# Analysis of Recombination Property of CIGS Solar Cells with Gradient Bandgap

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### Abstract

Cu(In,Ga)Se<sub>2</sub> (CIGS) layer for the state-of-the-art CIGS solar cell is generally grown by a three-stage possess, resulting in double graded material with varying [Ga]/([Ga] + [In]) (GGI) ratios across the thickness. Optimizing the gradient bandgap profile is of importance for obtaining high efficiency CIGS solar cells. In this work, we investigated the effect of the notch (*i.e.*, the position of the minimum bandgap) on the recombination property of the CIGS solar cell. The results show that when the notch moved from the front side to the bulk, the surface recombination drastically reduces. The optimized notch is 0.4  $\mu$ m for a 2  $\mu$ m-thick CIGS solar cell.

### 1. Introduction

Thanks to the high absorption coefficient, good stability, tunable bandgap, and low consumption of energy in the production process, Cu(In,Ga)Se<sub>2</sub> (CIGS) solar cells possess great potential in the photovoltaic market. CIGS layer is generally grown by three-stage method, resulting in double graded material with varying [Ga]/([Ga] + [In]) (GGI) ratios across the thickness (i.e., higher GGIs at the back and at the front, and lower GGIs in the middle). The Ga-grading has functions: (1) a back surface grading resulting in a gradually decrease of conduction band (CB) position, which assists the drift of free electrons to the front of the absorber, and (2) a front surface grading aiming at a specific alignment of the CBs at the CdS/CIGS interface to avoid a large barrier for electrons at the junction [1]. The nature of the Ga grading, for example front or back grading, slope, single or double grading, and position of the GGI minimum (typically referred as the "notch"), influences the solar cell parameters and therefore the final device performance. In this work, the notch was intentionally moved from 0.2, 0.4 to 0.6 µm (from the front of the CIGS layer) with keeping the constant height of the notch, and the recombination properties of these samples are analyzed in details.

# 2. Experimental method

CIGS thin films were grown on Mo-coated soda-lime glass substrates by a three-stage process using a molecular beam epitaxy system. We dedicatedly controlled the 2<sup>nd</sup> step of the three-stage process, and obtained three samples with different notch of 0.2, 0.4 and 0.6  $\mu$ m from the front of the CIGS layers (confirmed by the secondary ion mass spectrometry measurement). They are referred as samples 1, 2 and 3, respectively. The CdS layers were deposited on the CIGS film by chemical bath deposition (CBD) in order to form cell structures. Then, highly resistive i-ZnO and n-ZnO:Al layers were successively deposited by radio frequency magnetron sputtering method.

# 3. Results and discussion

Table I shows the photovoltaic parameters of samples 1, 2 and 3. The power conversion efficiency of sample 1 is 19.1%, which is the lowest one among the three samples. This is ascribed to the low short circuit current ( $J_{sc}$ ) and the low open-circuit voltage ( $V_{oc}$ ). Sample 2 has the best device performance with high  $V_{oc}$  and improved  $J_{sc}$ . The device performance of sample 3 is slightly lower than sample 2, mainly caused by the lowered  $V_{oc}$ .

Table I Photovoltaic parameters of samples 1, 2 and 3.

Sample	η	J <sub>SC</sub>	Voc	FF
	(%)	(mA/cm <sup>2</sup> )	(V)	
1	19.1	32.7	0.742	0.79
2	19.9	33.3	0.756	0.79
3	19.7	33.5	0.748	0.79

To understand the device physics of CIGS solar cells made by the three samples, we analyzed the recombination properties of them using the model reported by Li *et al* [2]. Fig. 1 shows the plots of light-intensity dependent opencircuit voltage (Suns-V<sub>oc</sub>) of samples 1, 2, and 3. Fig. 2 shows the plots of temperature dependent open-circuit voltage (V<sub>oc</sub>-T) of samples 1, 2, and 3. By combing the Sun-V<sub>oc</sub> and V<sub>oc</sub>-T results, the recombination parameters can be extracted. The recombination velocity of the (minority) carriers at the bias voltage can be classified into three regions, *i.e.*, the quasineutral region (QNR), the space charge (depletion) region (SCR), and the buffer/CIGS interface.  $R_0^b$ ,  $R_0^d$  and  $R_0^i$  are the recombination velocities when the bias voltage equals zero, at the QNR, SCR, and buffer/CIGS interface, respectively, where the minority carrier in these three regions are considered to be electrons, both electrons and holes (the number of electrons is approximately the same as that of holes), and holes, respectively. The derived recombination parameters are shown in Table II.



