Metal-Oxide Broken-Gap Tunnel Junction for Copper Indium Gallium Diselenide Tandem Solar Cells

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Abstract

A metal-oxide broken-gap heterojunction between p-Cu₂O and n-In₂O₃ is proposed and studied for use as a tunnel junction in polycrystalline CuIn_{1-x}Ga_xSe₂ (CIGS) based tandem solar cells using numerical device simulation. Specifically, a tandem solar cell with a CuGaSe₂ (CGS) absorber top cell and a CuInSe₂ (CIS) absorber bottom cell was considered. The ballistic transport model explains well the carrier transport in the broken-gap heterojunction. Broken-gap heterojunctions provide linear current-voltage characteristics even if one side is lightly doped and the junction resistance is much lower than typical values of series resistance in solar cells. However, electron affinities of metal oxides for broken-gap band alignment may induce an energy barrier between the tunnel junction and the top and bottom solar cells, degrading performance. These barriers can be reduced using buffer layers. For example, NiO and graded In₂O₃-ZnO buffer layers are proposed beneath CGS top solar cell and above the CIS bottom solar cell, respectively. With these buffer layers, the efficiencies of the top and bottom cells are 17.5% and 6.5% respectively. The modeled efficiency of the CGS/CIS tandem solar cell is 24.1% and there is virtually no significant efficiency loss due to the presence of the broken-gap junction.

Keywords – Broken-gap heterojunctions, Multi-junction photovoltaic cells, CIGS, Tunnel junction, Metal oxide, Device simulation.

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1. Introduction

Thin film multi-junction solar cells are among the most promising structures for third-generation photovoltaic (PV) devices because they have the potential to convert sunlight to electricity with high efficiency and at low cost [1,2]. Single-junction thin film solar cells show low cost [3] and high efficiency [4] compared to other solar cells. However, single-junction solar cell efficiencies are constrained by the Shockley-Queisser limit [5]. Further improvements require the use of multi-junction PV device architectures [1]. Crystalline multi-junction solar cells hold the world record efficiency [6], however, they are expensive to produce due to the need for epitaxial growth [7]. It would be desirable to make multi-junction solar cells based on low-cost thin polycrystalline films such as CdTe and $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ (CIGS).

In multi-junction PV devices two or more solar cells share the solar spectrum. The top cell should be transparent below the bandgap of its absorber and connected to the bottom cell with transparent contacts. When two solar cells are stacked monolithically, a reverse biased p-n junction forms at their interface. Typically tunnel junction (TJ) diodes are used between the solar cells to solve this problem.

This connection is one of the obstacles to making multi-junction solar cells based on polycrystalline films. The TJ requires a very heavily doped p-n junction with steep doping profiles at the interface [8]. However, the dopant concentration profile control in polycrystalline films is much more difficult to achieve owing to fast grain boundary diffusion [9,10]. Furthermore, some of the top cell layers require a high temperature deposition process to produce large grains and low trap densities. Thus, significant dopant diffusion in the bottom solar cell and inter-diffusion near the tunnel junction can occur. Furthermore, doping in most polycrystalline PV materials such as CIGS occurs via point defects, making precise doping

concentration control very difficult and compensation common. Finally, it is impossible to form heavily doped layers of both types due to compensation effects [11,12]. To avoid these difficulties, multi terminal methods have been demonstrated [13,14]. In CIGS solar cells, MoSe₂ on ZnO:Al, SnO:F and In₂O₃:Sn (ITO) make good ohmic contacts with CIGS absorber, however low transmittance is a problem [15,16,17]. More fundamentally, tandem devices formed by stacking cost more since one loses the advantages of monolithic integration.

In this article, we examine the possibility of using metal-oxide broken-gap heterojunctions as the tunnel junction in multi-junction CIGS solar cells. We investigated the I-V characteristics of p-Cu₂O/n-In₂O₃ junction. Early experimental results show ohmic behavior at a similar junction made from p-Cu₂O/n-ZnSnO₃ [18]. Here we also investigate monolithic CIGS-based tandem PV device with p-Cu₂O/n-In₂O₃ junction where the top and bottom cell absorbers were CuGaSe₂ (CGS) and CuInSe₂ (CIS) respectively, including the band alignment of broken-gap heterojunctions with top and bottom solar cells.

It is important to point out that major obstacles exist to realizing a high-efficiency tandem cell. The top (i.e. wide bandgap) cell is critical to the efficiency. Its larger V_{OC} means that it must provide about two thirds of the total power. CGS has a suitable band gap for the top solar cell in tandem devices. However, the best efficiency of CGS solar cells is only about 10%. This is due to a large bulk trap density [19] and poor band alignment between CGS and the buffer layer [20,21] which lead to a low open circuit voltage [22,23]. A second obstacle is thermal budget. The deposition of a low defect density wide bandgap absorber typically requires high temperature. A pore structure forms in the CdS upon annealing leading to a heavy diffusion of Ga into ZnO layer. Ga-assisted Cd diffusion may be responsible for the pore formation [24]. Furthermore, diffusion of Cd in the lower device counter dopes the absorber leading to a severe

