### Analysis for Non-radiative Recombination and Resistance Losses in Chalcopyrite and Kesterite Solar Cells

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### Abstract

Efficiency potential of future generation solar cells such as wide bandgap CIGSe(CuInGaSe<sub>2</sub>), CIGS(Cu-InGaS<sub>2</sub>). CZTS (Cu<sub>2</sub>ZnSnS<sub>4</sub>) and **CZTSSe** (Cu<sub>2</sub>ZnSn(S.Se)<sub>4</sub>) solar cells is discussed based on external radiative efficiency (ERE), and non-radiative recombination and resistance losses. The analytical results show CIGSe, CIGS, and CZTS(Se) solar cells have efficiency potential of 27.2%, 25%, and 22%, respectively. Regarding wide-gap CIGSe solar cells, lattice mismatching between CIGSe active layer and buffer layer, and increase in non-radiative recombination center density with increase in bandgap energy of CIGSe materials and solar cells are suggested as non-radiative recombination losses in wide-gap CIGSe solar cells. Regarding CZTS(Se) solar cells, existence of unknown recombination loss and resistance loss due to low carrier mobility compared to CIGSe materials are shown in addition to surface and bulk recombination losses.

### 1. Introduction

Thin-film chalcopyrites and kesterites such as CIGSe (CuInGaSe<sub>2</sub>), CIGS (CuInGaS<sub>2</sub>)) and CZTS (Cu<sub>2</sub>ZnSnS<sub>4</sub>), CZTSSe (Cu<sub>2</sub>ZnSn(S,Se)<sub>4</sub>) can potentially achieve high efficiency because of their direct bandgaps [1-3]. Meanwhile, the low areal manufacturing cost of these materials make them very cost competitive to other photovoltaic technologies. Nevertheless, state-of-the-art efficiencies of those solar cells are much lower than their efficiency limits, as shown in Fig. 1. As a result, identifying the loss mechanisms in those materials and solar cell devices is important in order to realize higher efficiency.



Fig.1. Efficiency potential and present efficiencies of CIGSe, CIGS, CZTSe and CZTS solar cells in comparison with those of GaAs and Si solar cells.

In this paper, we will quantify the efficiency loss of widegap CIGSe, CIGS and CZTS(Se) solar cells by surveying their external radiative efficiency (ERE), and resistance loss. These discussions lead to the contributions of the loss from non-radiative recombination and the resistance losses.

### 2. Efficiency Loss of Solar Cells

We analyzes the efficiency loss by using external radiative efficiency (ERE) as expressed by

 $V_{oc} = V_{oc,rad} + (kT/q)\ln(ERE), (1)$ 

where the second term shows non-radiative voltage loss, and  $V_{oc, rad}$  is radiative open-circuit voltage and is given by [1-6],

 $V_{oc, rad} = (kT/q)ln(J_L(V_{oc, rad})/J_{0, rad} + 1), (2)$ where  $J_L(V_{oc, rad})$  is photo-current at open-circuit in the case of only radiative recombination and  $J_{0, rad}$  is saturation current density in the case of only radiative recombination.

Fill factor is dependent upon  $V_{oc}$  and ideal fill factor  $FF_0$  used in the calculation is empirically expressed by [7],

$$FF_0 = [v_{oc} - \ln(v_{oc} + 0.72)]/(v_{oc} + 1), (3)$$

where  $v_{oc}$  is normalized open-circuit voltage and is given by  $v_{oc} = V_{oc}/(nkT/q)$ , (4)

The fill factor is decreased as in crease in series resistance  $R_s$  and decrease in shunt resistance  $R_{sh}$  of solar cell increases and approximated by

 $FF \approx FF_0(1-r_s)(1-1/r_{sh}) \approx FF_0(1-r_s-1/r_{sh}), (5)$ 

where  $r_s$  and  $r_{sh}$  are normalized series resistance and normalized shunt resistance , respectively and given by

 $r_s = Rs/R_{CH}$ , (6)

$$\mathbf{r}_{\rm sh} = \mathbf{R}_{\rm sh} / \mathbf{R}_{\rm CH,} (7)$$

The characteristic resistance  $R_{CH}$  is expressed by [7]  $P_{CH} = V/I_{-}(8)$ 

 $R_{\rm CH} = V_{\rm oc}/I_{\rm sc}.$  (8)

In the calculation, highest values obtained were used as Jsc. Voc and FF were calculated by equations (1)-(8) and conversion efficiency potential of various solar cells were calculated as a function of ERE.