Fig. 2  $V_{oc}$ -T plots for samples 1, 2 and 3

Table II Recombination parameters of samples 1, 2 and 3.

ıple	$E_a$	$R_0^i$	$R_0^d$	$R_0^b$	$R_0^i/R_0^b$
San	(eV)	$(cm^{-2}s^{-1})$	$(cm^{-2}s^{-1})$	$(cm^{-2}s^{-1})$	
1	1.21	$2.5 \times 10^{4}$	5.0×10 <sup>9</sup>	3.5×10 <sup>4</sup>	0.70
2	1.24	$1.1 \times 10^{4}$	8.3×10 <sup>9</sup>	$2.8 \times 10^{4}$	0.40
3	1.24	9.3×10 <sup>3</sup>	2.3×10 <sup>9</sup>	5.0×10 <sup>4</sup>	0.19

From the listed recombination parameters, we can see that the sample 1 has the highest  $R_0^i$ , suggesting that the surface recombination in sample 1 is severe. Although no clear trend for  $R_0^b$  is found for the three samples, the ratio of  $R_0^i$ and  $R_0^b$  ( $R_0^i/R_0^b$ ) has a clear difference. For sample 1, the  $R_0^i/R_0^b$  is as high as 0.70, which is much larger than that of samples 2 and 3. This suggests that the surface recombination is drastically suppressed in samples 2 and 3. These results are also consistent with the estimated activation energy (E<sub>a</sub>). The E<sub>a</sub> of sample 1 is 1.21 eV, which is lower than its bandgap (1.25 eV), suggesting that the dominant recombination is surface recombination. On the other hand, the E<sub>a</sub> of samples 2 and 3 is 1.24 eV, which is nearly equals to its bandgap (1.25 eV), indicating a dominant recombination of bulk recombination.

It was reported that the device performance is dependent on both the defect density and the relative position between the notch and the SCR edge [3,4]. In the case of low defect density, when the notch is inside the SCR, the doublegradient bandgap is effective for achieving high efficiency. However, when the notch is outside the SCR, the gradient bandgap from the notch to the CIGS surface acts as a barrier that impedes the collection of photo-generated electrons, thereby increasing the recombination rate and decreasing cell efficiency. On the other hand, in the case of high defect density, to decrease the recombination current and improve the efficiency, a more positive gradient from the back contact to the surface is needed, namely, either a double-graded profile with strong BSF (for the notch inside the SCR).

The defect densities in samples 2 and 3 are assumed to  $10^{14}$  cm<sup>3</sup>, and the depletion width is derived to be 0.33 and 0.41 µm. Clearly, the notch of 0.4 µm (corresponding to sample 2) is near to the edge of the SCR, while the notch of 0.6 µm (corresponding to sample 3) is outside of the edge of the SCR. Therefore, the double-gradient profile is favorable for sample 2. However, the double gradient profile is not helpful to sample 3, because the gradient bandgap from the notch to the CIGS surface acts as a barrier that impedes the collection of photo-generated electrons, therefore increasing the recombination rate. This is consistent with the device performance listed in Table I.

#### **3.** Conclusions

 $2 \mu m$  CIGS samples with different notches were prepared, and the recombination properties were analyzed for CIGS solar cells. When the notch is moved from the near surface region to the bulk (*i.e.*, from 0.2 to 0.4 µm), the surface recombination is drastically reduced. With further moving the notch from 0.4 to 0.6 µm, although the surface recombination is also reduced, the notch is then located outside of the SCR. In this case, the front gradient bandgap acts as a barrier, impeding the photo-carrier collection, and therefore deteriorate the device performance. This study shed the light on how to design the bandgap profile for fabricating high efficiency CIGS solar cells.

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