Analysis of heterointerface recombination by $Zn_{1-x}Mg_xO$ for window layer of $Cu(In,Ga)Se_2$ solar cells

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Abstract

An adjustment of a conduction band offset (CBO) of a window/absorber heterointerface is important for high efficiency $Cu(In,Ga)Se_2$ (CIGS) solar cells. In this study, the heterointerface recombination was characterized by the reduction of the thickness of a CdS layer and the adjustment of a CBO value by a $Zn_{1-x}Mg_xO$ (ZMO) layer. In ZnO/CdS/CIGS solar cells, open-circuit voltage (V_{oc}) and shunt resistance (R_{sh}) decreased with reducing the CdS thickness. In constant, significant reductions of V_{oc} and R_{sh} were not observed in ZMO/CdS/CIGS solar cells. With decreasing the CdS thickness, the CBO of (ZnO or ZMO)/CIGS become dominant for recombination. Also, the dominant mechanisms of recombination of the CIGS solar cells are discussed by the estimation of an activation energy obtained from temperature-dependent current–voltage measurements.
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Keywords: $Zn_{1-x}Mg_xO$; $Cu(In,Ga)Se_2$; Recombination mechanism

1. Introduction

Chalcopyrite thin-film solar cells based on the absorber material of $Cu(In,Ga)Se_2$ (CIGS) have attained solar cell conversion efficiency close to 20% at laboratory scale (Contreras et al., 2005). The band gap energy (E_g) of the champion solar cell absorber was about 1.1 eV. This value is relatively low in comparison with an ideal E_g of solar cells, i.e., 1.4 eV. One of the important reasons for the degradation at 1.4 eV CIGS solar cell is mismatching of a conduction band offset (CBO) of CdS/CIGS layers. Theoretically, if the conduction band level of the window layer is lower than that of CIGS (negative CBO), an interface recombination between window/CIGS layers become dominant (Minemoto et al., 2001). In the laboratory scale, $Zn_{1-x}Mg_xO$ (ZMO) was researched for a novel window layer to adjust the CBO of window/CIGS layers to positive.

The E_g of ZMO (E_{gZMO}) can be controlled by Mg contents without large shifting of valence band maximum. Thus, the CBO can be controlled precisely; the CBO increases in proportion to the E_{gZMO}. A high conversion efficiency of CIGS solar cells with the ZMO window layer was reported (Hultqvist et al., 2007), indicating that the ZMO window layer is suitable for CIGS solar cell.

In this study, the effects of the band diagram of window/ buffer/CIGS layers and the buffer layer thickness on the electronic properties of CIGS solar cells were discussed. To change the band alignment, ZnO or ZMO were used as the window layer. Also, a CdS film was used as a buffer layer and its thickness was varied from 0 to 80 nm.

2. Experimental

Fig. 1 shows the schematic structure of the CIGS solar cell with different heterointerface structures. The process of our solar cell fabrication is as follows: CIGS films were deposited on Mo/soda-lime glass (SLG) substrates by

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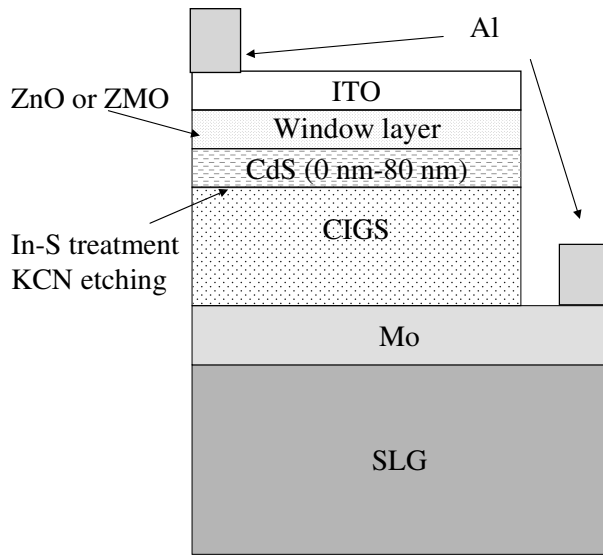 E-mail address: ro007038@se.ritsumei.ac.jp (K. Tanaka).