drop in open circuit voltage once the device is fully depleted [25]. The next possible problem is the use of CIS in the lower device. Although CIS has not demonstrated an efficiency as high as CIGS, Solar Frontier recently demonstrated a low Ga content 20.9% cell with a bandgap of only 1.05 eV [26]. Since this low concentration of gallium only increases the desired top cell from 1.65 to 1.70 eV, this problem has largely been resolved. As a result of the first two technical limitations, the device efficiency predicted here cannot be realized today. However, progress is being made. Not only are the efficiencies of CGS solar cells rising [27,28], but alternative wide bandgap CIGS-based materials are also being explored [29]. Shafarman has been developing $\text{Cu}_x\text{Ag}_{1-x}\text{In}_y\text{Ga}_{1-y}\text{Se}_2$ [30] and has recently demonstrated relatively high efficiency 1.4 eV devices. We have demonstrated very low trap density absorbers at 1.6 eV using UHV-deposited $\text{CuIn}_x\text{Al}_y\text{Ga}_{1-x-y}\text{Se}_2$ [29,31], but have not yet demonstrated a high efficiency device. In this work we focus on the effects of the broken-gap heterojunction under high performance conditions.

2. Metal oxide broken-gap heterojunction

While high conductivity transparent conducting oxides (TCOs) [32,33] are used as window layers in solar cells [34] they are difficult to heavily dope both electrons and holes making them poor candidates for tunnel junctions [35,36]. When the doping concentration is increased and Fermi level reaches the formation energy of a compensating defect, the net carrier concentration saturates in an effect called pinning [21]. Thus, one cannot form a heavily doped p-type film from materials such as ZnO , SnO_2 , In_2O_3 , Ga_2O_3 , and CdO . Similarly, one cannot form a heavily doped n-type film from Cu_2O , NiO and CuMO_2 ($\text{M}=\text{Al}$, In , Cr and Ga).

It is possible to use a heterojunction of an n-type and a p-type metal oxide for a tunnel junction. A broken-gap metal-oxide heterojunction is a promising design. This involves a

junction between two dissimilar materials where the conduction band edge of the n-type material is equal to or lower in energy than the valence band edge of the p-type material as shown in Fig. 1. Carriers can easily move across an interface with this band alignment by a nonlocal interband transition. As a result the junction has linear current-voltage (I-V) characteristics [37] even without heavy doping on both sides.

The electrical characteristics of the broken-gap heterojunction have been studied extensively in InAs/GaSb junctions [37-41]. The valence band edge of GaSb is between 0.48 and 0.53 eV higher than that of InAs. The band overlap ($\Delta\chi$ as shown in Fig. 1) is between 0.12 and 0.17 eV since band gaps of InAs and of GaSb are 0.36 eV and 0.71 eV, respectively [38]. The transport properties depend on the band bending near the junction interface. When an n-InAs/p-GaSb approaches flat band, the I-V characteristics are linear [38,39,40]. A resistance as low as $10^{-7} \Omega\text{-cm}^2$ can be achieved [41] suggesting no significant contribution to R_{series} .

When designing a broken-gap tunnel junction, the electron affinities of the materials are the most important properties. Low and high electron affinities are desired for the n- and p-type materials, respectively. P-type TCOs are rare. Cu_2O and CuAlO_2 are two of the most attractive materials for broken-gap tunnel junctions since they have the lowest electron affinities among the p-type TCOs. In n-type TCOs, SnO_2 , GaInO_3 and ZnSnO_3 are the most likely to form broken-gap band alignment with other TCOs for a similar reason [33].

There are few studies on broken-gap heterojunction with metal oxide films. Tanaka et al. studied the heterojunctions formed between Cu_2O and several different n-type TCOs including ZnO , ITO and In_2O_3 [42]. Unlike junctions with other n-type TCOs, the p- Cu_2O /n- In_2O_3 junction showed linear I-V characteristics while the p- Cu_2O /n- ITO junction showed nonlinear I-V characteristics with a low energy Schottky barrier [42]. The band alignment of these ohmic p-

Cu₂O/n-In₂O₃ junctions was not studied, however it can be estimated from the I-V results and the band alignment of the Cu₂O/ITO junction, and the electron affinity difference between ITO and n-In₂O₃. Recently, Deuermeier et al. analyzed the band alignment of p-Cu₂O/n-ITO by X-ray photoemission spectroscopy (XPS). They found that the conduction band edge of n-ITO is 0.2 to 0.7 eV higher than the valence band edge of p-Cu₂O depending on the ITO deposition conditions [43]. According to research results from multiple groups [33,44] the work function of In₂O₃ is 0.2 to 0.8 eV lower than that of ITO. From these results, it can be estimated that p-Cu₂O/n-In₂O₃ junctions have a broken-gap band alignment. The linear I-V characteristic supports this inference.

3. Device simulation.

Numerical simulation for the tunnel junction in a complete monolithic tandem solar cell requires current continuity and the Poisson equation, as well as a self-consistent treatment of quantum mechanical transport in the tunnel junction. However, well-known solar cell simulations do not have this capability. Thus, previous tandem device modeling has simply treated the tunnel junction as an ohmic contact between the top and bottom solar cells [45,46]. Here we use DESSIS – a commercially available multi physics device simulation tool for numerical simulation. Quantum transport at the broken-gap junction is solved by the Wentzel–Kramers–Brillouin (WKB) approximation. Device simulation is performed by self-consistently solving the current continuity equation, the Poisson equation and WKB approximation near the broken-gap junction interface. Optical absorption in the stacked multiple layers is calculated by transfer matrix methods [47].

