

# STRUCTURE OPTIMIZATION FOR A HIGH EFFICIENCY CIGS SOLAR CELL

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## ABSTRACT

This paper uses numerical simulation to study the effects of Ga concentration profile on the performance of  $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$  (CIGS) solar cell, including the effects of acceptor type Cu antisite defects whose concentration depends on Ga composition. These defects are the dominant deep traps in the CIGS material system. The concentration and spatial distribution of these traps affect the solar cell performance. The trap density model used in this work follows experimental reports in the literature. The trap concentration is  $4.3 \times 10^{15} \text{ cm}^{-3}$  for CIS ( $x=0$ ) and decreases to  $1.2 \times 10^{14} \text{ cm}^{-3}$  when the Ga mole fraction,  $x$ , reaches 0.24. The trap concentration increases exponentially above  $x=0.30$ . Applying this model to solar cells with uniform composition absorber layer predicts that the power conversion efficiency reaches a maximum value of 14.6%, at  $x=0.24$  and decreases with increasing Ga content above  $x=0.30$ , in good agreement with experimental results. When this model is used to simulate a solar cell where the Ga composition in the absorber layer is graded, the electric field produced by compositional grading improves the efficiency because of the reduced recombination rate. However compositions where  $x$  is higher than 0.45 lead to a drop in performance due to the high trap density and shorter lifetime. Both grading from the CdS/CIGS interface (forward grading), and back grading where the Ga concentration increases from the junction into the CIGS film were studied. In forward grading, the maximum efficiency is achieved when the Ga concentration is graded such that  $x$  decreases from 0.35 at the surface to 0.24 at  $0.4 \mu\text{m}$  into the CIGS film. In back grading, the maximum efficiency is achieved when  $x$  increases from 0.45 at the surface to 0.5 at  $0.4 \mu\text{m}$  into the CIGS film.

## INTRODUCTION

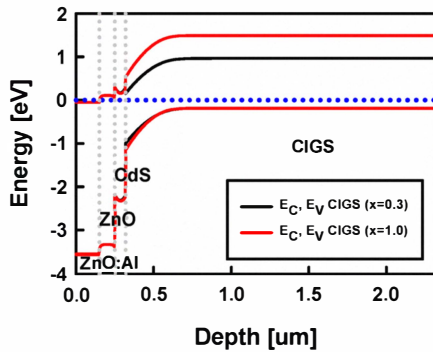
CIGS is the one of the most promising absorber materials for thin film photovoltaics (PV) because it is a direct bandgap ( $E_g$ ) semiconductor with a high absorption coefficient. Moreover, its bandgap can be tuned over a wide range (1.0 to 1.68 eV) by varying the Ga concentration in the film [1]. According to detailed balance limit calculations, the maximum efficiency of a single junction CIGS PV cell should be obtained when its band gap is near 1.4 eV, which corresponds to a Ga mole fraction of about 0.60. However, the reported maximum efficiency of CIGS PV cells is achieved when the Ga composition is about 0.30, corresponding to an  $E_g$  of 1.1 eV [2]. The experimental efficiencies of CIGS PV cells do

not increase for Ga concentrations above 0.30. This discrepancy between the real devices and the expected behavior of efficiency with increasing Ga concentration is explained by the dependence of trap density on Ga concentration [3]. The major deep trap in CIGS is known as the Cu antisite defect whose energy is located  $\sim 0.3$  eV above the valence band. The concentration of these traps reaches a minimum value at  $x \sim 0.30$  and coincides with the Ga concentration in the highest efficiency solar cells. Unfortunately, the trap concentration increases exponentially above 0.30 negating any expected increase in efficiency due to an increase in the band gap [3].