# **3.** Analysis for Efficiency Potential of CIGSe, CIGS, CZTS(Se) Solar Cells

Figure 2 shows calculated efficiency of CIGSe, CIGS and CZTS(Se) solar cells as a function of ERE and efficiency values for those solar cells ever reported [8-11]. As shown in Fig. 2, CIGSe solar cells have efficiency potential of 27.2% with normalized resistance rs+1/rsh of 0.025 and by improving in ERE into 30% from around 3%.

Although high efficiency of 23.35% has been attained with the CIGSe solar cells [11], wide-gap CIGSe solar cells has shown much lower efficiency with 16.9% [12] due to

larger voltage loss. As shown in Fig. 2, CIGS solar cells have efficiency potential of 25% with normalized resistance rs+1/rsh of 0.025 and by improving in ERE into 10% from around 0.05%.

CZTS and CZTSSe solar cells consists of earth abundant elements and therefore have the potential of achieving very low areal cost as pointed out by Katagiri et al., [13]. However, compared to CIGSe solar cells, CZTSSe solar cells have much lower efficiency (12.6%) [11]. As shown in Fig.2, the CZTS(Se) solar cells can achieve a efficiency of about 22% by realizing a  $r_s + 1/r_{sh}$  value of 0.05 and a ERE value over 1%.



Fig.2. Calculated efficiency of CIGSe, CIGS and CZTS(Se) solar cells as a function of ERE and efficiency values for those solar cells ever reported.

### 4. Non-Radiative Recombination Loss in CIGSe, CIGS and CZTS(Se) Solar Cells

Figure 3 shows correlations between experimental values of minority-carrier lifetime and calculated values by considering deep-level (DL) limited non-radiative recombination lifetime  $\tau_{nonrad}$  in addition to lattice mismatching (LM) of CdS layer and CIGSe active layer as a function of bandgap energy in CIGSe solar cells. Increase in density of non-radiative recombination centers with increase in Eg of CIGSe materials is thought to be another reason.



Fig.3. Correlations between experimental values of minoritycarrier lifetime and calculated values by considering deeplevel (DL) limited non-radiative recombination lifetime  $\tau_{nonrad}$ in addition to lattice mismatching (LM) of CdS layer and CIGSe active layer as a function of bandgap energy in CIGSe solar cells.

## 5. Resistance Losses in CIGSe, CIGS and CZTS(Se) Solar Cells

Figure 4 shows changes in fill factor FF of CIGSe, CIGS and CZTS(Se) solar cells [8-12] as a function resistance loss  $r_s+1/r_{sh}$  estimated by using (6) and external radiative efficiency (ERE) estimated by using (2) in comparison with calculated results for effects of resistance loss and ERE upon FF calculated by using (1)-(6). Especially, problems of the CZTS(Se) solar cells are lower ERE and higher resistance loss compared to those of CIGSe solar cells. It is known that the CZTS and CZTSe materials have lower carrier mobility compared to CI(G)Se materials because of higher effective mass of electron and hole  $m_e^*=0.19$  and  $m_h^*=0.47$  (Person, 2010) in CZTS,  $m_e^*=0.08$  and  $m_h^*=0.255$  [15] in CZTSe compared to  $m_e^*=0.09$  and  $m_h^*=0.092$  [16] in CISe.



Fig.4. Changes in fill factor FF of CIGSe, CIGS and CZTS(Se) solar cells as a function resistance loss estimated by using eq. (6) and external radiative efficiency (ERE) estimated by using eq. (2) in comparison with calculated results for effects of resistance loss and ERE upon FF calculated by using eq.(1)-(6).

### 6. Summary

Potential efficiencies of CIGSe, CIGS and CZTS(Se) solar cells were discussed by using non-radiative recombination and resistance losses.

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