4. Transport models and simulation results of p-Cu₂O/n-In₂O₃ heterojunction.

4.1 Nonlocal interband transition model vs. ballistic transport model.

Fig. 2a shows the equilibrium band diagram of the p-Cu₂O/n-In₂O₃ heterojunction. As previously shown for the Cu₂O/ITO heterojunction [43], the band alignment can vary with film deposition conditions. We varied the band overlap from 0.0 eV to 0.2 eV to study the effect. For these calculations, the doping concentrations on both sides of the junction were taken to be $1.5 \times 10^{19} \text{ cm}^{-3}$ and the thickness of each layer was set to 200 nm. According to the Anderson model [48], the Fermi level should be constant. Also, the energy band discontinuity must be maintained at the interface. The energy bands bend at the interface to satisfy these requirements [48]. As shown in Fig. 2b, band bending induces a carrier accumulation on both sides of the junction. The wider the band overlap ($\Delta\chi$), the higher the accumulation layer concentrations.

Next we studied transport. An accurate solution for carrier transport in a broken-gap heterojunction can be obtained by solving Schrodinger's and Poisson's equations self-consistently [49,50]. Quantum transport near the junction interface can also be treated by the WKB approximation. Carrier transport is modeled by solving both the interband transition and the drift-diffusion transport in the quasi-neutral region simultaneously. The band alignment of the heterojunction affects both the electric field and the carrier concentration at the interface as described above [51]. Clearly these are important for the drift-diffusion model. Band bending at the interface is also very important since the shape of the potential strongly affects the transmission coefficient.

In addition to interband transition at the interface, ballistic transport may occur between the edge of the charge neutral region and the junction interface ((3) in Fig. 3) when the accumulation width is narrow and the field is large. Ballistic transport occurs when electrons

travel without losing energy by scattering [52]. Electrons in the accumulation region are accelerated by a strong built-in electric field, reaching velocities substantially higher than the saturated or terminal velocity. This is the so-called velocity overshoot effect. The electrons eventually scatter and lose the kinetic energy acquired from the field if the accumulation region is wide enough [52]. Since the scattering rate increases with kinetic energy, ballistic transport happens within a narrow region. Thus, electrons can move ballistically across the accumulation region only if the accumulation width is narrower than about 10 nm [52].

In this work, we simulate ballistic transport from the edge of charge neutral region to the junction interface using the WKB approximation since ballistic transport conserves the sum of the kinetic and potential energies. In this model the transmission probability can be calculated for arbitrary potential shapes. The carrier energy can be larger or smaller than the potential barrier. Interband tunneling current from the valence band to the conduction band (J_{cv}) is given by

$$J_{cv} = -q \int_{0^+}^{\infty} [R_{cv}(x) - G_{cv}(x)] dx, \quad (1)$$

where the difference between the recombination (R_{cv}) and generation rates (G_{cv}) is given as

$$R_{cv}(x) - G_{cv}(x) = \frac{A_{cv}^*}{qk} \left(\frac{dE_v(x)}{dx} \right) \Gamma_{cv}(\varepsilon, x) \times \left[T_p(x) \log \left\{ 1 + \exp \left(\frac{E_{fp}(x) - \varepsilon}{kT(x)} \right) \right\} - T_n(0^-) \log \left\{ 1 + \exp \left(\frac{E_{fn}(0^-) - \varepsilon}{kT(0^-)} \right) \right\} \right] \quad (2)$$

In Eq. 2, A_{cv}^* is the Richardson constant, $E_{fp,n}$ is Fermi level of hole and electron, ε is the carrier energy, E_v is the valence band edge energy, q is charge, k is the Boltzmann constant, T is temperature and T_n and T_p are the transmission coefficients at the interface which is due to velocity mismatch for electrons and holes, respectively [47]. Here $x=0^-$ refers to the position

where tunneling begins. We assume that the transmission coefficients are unity since the carriers that move across the junction recombine quickly with the majority carriers. The tunneling probability (Γ_{cv}) is given by

$$\Gamma_{cv}(\varepsilon, x) = \exp \left[-2 \int_0^r \kappa(x', \varepsilon) dx' \right], \quad (3)$$

where, κ , ε and x are the wave vector, the energy of carriers and position respectively. The wave vector, κ , is

$$\kappa = \frac{\kappa_C \kappa_V}{\sqrt{\kappa_C^2 + \kappa_V^2}}, \quad (4)$$

where,

$$\kappa_{C,V} = \frac{\sqrt{2m_0 m_{e,h}^* \pm (E_{C,V}(x) - \varepsilon)}}{\hbar}, \quad (5)$$

$\hbar, m_e, m_h, E_C$ and E_V are the reduced Planck constant, the effective masses of the electron and the hole and the conduction band edge energy of n-type material and the valence band edge energy of the p-type material, respectively [47]. Parameters used in the simulations are listed in Table 1. Parameters for the CIGS solar cell simulations were taken from Song et al. [53].

We studied the I-V characteristics of a p-Cu₂O/n-In₂O₃ broken-gap heterojunctions and compared the two tunneling models described above. Even though a band overlap exists, the I-V characteristic of the broken-gap junction is linear as proven in n-InAs/p-GaSb junction.