One of merits of a tunable bandgap is that the band structure of the absorber can be engineered to improve the transport properties of photo-generated carriers. Among the reported CIGS growth processes, the NREL three step process shows especially high performance. This process involves the regrowth of the CIGS films by the high temperature ( $590\text{--}600^\circ\text{C}$ ) deposition of  $\text{Cu}_x\text{Se}$  on an  $(\text{In,Ga})\text{Se}_2$  film. This process not only increases the grain size but also forms a Ga composition gradient through the film. This grading of the Ga composition induces electric fields in the charge neutral region which improves the transport of carriers. However, until now, models only studied the transport effects without taking into consideration the effects of the increase in trap concentration due to increasing Ga concentration [4]. This paper investigate the effects of grading the Ga concentration near the junction while including the reported Ga-related trap density and finding the optimum Ga profile [5]. Only the Cu antisite defect is considered in this work because it is the major deep trap in the bulk CIGS absorber.

## DEVICE SIMULATION DETAILS

The structure of the CIGS PV cell used for simulation consists of 150 nm thick n-type ZnO:Al, 100 nm thick n-type ZnO, and 70 nm n-type CdS all on a  $2 \mu\text{m}$  thick p-type CIGS. The Ga concentration in the film is varied as a function of position by varying  $x$  in  $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ . As examples, the band diagram for solar cells with a CIGS film where  $x=0.3$  and  $x=1.0$  (CGS) are shown in Fig. 1 at thermal equilibrium.



**Figure 1** Energy band diagram for ungraded  $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$  PV cells.

The physical parameters used in the simulations are shown in Table 1. Due to the lack of data on the compositional dependence of some of the physical parameters, the dielectric constant and electron affinity are assumed to vary linearly with Ga composition and mobility and doping concentration are assumed to be independent of composition. The absorption coefficient as a function of Ga composition is adopted from Paulson's work [5].

	CIGS	CdS	ZnO	ZnO:Al
Dielectric constant [6]	x=0: 15.1 x=1: 10.1	8.28	7.8	7.8
Electron affinity [eV] [7]	x=0: 4.57 x=1: 3.98	4.24	4.25	4.25
Lifetime [ $\mu\text{s}$ ] [8]	0.03	3	3	3
Mobility [ $\text{cm}^2/\text{V}\cdot\text{s}$ ] [6]	150	100	45	45
Doping [ $\text{cm}^{-3}$ ] [3]	p-type $1 \times 10^{16}$	n-type $5 \times 10^{15}$	n-type $1 \times 10^{17}$	n-type $5 \times 10^{19}$

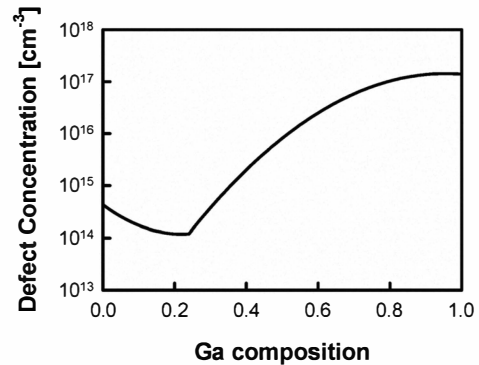
**Table 1** Physical parameters used for the simulation.

DESSIS, a commercially available 2D hydrodynamic drift and diffusion package was used for numerical simulation. DESSIS was linked to OPTIK, a software package that simulates light absorption and carrier generation in response to AM1.5 exposure.

