. Major et al. (2014) report that Cl-doping can shallow the depletion region. Li et al. (2014) point out that Cl-Te interaction at the grain boundaries (GB) of CdTe creates p-n junctions near GB which promotes the capability of carrier-collection so that the optical current increases.

All these investigations have indicated that carrier generation is highest in the vicinity of the CdS/CdTe junction. The mixing between CdS and CdTe homogenizes the CdS/CdTe interface (Major and Durose, 2009) and increases the minority carrier lifetime therefore improving the fill factor and the open circuit voltage (Kranz et al., 2014). Moreover, the inter-diffusion at the CdS/CdTe junction reduces the optical absorption loss by consuming CdS window layer (Korevaar et al., 2013) and results in the formation of low band gap alloy $CdS_{1-y}Te_y$ and $CdTe_{1-x}S_x$ that reduces the response at shorter wavelength and slightly extends response at longer wavelength (Mathew et al., 2012). However, those studies do not investigate the combined influence on EQE caused by inter-diffusion. Thus a quantitative analysis of S-Te inter-diffusion which includes all positive and negative impacts on EQE will benefit the fabrication of better CdTe solar cells.

Comparing with Lift-off (Albin et al., 2002), sputtering (Fritsche et al., 2005) and other invasive techniques (Enríquez et al., 2007; Major et al., 2012), X-ray diffraction(XRD) and spectroscopic ellipsometry (SE) are non-destructive and powerful techniques to characterize the S-Te inter-diffusion in CdS/CdTe heterojunction (Kim et al., 2013; Pan et al., 2011). A reasonable SE analysis needs pre-information of the heterojunction structures. With the help of XRD detection, McCandless et al. (1997), McCandless et al. (2002) report the possibility of phase segregation in CdS_yTe_x system, but it is now still under controversy (Santana-Aranda and Meléndez-Lira, 2001; Al-Ani et al., 1993; Murali et al., 2009). However, most of these XRD measurements are operated on the synthesized "CdS_yTe_x compound" rather than the "CdS_yTe_x compound layer" in real heterojunction (McCandless et al., 2002; Santana-Aranda and Meléndez-Lira, 2001; Al-Ani et al., 1993; Murali et al., 2009),

* Corresponding author.
E-mail address: binlv@zjut.edu.cn (B. Lv).

http://dx.doi.org/10.1016/j.solener.2016.07.030
0038-092X/

which may fail to give the real information of S-Te inter diffusion in solar cells. Moreover, it is difficult to explain the slow drops in EQE at CdS absorption edge (Major et al., 2014) due to the lack of accurate knowledge of CdS_yTe_x compound. Though we have proposed an approximate method to fit this feature of EQE spectra (Lv et al., 2015), it is unsatisfactory because the layer structure used in EQE fitting is inconsistent with the one in SE analysis.

In the present, we deposite CdS/CdTe heterojunction by close space sublimation (CSS) with the structure of Glass/CdS/CdTe followed by $CdCl_2$ annealing. In order to identify the phase of CdS_yTe_x compound and its possible change due to the CdTe depositing, we suppress the CdTe sublimation at different stage during the deposition to prepare the heterojunctions that have different CdTe thickness (sample s_2 and s_3) but experience the same temperature process. The CdS_yTe_x compound in heterojunction is investigated by XRD and its optical constant is measured and analyzed by SE. The complete solar cell (sample s_4) is also fabricated with the same condition but adding the back contact layer Cu_xTe and electrodes ITO and Cu with the structure Glass/ITO/CdS/CdTe/Cu_xTe/Cu. Combing the optical constant of each layer, we simulate the EQE of the solar cell. The quantitative analysis of influence of S-Te inter-diffusion on optical absorption and EQE are presented for the first time.