Fig. 4 compares the I-V characteristics of the p-Cu₂O/n-In₂O₃ junction calculated using the interface interband transition model (Fig. 4a) and the ballistic transport model (Fig. 4b). Under near flat-band conditions where the band overlap is zero, both tunneling models predict linear I-V characteristics in the reverse bias region. However significant differences exist

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5 between the two model predictions when there is band overlap. A cutoff voltage (V_C) appears for
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7 the interface interband transition model in reverse bias when the band overlap is wider than 0.1
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9 eV. Since the junction must be operated in reverse bias in multijunction solar cells, only small
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11 voltage drops can be allowed.
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15 Band bending creates an electric field which induces a drift current toward the junction.
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17 At thermal equilibrium, the carrier concentration profile must be such that the induced diffusion
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19 current cancels the drift current for both carriers. According the simulation results shown in Fig.
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21 4a, even if a small bias is applied, when carriers are accumulated at the interface the diffusion
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23 current cancels the drift current. Thus no significant current flows. From this effect, we can
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25 estimate the cutoff voltage analytically by calculating a flat band voltage at which carriers are
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27 not accumulated. As shown in Fig. 2a, the energy difference from the valence band edge of p-
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29 type area to the conduction band edge of n-type area in the charge neutral region is 49 meV.
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31 When the band overlaps are 0.1 and 0.2 eV this difference is -51 mV and -0.151 V respectively.
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33 The corresponding cutoff voltages calculated by simulation are -61 mV and -0.16 V, respectively,
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35 in good agreement with the analytical calculation. A wider band overlap increases the band
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37 bending and so requires a larger reverse bias to remove the accumulated carriers at the interface.
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44 Under forward bias, band bending and therefore carrier accumulation increases at the
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46 interface. The diffusion current by accumulated carriers also increases and cancels out the drift
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48 current. An applied reverse bias reduces the band bending and the accumulated carrier
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50 concentration. The current does not flow until the accumulated carriers are removed. After the
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52 band is flat, majority carriers are injected to the interface by drift, thus current flows through the
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54 device. When the band overlap is zero no carriers are accumulated at thermal equilibrium.
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56 Carrier accumulation begins at 0.124 V in forward bias. Thus current flow below 0.124 V and
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5 peak voltage (V_P) is observed in I-V characteristics. However, the experimentally measured I-V
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7 characteristics of InAs/GaSb broken-gap heterojunctions with band overlap do not show a cutoff
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9 voltage. Thus, the interface transition model fails to explain the observed I-V characteristics [37-
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15 By contrast, the I-V characteristics of a broken-gap heterojunction predicted using a
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17 ballistic transport model is linear and exhibit current flow both in forward and reverse bias as
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19 shown in Fig. 4b. Since ballistic transport occurs directly between the charge neutral region and
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21 the interface, the transmission coefficient depends only on the barrier shape and not on the
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23 profiles of accumulated carriers near the interface. For carriers to move ballistically the charge
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25 accumulation width should be narrower than the ballistic mean free path and the electric field
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27 should be high. In the p-Cu₂O/n-In₂O₃ junction studied here, the charge accumulation widths on
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29 both sides of the junction are less than 4 nm as shown in Fig. 2 and the maximum electric field is
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31 1 MV/cm. These narrow depletion widths and high electric fields lead to carrier conduction by
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33 ballistic transport across this junction. Increasing the energy band overlap produces a higher
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35 electric field at the interface making ballistic tunneling more likely. The resistance due to
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37 ballistic transport is determined by the transmission coefficient. When the transmission
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39 coefficient is one, the resistance of ballistic transport at the interface is lower than the series
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41 resistance of the charge neutral region. As a result, the series resistance of junction does not
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43 determine the I-V characteristics. Thus, the I-V characteristics do not depend on the width of the
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45 band overlap ($\Delta\chi$). This is the reason that a broken band-gap junction can achieve a junction
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47 resistance as low as $10^{-7} \Omega\text{-cm}^2$ in InAs/GaSb junctions. We note that in a tandem device
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49 operating under unconcentrated sunlight will generate about 20 mA/cm². For a 1 mV potential
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drop at the tunnel junction, the maximum allowable resistance could be as high as $5 \times 10^{-2} \Omega\text{-cm}^2$, suggesting that a broken-gap tunnel junction could easily achieve this goal.

4.2 The effect of doping concentration.

One of difficulties in fabricating a tunnel junction is maintaining steep doping profiles near the junction in the heavily doped n- and p-type layers. However, the energy band alignment of the broken-gap heterojunction is such that the Fermi level is located in the conduction and valence bands of the n- and p-type layers, respectively, and conduction can occur even when these layers are only lightly doped. Although many n-type TCOs can be doped higher than $1 \times 10^{20} \text{ cm}^{-3}$, heavily doped p-type TCOs are much more difficult to achieve. We therefore investigate the effect on hole concentration in Cu_2O when the electron concentration in In_2O_3 is $5 \times 10^{19} \text{ cm}^{-3}$. The thicknesses of n and p-type layers were fixed at 200 nm.