## RESULTS AND DISCUSSION

### Trap model and cells with uniform composition

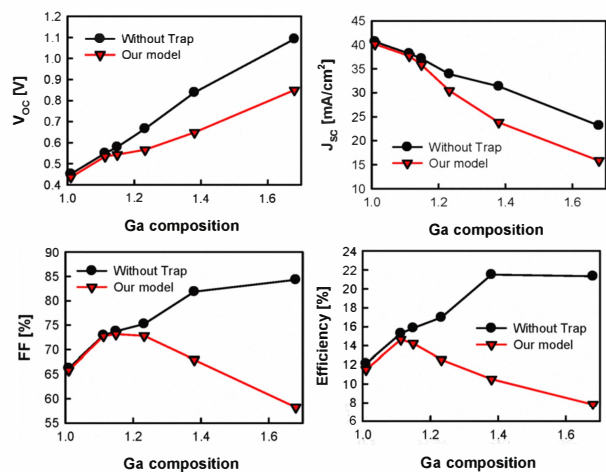
In the CIGS literature, two characteristic traps are reported as major deep traps: the Cu antisite (acceptor like) and the Cu interstitial or the In antisite (donor like) defects. The Cu antisite is particularly important because of its higher activation energy ( $\sim 0.3$  eV) and dependency on Ga concentration. Because it is an acceptor-like trap in p-type CIGS, it is the dominant trap in the bulk. Thus, it is reasonable to consider only this defect when studying grading in the bulk. Based on the work of Hanna et al, a trap concentration model, shown in Fig. 2, was constructed [3].



**Figure 2** Variation of the defect concentration with Ga composition (x) used to model the interdependence of these variables in CIGS films.

In this model, the trap concentration is  $4.3 \times 10^{15} \text{ cm}^{-3}$  at  $x=0$  and decreases to  $1.2 \times 10^{14} \text{ cm}^{-3}$  at  $x=0.24$ . Above  $x=0.3$ , trap concentration increases sharply, reaching  $1 \times 10^{17} \text{ cm}^{-3}$  at  $x=1$ . Most of Hanna's work is based on single stage growth and, consequently, the trap density is higher than that have been achieved with the three stage NREL process, particularly at the minimum ( $x=0.3$ ). The trap density values for films grown by the NREL process at  $x=0.3$  was used in this work, but the values corresponding to Hanna's results at  $x=1$  were retained. The activation energy of traps is 0.3 eV above valence band and is constant for all Ga compositions.

Fig. 3 shows a comparison of the PV figures of merit for ungraded cells with and without traps where the trap dependence on Ga concentration follows the model shown in Fig. 2.



**Figure 3** A comparison between the PV figures of merit of perfect trap-free CIGS PV cells and solar cells with traps concentrations given by Fig. 2.

Without traps, the CIGS solar cell has a maximum efficiency at  $x=0.66$ . At this value,  $E_g$  is 1.38 eV, in good agreement with that predicted from the Shockley-Queisser detailed balance calculations. With traps, the efficiency increases with  $E_g$  until  $x=0.3$ , but then decreases to 7.8% at  $x=1$ . At high Ga concentrations, the increased trap density causes the short circuit current ( $J_{sc}$ ) to decrease sharply, degrading the power conversion efficiency. The current flow mechanism changes from drift-diffusion to Shockley-Reed-Hall recombination at high Ga and trap concentrations. At  $x=1.0$ , the open circuit voltage ( $V_{oc}$ ) is 0.85 V. All these predictions are in good agreement with measurements reported in literature [9]. The validated model can now be used to explore how grading Ga concentration near the junction would affect the solar cell figures of merit.

### Forward grading

Previous modeling research has suggested that forward Ga composition grading is the most effective way to increase both  $V_{oc}$  and the fill factor (FF) [4]. This means that increasing the bandgap at the CIGS/CdS interface dominates over the effects of increased trap density. However, experimental data does not demonstrate an unambiguous improvement by forward grading. This is in contrast to the improvement by backward grading, which is experimentally obvious. How to grade the Ga composition near the junction is unclear because of the competing effects of increasing the bandgap and increasing the trap density at the interface by increasing the Ga composition. Thus the effect of Ga forward grading should be analyzed carefully.

Forward grading induces an electric field which retards the transport of electrons. Thus, the grading should be confined to the space charge region (SCR) where the field caused by the junction can overcome the field due to grading. This allows photo-generated electron hole pairs to be separated without recombination. According to the DESSIS simulations, the width of the SCR on the CIGS side of the junction is  $\sim 0.38 \mu\text{m}$ . The width of the forward grading is therefore taken to be  $0.38 \mu\text{m}$ .