2. Experimental

The CdS films were grown by chemical bath deposition method (CBD) and CdTe films were deposited using a domestic close space sublimation system. In order to obtain reliable fitting results from SE analysis for multilayers, the commercial glass coated with 180 nm of ITO was only used as substrate in solar cells (fabricated with sample s_4) because the fewer layers involved in analysis, the more accurate the result is. Thus the CdTe monolayer film, CdS monolayer film (sample s_1) as well as CdS/CdTe heterojunctioin (sample s_2 and s_3) were prepared on TEC-15 glass and were investigated by XRD (Siemens, D5000H, the resolution of scanning is 0.02°) and SE (J.A. Woollam, T-solar). In order to obtain an observable XRD signal of CdS_yTe_x compound, the heterojunction should locate no deeper than 2000 nm from the surface. Moreover, the CdS_yTe_x compound we studied in mutilayers should has the same phase as that in complete solar cell. We achieved this goal by controlling the temperature of CdTe source. As is well known, CSS is an evaporation process, the depositing and decomposing on substrate will get into an equilibrate status when the source and substrate have the same temperature so that the film thickness will stop increasing. As is showed in Fig. 1(a), the different substrates on which the heterojunction deposited were designed to go along the same temperature curve (solid line) up to 570 °C to acquire the CdS_yTe_x compound with the same phase (Lane et al., 2000) for samples s_2, s_3 and s_4. Meanwhile, the source temperature, take s_2 for example, departed from the substrate temperature at t_1 and established a temperature gradient of 60 °C between them. Then the source stopped heating at 530 °C (at t_2) until the substrate caught up with it at t_3. Finally they went over the following process with the same temperature as is showed by red dash line in the Fig. 1(a). For s_2 the CdTe thickness had stopped increasing since the substrate reached 530 °C. We named this temperature that the thickness of CdTe stops increasing as cut-off temperature. Because the sublimation temperature of CdTe at 2 kPa is considered as 500 °C approximately (Seth et al., 1999), the cut-off temperature was set as 530 °C and 570 °C for s_2 and s_3 respectively to achieve the heterojunction with different CdTe thickness. It should be noted that s_4 was deposited on commercial ITO glass coated with CdS layer and was used to fabricate the solar cell, thus the source kept being hotter than substrate until the end of CSS process to acquire thick CdTe layer (~8 μm). For all samples, after deposition process, a saturated $CdCl_2$ methanol solution was dipped on the surface of CdTe films and annealed at 430 °C for 30 min. Their morphologies were also observed by atomic force microscope (AFM, Veeco Dimension 3100) with tapping mode. The thicknesses of as deposited CdS and CdTe layers were verified by the stylus surface profilometry (Vecco, Dektak6M) and were used as parameters in SE analysis. The transmittance spectra of multilayer which was measured by UV–vis spectrophotometer (Varian, Cary50Probe) was used as supplement for SE analysis to promote the accuracy of results. In order to perform reliable SE measurements on heterojunction, we set glass as substrate layer for s_2 and s_3 to avoid the problem of backside substrate reflections from CdTe/air interface. In this configuration, the backside substrate reflections from glass/air interface can be diminished by sticking a frosted tape onto the backside of the glass. On the contrary, the glass was set as top layer in the investigation of s_4 because the CdTe layer is too thick as a top layer that SE cannot detect the signal of heterojunction. In this configuration, the 60° fused silica prism and the index-coupling fluid was used to suppress the incoherent top surface reflections as has been illuminated in our previous work (Lv et al., 2015). The insets of Fig. 3 (c) and (e) have shown these two kinds of configuration of SE measurement. The fabrication of solar cells just followed the process of s_4. After $CdCl_2$ annealing, the CdTe layer was etched for 15 s. Then Cu_xTe was deposited as back-contact layer via vacuum co-evaporation of Cu and Te with optimal parameters. After annealing with Ar at 250 °C, the solar cells were completed with conductive silver painting. The details of preparation of each layer are listed in Table 1. Finally, the EQE spectrum of solar cell was obtained by quantum efficiency measurement system (PV Measurements, QEX10) and the conversion efficiency was measured by I-V test system (Newport, PVIV).

3. Results and discussions

During CdTe deposition, alloying between CdS and CdTe at the CdS/CdTe heterojunction is a function of the growth temperature. Here the phase and structural properties of CdS_yTe_x compound that has been heated up to 570 °C are studied on the basis of XRD scanning. Instead of glancing incidence XRD, a conventional XRD scan is carried out to characterize the heterojunction with different CdTe thickness as is showed in Fig. 1(b). The characteristic peak position of each sample is listed in Table 2. At the same time, the AFM images of these samples are showed in Fig. 2(a). As increasing amounts of CdTe are deposited on the surface, the morphological feature of large grain appears gradually in the AFM images. Sample s_1 is a glass substrate coated with CdS monolayer film showing the characteristic peak of hexagonal (002) and (103) of CdS only. Meanwhile, sample s_4 which goes through the entire deposition process shows the characteristic peaks of CdTe with cubic phase, for a large amount of CdTe are deposited on the heterojunction as the surface layer. For the case of s_2, the CdTe depositing occurred during the substrate temperature increasing from 440 °C to 530 °C, and then the CdS/CdTe heterojunction experiences a heating process up to 570 °C with a fixed CdTe thickness. With the help of high temperature process, the recrystallization occurred and more characteristic peaks of hexagonal CdS such as (100) and (101) have been detected as is showed by XRD pattern of s_2. There are three features in the XRD pattern of s_2: Firstly, both of CdS and CdTe exhibit the characteristic peaks in one XRD pattern for the CdTe is not thick enough to cover the signal of CdS. Secondly, the characteristic peaks of CdS and CdTe exhibit a little shifting and split comparing with the corresponding peaks of s_1 and s_4. We attribute this shifting to the formation of the CdS-like alloy $CdS_{1-y}Te_y$ and