The model results show a peak voltage (V_P) or cutoff voltage (V_C) in I-V characteristics when the hole concentration is low. Fig. 5a shows the typical I-V characteristics and energy band diagrams in each different carrier transport region of the p- Cu_2O /n- In_2O_3 junction with a hole concentration in Cu_2O of 10^{17} cm^{-3} . At thermal equilibrium (point A), the Cu_2O band is pulled down near the interface due to the heavy dopant concentration in the In_2O_3 . Thus the valence band edge of Cu_2O in the charge neutral region is higher than the conduction band of In_2O_3 . In reverse bias (point B), band bending increases the electron concentrations in p- Cu_2O at the interface. Electrons are injected into the n- In_2O_3 across the junction by interband transition. Under a small forward bias, electrons move from n- In_2O_3 to p- Cu_2O by not only diffusion but also interband transition at the interface. This continues until the valence band edge of Cu_2O is equal to the conduction band edge of In_2O_3 (point C). At this point the interband transition at the

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5 interface is blocked by the band gap of Cu_2O and only the small diffusion current remain. Thus
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7 the current changes abruptly (point C). This abrupt current change produces the negative
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9 differential resistance (NDR) often associated with tunnel junctions. NDR of a broken-gap
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11 heterojunction was observed in InAs/GaSb heterojunction at moderate doping concentration
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13 when the dopant concentrations of n-type InAs and p-type GaSb is 2×10^{17} and $5 \times 10^{18} \text{ cm}^{-3}$
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15 respectively [54]. Since the diffusion current increases exponentially with voltage in this regime,
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17 at sufficiently high voltage (point D), one finds a measurable current once again. The peak
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19 voltage is the voltage which makes the energy band flat. It is determined by the difference
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21 between the valence band edge of Cu_2O in charge neutral region and the conduction band edge
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23 of In_2O_3 in charge neutral region at thermal equilibrium. When valence band edge of Cu_2O is
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25 higher than the conduction band edge of In_2O_3 the peak voltage becomes positive. In the reverse
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27 bias case, the peak voltage changes to a cutoff voltage since carriers cannot transport across the
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29 junction until the energy band becomes flat. Thus at sufficiently low carrier concentrations the
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31 peak voltage becomes the cutoff voltage.
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39 Fig. 5b shows the band diagrams of p- Cu_2O /n- In_2O_3 with Cu_2O dopant concentrations of
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41 1×10^{16} , 2×10^{17} and $1 \times 10^{18} \text{ cm}^{-3}$. For the last two, the cutoff voltage is positive. When the dopant
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43 concentration of Cu_2O becomes $1 \times 10^{16} \text{ cm}^{-3}$ the valence band edge of Cu_2O is lower than the
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45 conduction band edge of In_2O_3 and cutoff voltage is -0.11 V. No peak voltage is observed. Thus,
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47 broken-gap junctions provide low resistance ohmic junctions, however, both sides of the junction
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49 need to be at least moderately doped. This is in sharp contrast to conventional tunnel junctions
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51 which require very heavy doping on both sides of the junction.
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59 **5. Top and bottom single solar cells with $\text{Cu}_2\text{O}/\text{In}_2\text{O}_3$ heterojunction interface.**

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Next, the performance of top and bottom CIGS-based solar cells with a p-Cu₂O/n-In₂O₃ tunnel junction was investigated. For tandem PV devices, the optimized band gaps of the top and the bottom solar cells under AM 1.5 illumination are 1.64 eV and 0.94 eV, respectively [55]. The band gap of the CIGS material system approximately covers this range and can be varied from 1.01 eV for CuInSe₂ (CIS) to 1.68 eV for CuGaSe₂ (CGS). Thus, we chose CGS and (CIS) for the absorber layers in the top and bottom cells, respectively.

5.1 Top CGS solar cell to Cu₂O heterojunction interface.

The device structures and performance results of top solar cells with a broken-gap heterojunction are shown in Fig. 6a. The window layers were comprised of a 150 nm thick n-type ZnO:Al and a 100 nm thick n-type ZnO. The dopant concentrations of the 150 nm thick and 100 nm thick n-ZnO were 10^{19} cm^{-3} and 10^{17} cm^{-3} , respectively. A 70 nm thick n-type ($5 \times 10^{15} \text{ cm}^{-3}$) CdS was used as a buffer layer between the CGS and the n-ZnO. A 1.6 μm thick p-type (10^{16} cm^{-3}) CGS layer was used for the absorber layer. A 10 nm thick MoSe₂ was used for the contact layer between the top solar cell and the broken-gap heterojunction. The valence band edge of MoSe₂ (at 5.6 eV below vacuum level) is close to valence band of CGS (at 5.68 eV below vacuum level). As a result, MoSe₂ forms an ohmic contact with CGS. We assumed that this layer has the same optical (n-k) parameters as sputtered MoSe₂ [56]. The doping concentration of MoSe₂ was taken to be 10^{18} cm^{-3} . Since Cu₂O is a p-type material (10^{19} cm^{-3}) it should contact the CGS absorber of the top cell. A 100 nm thick p-type Cu₂O was placed below the MoSe₂ to complete the top cell.

Fig. 6b shows the valence band diagrams near the interface between the top solar cell and ideal ohmic contact (solid lines), Cu₂O (dotted line) and NiO buffer and Cu₂O (dashed line).

When the bottom contact is ohmic, the valence band of CGS bends toward the Fermi level. Holes in valence band of CGS move easily to the bottom contact because there is no barrier between the top solar cell and the bottom contact. The reported valence band edges of MoSe₂ and Cu₂O are 5.6 eV [57] and 5.1 eV [43], respectively, so that a 0.5 eV energy difference exists between these two materials. Therefore, when Cu₂O is directly contacted with MoSe₂ an energy barrier is formed on the valence band of CGS. Since the extremely thin layer of MoSe₂ is fully depleted and the dopant concentration of CGS is lower than that of Cu₂O, CGS is depleted from the bottom contact. This barrier would block hole transport to the tunnel junction. To reduce this barrier, we introduced a p-type buffer layer between the MoSe₂ and Cu₂O. The valence band edge of buffer materials is located between the valence band edge of CGS and Cu₂O. NiO is a good candidate as shown in Table 1 [44]. When 50 nm of p-type (10^{18} cm^{-3}) NiO is inserted between MoSe₂ and Cu₂O, the barrier height in CGS is reduced from 0.26 eV to 0.12 eV. Another barrier is generated in NiO at the interface between NiO and Cu₂O, however, due to the high dopant concentration in NiO, the barrier height and width is narrow (7 nm) and low (0.1 eV). Therefore it does not affect hole transport.