Six different structures are shown at the top of Fig. 4. The middle and bottom figures show the performance of these devices. The efficiency reaches a maximum value when the Ga concentration at the junction reaches  $x=0.35$  and then decreases with increasing Ga composition. The initial efficiency increase is primarily due to an increase in  $E_g$  and consequently, an increase in  $V_{oc}$ , and to a lesser extent due to a small increase in  $J_{sc}$ . The increase of  $J_{sc}$  is believed to be due to a reduction of the conduction band offset at the interface between the CIGS and the CdS films. As shown in Fig. 1, a conduction band barrier exists at interface between CdS and CIGS for  $x=0.3$ . **This barrier** can prevent transport of photo-generated electrons. The conduction band offset is reduced because the change in the band gap reduces the electron affinity (i.e., valence band remains approximately constant). With increasing  $E_g$ ,

this barrier is reduced which mitigates the loss of electrons at the interface. Above  $x>0.4$ , the  $J_{sc}$  decreases due to the effects of traps. This decrease counterbalances and eventually overwhelms the increase in  $V_{oc}$  and reduces the overall efficiency.

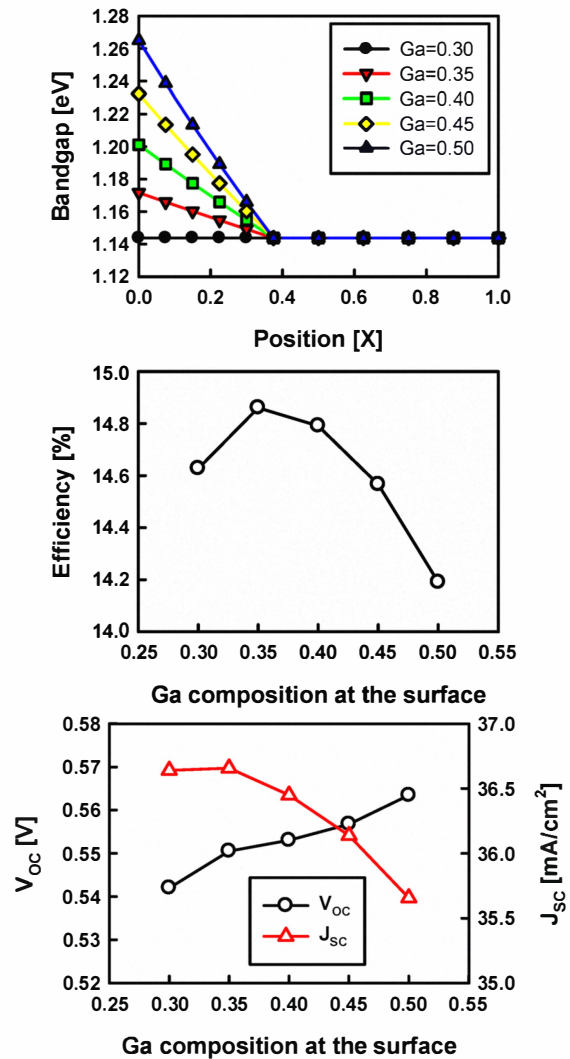
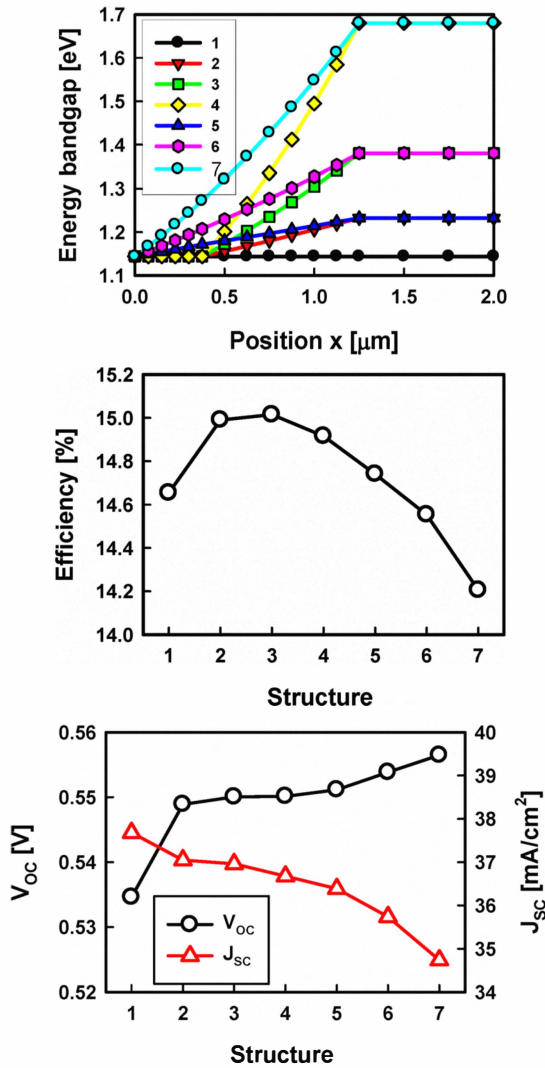