Fig. 1. Structure of the CIGS solar cell with different heterointerface structures.

three-stage evaporation process (Negami et al., 2001). KCN-etching (1 wt.% for 1 min), In–S treatment (Hashimoto et al., 2000) and the annealing at 250 °C for 30 min in N_2 atmosphere were performed for the CIGS surface cleaning and modification. The CdS layers with the thickness of 0, 10, 30, 50 and 80 nm were deposited on the CIGS films (Hashimoto et al., 2001). Then, ZnO or ZMO as the window layer, ITO as the transparent conductive oxide and Al as the front electrode were deposited. The CBO was determined from the E_g of CIGS (E_{gCIGS}) and ZMO (E_{gZMO}) layers with the assumption that the valence band offset between CIGS and ZMO layers is the fixed value of 2.30 eV (Minemoto et al., 2001) in this composition range of both layers. The E_{gCIGS} was 1.18 eV, which was deduced by Ga/(In + Ga) ratio of 0.24 measured by energy-dispersive X-ray spectroscopy. The E_{gZMO} was 3.68 eV (Mg/(Zn + Mg) = 0.20) which was determined by transmittance spectra. Thus, the CBO value was determined to +0.20 eV. Current–voltage measurements of the devices were measured under AM 1.5 and 100 mW/cm^2 illumination at 25 °C.

The dominant mechanism of recombination (interface or space charge region) was analyzed by the activation energy of recombination (E_a) obtained from the temperature dependent current–voltage (TIV) measurement (Turch et al., 2002). The TIV measurements were performed using a cryostat cooled with liquid-N$_2$ and heated using a heater controlled by a Cryocon Model 34 temperature controller. A xenon lamp serves for illuminating the sample. The intensity of illumination was controlled to 1 sun by adjusting the short-circuit current (J_{sc}) of the cell to be the identical J_{sc} under 1 sun created with solar simulator already calibrated with the standard solar cell. Four measurements were performed in the temperature range at 320–250 K. The evaluation of the TIV measurements uses the J_{sc} and the open-circuit voltage (V_{oc}) at the various temperatures.

The independence of J_{sc} and V_{oc} is given by Turch et al. (2002)

$$J_{sc} = J_0 \exp\left(\frac{qV_{oc}}{AkT}\right) = J_{00}\exp\left(\frac{qV_{oc}}{AkT}\right)\exp\left(\frac{-E_a}{AkT}\right) \quad (1)$$

where A and J_0 are ideality factor and saturation current density of the diode, kT/q is the thermal voltage, J_{00} is a weakly temperature-dependent prefactor, and E_a is the activation energy of recombination. Resolving Eq (1) for V_{oc} yields

$$V_{oc} = \frac{E_a}{q} - \frac{AkT}{q}\ln\left(\frac{J_{00}}{J_{sc}}\right) \quad (2)$$

If A, J_{sc}, and J_{00} are independent of temperature T, a plot of V_{oc} versus T should yield a straight line and the extrapolation of this line to $T \sim 0$ K gives the activation energy of recombination. If $E_a < E_{gCIGS}$, dominant recombination path is heterointerface. If $E_a \sim E_{gCIGS}$, dominant recombination path is space charge region (SCR).

3. Results and discussion

Fig. 2 shows the (a) V_{oc} and the (b) R_{sh} of the ZnO/CdS/CIGS and ZMO/CdS/CIGS solar cells as a function of thickness of CdS. In ZnO/CdS/CIGS solar cells, V_{oc} and R_{sh} decreased with reducing the thickness of the CdS layer. This is because that the CdS layer act as a buffer layer for the sputtering damage on the CIGS surface during the window layer deposition. If the thickness of the CdS layer is too thin, the defects which act as the site of the interface recombination are generated and also the heterojunction
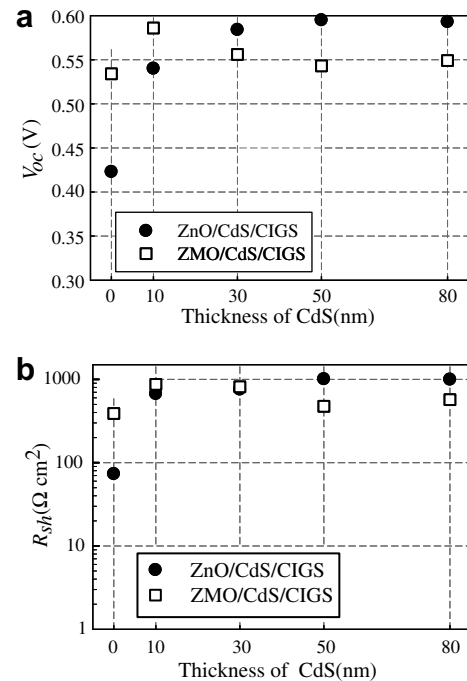