The I-V characteristics and the performance summary of the top solar cells in Fig. 6a are shown in Fig. 6c and Table 2 respectively. With an ideal ohmic bottom contact (solid line in Fig. 6c), the short circuit current (J_{SC}) and open circuit voltage (V_{OC}) are 18.77 mA/cm² and 1.154 V respectively and the efficiency of top solar cell is 18.7%. When Cu₂O is connected directly to MoSe₂ (dotted line in Fig. 6c) J_{SC} and V_{OC} are 18 mA/cm² and 1.134 V and the efficiency decreases to 17.0%. The J_{SC} loss, 5%, is the main factor in reducing the efficiency. The insertion of the NiO buffer layer between MoSe₂ and Cu₂O recovers J_{SC} to 18.44 mA/cm² by reducing the

barrier (dashed line in Fig. 6c). The efficiency rebounds to 17.9%, showing that the NiO buffer layer is effective in improving device efficiency.

5.2 Bottom CIS solar cell to In₂O₃ heterojunction interface.

Fig. 7a shows the device structures that were simulated and the performance of bottom solar cells with a broken-gap heterojunction. A 100 nm thick n-type ZnO (10^{17} cm^{-3}) was used for the n-side of the p-n junction and a 70 nm thick n-type ($5 \times 10^{15} \text{ cm}^{-3}$) CdS buffer layer was placed between the n-type ZnO and 2 μm thick p-type (10^{16} cm^{-3}) CIS absorber. In single junction solar cells, low resistivity TCOs are deposited on top of the ZnO window layer to reduce the series resistance due to lateral conduction in resistive ZnO. However, in the bottom cell, current only flows vertically. Lateral conduction occurs only in the top cell. Therefore, a TCO window layer is not required in the bottom solar cell.

Conduction band diagrams of bottom solar cells are shown in Fig. 7b. With In₂O₃ on top of the bottom cell, an energy barrier is formed in the conduction band at the interface between ZnO and In₂O₃ (dotted line in Fig. 7b). This happens because the electron affinity of In₂O₃ is lower (5.1 eV [44] below the vacuum level) than that of ZnO (4.5 eV [33] below the vacuum level). It has been reported that a low resistivity TCO can be formed [58]. Then the composition of In₂O₃-ZnO film (IZO) can be graded to eliminate the barrier. Fig. 7b shows the conduction band diagrams of top solar cells with 100 nm thick In₂O₃ and 50 nm thick In₂O₃ and 50 nm thick compositionally graded ZnO to In₂O₃ from top surface of the bottom solar cell removing the energy barrier between In₂O₃ and ZnO.

The I-V characteristics and performance summary of top solar cells in Fig. 7a are shown in Fig. 7c and Table 3 respectively. With an ohmic contact on top of the bottom cell, J_{SC} and V_{OC}

are 38.52 mA/cm^2 and 0.493 V respectively. The efficiency of the bottom solar cell is 14.3% under AM 1.5 illumination. However, the bottom solar cell must share the solar spectrum with top cell. We calculated the component of the solar spectrum reaching the bottom cell assuming the full tandem structure (screened spectrum). Then J_{SC} , FF, and V_{OC} are 18.76 mA/cm^2 , 75.1% and 0.473 V respectively, and the efficiency decreases to 6.67%. With In_2O_3 on top of the bottom solar cell, the power conversion efficiency decreases to 5.77% under the screened spectrum. The decrease in efficiency is due to the reduction in the J_{SC} and FF to 17.86 mA/cm^2 and 68.18% respectively compared to the bottom cell with an ohmic contact. The energy barrier in ZnO at the interface between ZnO and In_2O_3 hinders electron transport and induces a kink in the I-V characteristic near the open circuit voltage as shown in Fig. 7c. This kink degrades the FF. According to Gloeckler et al. this forward bias kink is due to an electron barrier in the conduction band at the CIGS/CdS interface. The kink occurs when the conduction band edge of CdS is much higher than that of CIGS [59]. Similarly, the large conduction band discontinuity between In_2O_3 and ZnO depletes electrons in ZnO and moves the conduction band of CdS upward compared to the bottom cell with an ohmic contact (Fig. 7b). This shift in the conduction band of CdS blocks electron transport at high forward bias and degrades the FF. A graded In_2O_3 -ZnO layer between In_2O_3 to ZnO restores the efficiency to 6.65%, the J_{SC} to 18.7 mA/cm^2 and the fill factor to 75.1%.