Figure 4 Band diagram for six different forward graded solar cell structures (top) and their PV performance (middle, bottom).

### Back grading

The mechanism by which back grading improves solar cell efficiency is well known and understood in absence of traps. Back grading increases the electric field outside the SCR; this induced electric field helps the separation and transport of the photo-generated holes, improving both  $J_{sc}$  and the overall power conversion efficiency. If the light absorption exceeds the width of the SCR, it also assists in

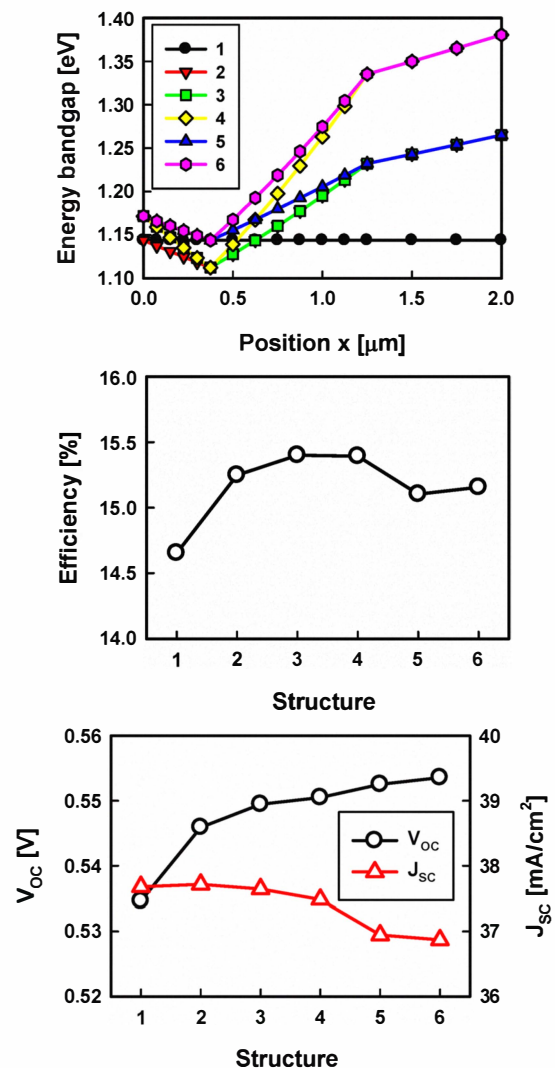
the collection of electrons which are swept back into the SCR and out through the CdS.



**Figure 5** Band diagram for seven back graded solar cells structures (top) and their PV performance results (middle, bottom). A constant concentration in the SCR gives the best performance.