Fig. 2. (a) V_{oc} and (b) R_{sh} of ZnO/CdS/CIGS and ZMO/CdS/CIGS solar cells as a function of thickness of CdS.
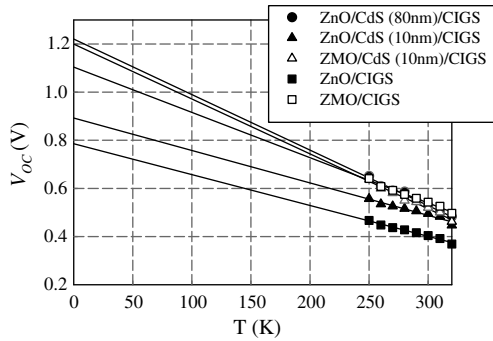
Fig. 3. V_{oc} of ZnO/CdS/CIGS, ZnO/CdS (10 nm)/CIGS (CBO: −0.28 eV) and ZMO/CdS (10 nm)/CIGS (CBO: +0.20 eV), ZnO/CIGS (CBO: −0.28 eV) and ZMO/CIGS (CBO: +0.20 eV) solar cells as a function of temperature.

is formed by ZnO and CIGS which have a negative CBO value increasing the interface recombination. In contrast to ZnO/CdS/CIGS solar cells, significant reductions of V_{oc} and R_{sh} were not observed in ZMO/CdS/CIGS solar cells. The reduction of the CdS thickness should increase the defects at the CIGS surface; however, the heterojunction is formed by ZMO and CIGS which have a positive CBO value reducing the interface recombination. With decreasing the thickness of the CdS layer, the CBO of the window/CIGS layers become dominant for recombination than the CBO of the CdS/CIGS layers.

Fig. 3 shows the V_{oc} of ZnO/CdS/CIGS, ZnO/thin-CdS (10 nm)/CIGS (CBO: −0.28 eV) and ZMO/thin-CdS (10 nm)/CIGS (CBO: +0.20 eV), ZnO/CIGS (CBO: −0.28 eV) and ZMO/CIGS (CBO: +0.20 eV) solar cells as a function of temperature. The extrapolated V_{oc} values at 0 K, corresponding E_a/q, for CdS/CIGS, ZnO/thin-CdS (10 nm)/CIGS, ZMO/thin-CdS (10 nm)/CIGS, ZnO/CIGS and ZMO/CIGS are 1.22, 0.89, 1.20, 0.786 and 1.12 V, respectively. In the ZnO/CdS/CIGS solar cell, the dominant recombination path is SCR because E_a is almost equal to E_{gCIGS}. However, the reduction of the CdS thickness to 0 nm or 10 nm, E_a of the ZnO/thin-CdS (10 nm)/CIGS and ZnO/CIGS solar cell is lower than E_{gCIGS}, indicating that the dominant recombination path is the ZnO/CIGS heterointerface. In contrast, the adjustment of the CBO with ZMO makes the E_a of ZMO/thin-CdS (10 nm)/CIGS and ZMO/CIGS solar cells to almost equal to E_{gCIGS}, indicating that the dominant recombination path is SCR. These results indicate that the adjustment of

the CBO affected to the recombination paths and the ZMO window layer is effective to reduce the interface recombination in the CIGS solar cells.

4. Conclusions

The heterointerface recombination in the CIGS solar cells was characterized by the reduction of the thickness of a CdS layer and the adjustment of the CBO of window/CIGS layers by ZMO. In the ZnO/CIGS solar cell, V_{oc} and R_{sh} decreased with reducing the thickness of the CdS layer. In contrast, V_{oc} and R_{sh} did not decrease in the ZMO/CIGS solar cell. With decreasing the CdS thickness, the CBO of (ZnO or ZMO)/CIGS become dominant for recombination. The E_a of the ZnO/thin-CdS (10 nm)/CIGS solar cell is lower than the E_{gCIGS}, indicating that the dominant recombination path is heterointerface. In contrast, the E_a of the ZMO/thin-CdS (10 nm)/CIGS solar cell is almost equal to E_{gCIGS}, indicating that the dominant recombination path became SCR. These results indicate that the adjustment of the CBO affected to the recombination paths and the ZMO window layer is effective to reduce the interface recombination in the CIGS solar cells.

Acknowledgements

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