6. CGS/CIS Tandem solar cell

Fig. 8a shows the structure and band diagram for an optimized CGS/CIS tandem solar cell. The design shown in Fig. 8a incorporates the lessons from previous sections. Specifically, the top solar cell is comprised of a $1.6 \mu\text{m}$ thick p-type CGS absorber with ZnO:Al/ZnO window

layers, a CdS buffer layer and a MoSe₂ contact layer. The bottom solar cell is comprised of a 2.0 μm thick p-type CIS absorber with a ZnO window layer and a CdS buffer layer. The Cu₂O-In₂O₃ broken-gap heterojunction is used to connect the top and bottom solar cells in series. A NiO buffer layer is used in the top cell between the MoSe₂ and the Cu₂O layers. Similarly, a graded In₂O₃-ZnO layer is inserted in the bottom cell between the In₂O₃ and ZnO layers. The band diagram at thermal equilibrium is shown on the right of Fig. 8a.

The performance of the CGS/CIS tandem solar cell is shown in Table 4 and Fig. 8a. Fig. 8b shows the I-V characteristics of the top, bottom, and tandem solar cells. With a p-Cu₂O/n-In₂O₃ broken-gap heterojunction, the tandem CGS/CIS solar cell works successfully. The efficiency of the tandem solar cell is 24.1% while the efficiencies of the top and bottom cells are 17.5% and 6.7% respectively. The V_{oc} of the tandem device (1.62 V) is equal to the sum of the V_{oc} for the top and bottom PV cells (1.14 V, and 0.47 V, respectively). Due to current continuity, the J_{sc} of a tandem cell is limited by lowest value of the two cells. For this device, J_{sc} is 18.5 mA/cm^2 , close to that of the top cell. Further structure optimization could be done to increase the current generated by the top cell thereby improving the overall efficiency. The FF of the tandem PV cells is substantially lower than that for the top cell (82.9%). Due to the narrower bandgap of CIS compared to CIGS, a higher energy barrier forms at the CdS/CIS interface. This barrier impedes electron transport, reducing the FF of the bottom cell to 75.1% (Fig. 8b). The FF of the tandem cell is determined by the sum of FFs of top and bottom solar cells weighted by efficiency. Thus it becomes 80.5%. The efficiency of a tandem solar cell is the sum of the efficiencies of top and bottom solar cells. The efficiencies of top and bottom cell in tandem solar cell are similar to the results of single solar cells when one takes into account screening by top cell. The ideal maximum efficiency of a CGS/CIS tandem solar cells is 25.3%, the sum of the top and bottom

solar cells with ohmic contacts. With p-Cu₂O/n-In₂O₃ broken-gap heterojunction, the efficiency of CGS/CIS tandem cell is 24.1% in this work. This efficiency degradation is mainly due to the energy barrier between the top cell and p-Cu₂O. New process techniques such as compositional grading can reduce this barrier and improve the efficiency to a value close to the ideal case. The broken-gap heterojunction is a promising tunnel junction candidate for connecting top and bottom solar cells in a multi-junction PV device without performance loss.

Finally, we note that the quoted maximum efficiency, 25.3%, is well below the Shockley-Queisser limit of 42.3% for an optimal cell [60]. The value we predict is a strong function of the assumptions. Our assumption of trap-free absorbers is clearly extremely optimistic. In state of the art CIGS, bulk traps do not significantly limit efficiency, however this is not true to CIS and CGS at this writing. Assuming these absorbers could be developed, further improvements could be made to approach this limit. Here we assumed uniform composition and doping. The types of grading used in champion single junction CIGS devices would improve efficiency. The band offset barrier described above could be reduced by modifying the buffer layer composition. The layer thicknesses could be optimized. In particular, the buffer layer thicknesses chosen for this simulation will lead to significant absorption.

7. Conclusion

A broken-gap p-n heterojunction, where the conduction band edge of the n-type material is equal to or lower in energy than the valence band edge of the p-type material, is studied as a potential tunnel junction in CIGS-based tandem solar cells. The broken-gap junction has a low resistance and linear I-V characteristic in both forward and reverse bias. The effectiveness of a specific broken-gap heterojunction between p-type Cu₂O and n-type In₂O₃ in a multi-junction

solar cell was studied using numerical simulation with DESSIS, a commercially available device simulator. Carrier transport across the p-Cu₂O/n-In₂O₃ broken-gap heterojunction occurs by ballistic transport. The junction has linear I-V characteristics with a resistance much lower than conventional tunnel junctions even when Cu₂O is only moderately ($2 \times 10^{17} \text{ cm}^{-3}$) doped. Junction properties were improved further by inserting buffer layers between the tunnel junction and the absorbers in both top and the bottom cells to minimize the energy barriers between the tunnel junction and the solar cells. With an optimized tunnel junction structure, the efficiency of a CGS/CIS tandem PV cells was 24.1% predicted. Importantly, there are no significant losses in efficiency due to the presence of the p-Cu₂O/n-In₂O₃ broken-gap junctions as compared to the total efficiency of separate bottom and top solar cells. Thus, a p-Cu₂O/n-In₂O₃ broken-gap tunnel junction is an attractive approach for connecting solar cells in polycrystalline CIGS-based multi-junction PV devices.

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Figure captions

Fig. 1. Band alignment of broken-gap heterojunctions.

Fig. 2. (a) The band diagram and (b) carrier concentrations for a $\text{Cu}_2\text{O}/\text{In}_2\text{O}_3$ broken-gap heterojunction near the band overlap region for different values of the band overlap (χ) between 0.0 eV and 0.2 eV. In (a) the solid and dotted lines represent the valence and the conduction bands, respectively. In (b) the solid and dotted lines represent the hole and electron concentrations, respectively.