However, Ga compositions greater than 0.24 can lead to recombination in the SCR which reduces efficiency Fig. 5 shows the band diagram of the structures constructed to examine the effects of various back grading strategies. Two kinds of back-graded structures were studied; one group had a uniform composition ( $x=0.3$ ) in the space charge region and linearly increasing Ga concentration from the end of the SCR at  $0.4 \mu\text{m}$  to  $1.25 \mu\text{m}$  (structures 2, 3 and 4). The other group of structures had linearly increasing Ga concentration from the surface to  $1.25 \mu\text{m}$  into the CIGS film (structures 6, 7 and 8). A uniform composition from  $1.25 \mu\text{m}$  to the bottom contact was

assumed in all structures. The compositions of structure 5, 6, and 7 are increased from  $x=0.3$  at the surface to 0.45, 0.66 and 1.0 at  $1.25 \mu\text{m}$ , respectively. Structure 1 represents a uniform composition as a reference. The results of two groups show a vivid contrast. The efficiencies of solar cells with a uniform composition in the SCR show improvement from 0.25% to 0.36%. In contrast, structures with linear grading from the surface towards  $1.25 \mu\text{m}$  into the film do not show a corresponding improvement in efficiency with the exception of structure 5. As shown in Fig. 5, the  $V_{oc}$  increase is the dominant factor for efficiency improvement.  $J_{sc}$  decreases in all structures with a Ga composition gradient. Back grading generates an electric field, which should increase the drift velocity and reduce recombination. However, clearly this effect



**Figure 6** Band diagram for solar cell structures with both types of grading (top) and the corresponding PV cell performance results.



is more than compensated for and the reduction in efficiency observed in Fig. 5 is caused by the high trap density.

Compared to forward grading, back grading has a large process window in composition grading. That is, a wide range in compositions (structures 2, 3, and 4) give very similar performance. Furthermore, back grading gives a more significant improvement in performance. These results can explain the difficulty in observing forward grading effects compared to back grading.

### Double side grading

The above study showed that, for a range of concentrations, both forward and back grading can improve the efficiency of a PV cell. On this basis, the optimum structures with both grading types combined were studied. Fig. 6 shows the band diagram of structures with a non-monotonic Ga composition gradient. Structure 1 again represents a uniform composition as a reference and structure 2 mimics the Ga concentration profile in the 19.2% efficient CIGS solar cell from NREL [10]. Structures 3 and 4 have a forward gradient of 0.35 to 0.24; structures 5 and 6 have a forward gradient of 0.35 to 0.30. Structure 2 and 3 have a back gradient of 0.24 to 0.45 and structures 4, 5, and 6 have a back gradient of 0.24 to 0.66, 0.30 to 0.45 and 0.30 to 0.66 respectively. The structures which have  $x=0.24$  at the end of the SCR show good efficiency.  $V_{OC}$  gains of these structures are lower than others with  $x=0.3$  because of the reduced band gap, however,  $J_{SC}$  losses become negligible due to low trap density. Structure 3 has the best efficiency, 15.4%. Compared to the NREL structure, a higher surface Ga composition can only improve efficiency very slightly. For back grading, the bottom composition change does not have much effect on efficiency in the range of 0.45 to 0.66.

### CONCLUSION

The effect of uniform Ga concentration and Ga grading in CIGS solar cells was studied using a model that includes the variation of trap density as a function of Ga composition. The trap model is based on published experimental data. For a simple, nongraded cell, the best efficiency is found to be near a Ga concentration of 0.66. At this value,  $E_g$  is 1.38 eV, in good agreement with Shockley-Queisser balance calculations. Taking into account the effect of traps, the optimum Ga concentration is 0.30, in good agreement with literature results for CIGS devices. It was found that a Ga concentration gradient that increases from the heterojunction into the CIGS film increases the  $V_{OC}$ , but for compositions higher than that of the NREL three-step process, the voltage increase comes at the expense of reduced  $J_{SC}$ . Increased field due to decreased Ga concentration in the SCR may increase  $J_{SC}$ .  $J_{SC}$  begins to decrease when the surface Ga concentration exceeds 0.35.

### ACKNOWLEDGEMENT

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