Fig. 3. Possible current transport mechanisms in broken-gap heterojunctions: (1) interband transition at the interface (2) drift-diffusion and (3) ballistic transport.

Fig. 4. Calculated I-V characteristics for (a) the interface-interband transition model and (b) the ballistic transport model for different values of the band overlap (χ) between 0.0 eV and 0.2 eV.

Fig. 5. (a) I-V characteristics of 10^{17} cm^{-3} p- Cu_2O and $5 \times 10^{19} \text{ cm}^{-3}$ n- In_2O_3 broken-gap heterojunction and pictorial band diagrams for each transport region, (b) band diagrams of $5 \times 10^{19} \text{ cm}^{-3}$ Cu_2O with 10^{16} , 2×10^{17} and 10^{18} cm^{-3} In_2O_3 .

Fig. 6. (a) Three top solar cell structures with different bottom contacts for comparison (1) an ohmic contact, (2) using Cu_2O only, and (3) using Cu_2O with a NiO buffer layer and comparison of calculated (b) valence band diagrams and (c) I-V characteristics of CuGaSe_2 top solar cells with different bottom contacts.

Fig. 7. (a) Three bottom solar cell with top contact structures for comparison (1) an ohmic contact, (2) using In_2O_3 only, and (3) using In_2O_3 /graded In_2O_3 -ZnO layer,

comparison of calculated (b) conduction band diagrams and (c) I-V characteristics of CuInSe₂ bottom solar cells with different top contacts.

Fig. 8. (a) The optimized tandem CGS/CIS solar cell structure and its band diagram and (b) I-V characteristics of just the CGS (top cell), just the CIS (bottom cell) and the tandem CGS/CIS tandem solar cell in (a).

Table 1

Physical parameters for simulation.

Material	Dielectric Constant	Band gap [eV]	Electron Affinity [eV]	Mobility [cm ² /Vs]	Effective Tunneling mass
CGS	10.07	1.68	4.0	N:100, P: 45	
MoSe ₂	18.0	1.2	4.4	N:45, P: 15	
NiO	11.9	3.6	1.6	N:45, P: 2	
Cu ₂ O	7.11	2.1	3.0	N:45, P: 15	m _h : 0.84 [61]
In ₂ O ₃	3.95	3.5	5.1	N:45, P: 15	m _e : 0.35 [62]
ZnO	7.8	3.441	4.5	N:45, P: 15	
IZO	3.95-7.8	3.5	5.0 – 4.5	N:45, P: 15	

Table 2

The simulation results of top PV cells shown in Fig. 5a with various different top contacts.

Structure	Top Cell	Reference	BGJ	Buffer/BGJ
			ZnO:Al, n-type, 1×10^{19} , 150 nm	
			ZnO, n-type, 1×10^{17} , 100 nm	
			CdS, n-type, 5×10^{15} , 70 nm	
			CuGaSe ₂ , p-type, 1×10^{16} , 1.6 μm	
			MoSe ₂ , p-type, 1×10^{18} , 10 nm	
	Broken-gap junction	Ohmic Contact	Cu ₂ O, 1.5×10^{19} , 100 nm	NiO, 1×10^{18} , 50 nm
				Cu ₂ O, 1.5×10^{19} , 50 nm
Performance	Efficiency [%]	18.66	16.99	17.90
	V _{oc} [V]	1.154	1.134	1.144
	J _{sc} [mA/cm ²]	18.77	17.97	18.44
	FF [%]	86.15	83.34	84.86

Table 3

The simulation results of bottom PV cells shown in Fig. 6a with various different top contacts.

		Reference		BGJ	Buffer/BGJ
		Broken-gap junction	Ohmic Contact	In ₂ O ₃ , 1×10 ¹⁹ , 100 nm	In ₂ O ₃ , 1×10 ¹⁹ , 50 nm IZO, 1×10 ¹⁹ , 50 nm
Structure	Bottom Cell	ZnO, n-type, 1×10 ¹⁷ , 100 nm			
		CdS, n-type, 5×10 ¹⁵ , 70 nm			
		CuInSe ₂ , p-type, 1×10 ¹⁶ , 2.0 μm			
Performance	Intensity	1 Sun		Top PV cell screened	
	Efficiency [%]	14.26	6.67	5.77	6.65
	V _{oc} [V]	0.493	0.473	0.474	0.473
	J _{sc} [mA/cm ²]	38.52	18.76	17.86	18.70
	FF [%]	75.10	75.13	68.18	75.12

Table 4

The performance of top, bottom and CGS/CIS tandem PV cells.

	Top Cell	Bottom Cell	Tandem Cell
Efficiency [%]	17.5	6.47	24.1
V_{oc} [V]	1.14	0.473	1.62
J_{sc} [mA/cm ²]	18.5	18.5	18.5
FF [%]	82.9	73.9	80.5

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Fig. 1

Fig. 2a

Fig. 2b

- ➡ (1) Interface Tunneling
- ➡ (2) Drift-Diffusion
- ➡ (3) Ballistic Tunneling

Fig. 3

Fig. 4a

Fig. 4b

Fig. 5a

Fig. 5b

(1) Ohmic contact

(a)

(2) Cu₂O

(3) NiO/Cu₂O

Fig. 6b

Fig. 6c

(a)
(1) Ohmic contact

(2) In_2O_3

**(3) In_2O_3 /
 In_2O_3 -ZnO grading**

Fig. 7a

Fig. 7b

Fig. 7c

Fig. 8a

Fig. 8b