

Minority carrier transport length of electrodeposited Cu_2O in $\text{ZnO}/\text{Cu}_2\text{O}$ heterojunction solar cells

Yingchi Liu,¹ Hubert K. Turley,² John R. Tumbleston,¹ Edward T. Samulski,² and Rene Lopez^{1,a)}

¹Department of Physics and Astronomy, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599, USA

²Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599, USA

(Received 21 February 2011; accepted 28 March 2011; published online 21 April 2011)

The minority carrier transport length is a critical parameter limiting the performance of inexpensive Cu_2O - ZnO photovoltaic devices. In this letter, this length is estimated to be ~ 430 nm for electrochemically deposited Cu_2O by linking the cell's carrier generation profile with back and front incident photon-to-electron conversion efficiency measurements to a one-dimensional transport model. This critical length explains the losses typically presented by these devices and appears to correlate well with the microcrystalline film structure. The consequences of the magnitude of the length on device design with the aim of improving solar cell performance are described. © 2011 American Institute of Physics. [doi:10.1063/1.3579259]

The need for sustainable energy technologies has invigorated research in many photovoltaic systems with increasing emphasis placed on balancing cost and performance. To this end there has been a renewal of interest in solar cells based on cuprous oxide (Cu_2O) as the active layer because this semiconductor shows many important characteristics useful for solar cells production. These include low raw material cost, a direct energy gap (~ 2.1 eV), nontoxicity, long term stability, and it is amenable to low cost scalable fabrication process such as electrodeposition.¹ However, the fundamental limitations of Cu_2O , one of the earliest semiconductors to be studied, have not been overcome. In particular, the difficulty of fabricating n-type Cu_2O , homojunctions remains a barrier to the realization of Cu_2O based solar cells. More recently transparent conducting oxide (TCO)/ Cu_2O heterojunction solar cells have been pursued, especially $\text{ZnO}/\text{Cu}_2\text{O}$. Although the theoretical limit of the power conversion efficiency of Cu_2O based solar cell is about 18%,² the highest efficiency of electrodeposited $\text{ZnO}/\text{Cu}_2\text{O}$ device reported is 1.28%.¹ An inadequate minority carrier transport length has been implicated as an important factor behind this poor performance.³

In this letter, we report the minority carrier transport length in an electrodeposited Cu_2O layer. Using a simple physical model for carrier transport and recombination, namely, that the minority carriers (electrons in Cu_2O) diffuse to a depletion layer with an approximately constant diffusion coefficient and life time, the minority transport length is determined by analyzing the ratio of incident photon to electron conversion efficiency (IPCE) measured under front (glass) and back (gold) illumination. The transport length is found to be ~ 430 nm, significantly shorter than what other researchers have estimated in the past (discussed below) but consistent with the crystallite size of electrochemically deposited films. This finding provides insights into the performance difficulties and potential cell design alternatives for this material.

We fabricated the $\text{ZnO}/\text{Cu}_2\text{O}$ solar cell by electrodeposition¹ of Cu_2O on ZnO precoated glass substrates. ZnO film was deposited by pulsed laser deposition (PLD) using 99.99% purity ZnO target. To get good conductivity ZnO film with a surface receptive to Cu_2O growth, we deposit two layers of ZnO . First, a ZnO layer ~ 200 nm thick is deposited on glass substrate at 200°C with 10 mTorr O_2 . Second, a ZnO layer ~ 500 nm is deposited at room temperature with 200 mTorr O_2 . The Cu_2O layer was electrodeposited in an aqueous solution that contains 0.2 mol l^{-1} copper sulfate hydrate and 3 mol l^{-1} lactic acid. The solution pH is adjusted to 12.5 with a 1 mol l^{-1} KOH aqueous solution. The electrodeposition on glass/ ZnO substrate is carried out at 40°C with a current density of -0.9 mA/cm^2 for a total electric charge of 2 C cm^{-2} corresponding to the film thickness of $\sim 1.6\text{ }\mu\text{m}$. A 20 nm thick semitransparent gold layer was sputtered on Cu_2O as anode contact. The whole device was annealed on hot plate at 200°C for 1 h.

X-ray diffraction measurements confirm that Cu_2O is formed on the ZnO without the diffraction signatures of CuO (not shown). A scanning electron micrograph (SEM) of the cross section of the device is shown in Fig. 1, from which the

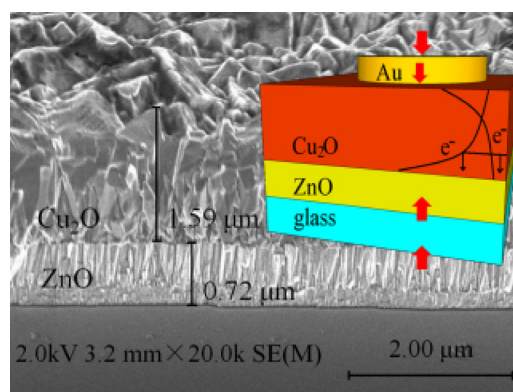


FIG. 1. (Color online) Cross-sectional SEM (45° tilt) of the $\text{ZnO}/\text{Cu}_2\text{O}$ solar cell. Inset: schematic of the complete device solar cell and electron generation profiles for front and back illumination.

^{a)}Electronic mail: rln@physics.unc.edu.

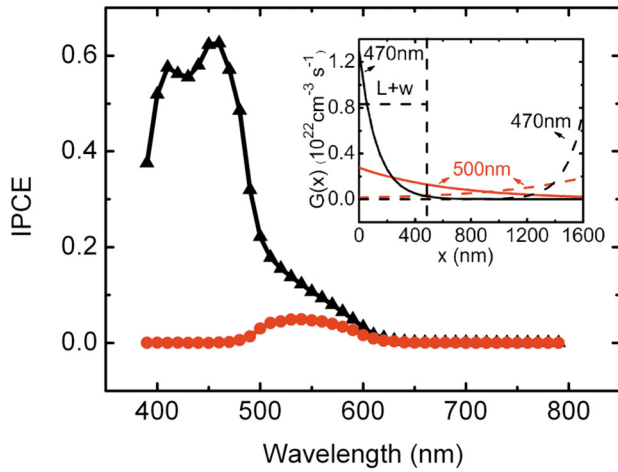


FIG. 2. (Color online) IPCE measurements with illumination from glass side (triangles on black line), and gold side (circles on red line), respectively. Inset: generation profile $G(x)$ of $\lambda=470$ nm and $\lambda=500$ nm. Solid lines are glass side illumination. Dashed lines are gold side illumination.

thickness of each layer of the device is assessed. The solar cells with $J_{sc}=3.16$ mA/cm² and a $V_{oc}=0.11$ V have been also characterized by current-voltage (I-V) scan, both in dark and under AM 1.5 conditions⁴ (front illumination). Figure 2 shows the IPCE measurements with illumination from both back and front of the cell. The J_{sc} calculated from the IPCE with front illumination is 3.49 mA/cm², which is consistent with our solar simulator measurement.

Recent work by Biccari *et al.*⁵ concluded that photoexcited electrons make the dominant contribution to the current in Cu₂O (>95%). The scale of the electron diffusion length in Cu₂O has been estimated previously^{5,6} using Gärtner's model⁷ for the photocurrent density. Their results range from 2 to 12 μ m. This would be an overestimation for electrodeposited Cu₂O given the typical low photocurrents obtained in these devices. In order to obtain the transport length in electrodeposited Cu₂O, we have modified Gärtner's model following the work of Soedergren *et al.*⁸ to obtain a self-consistent model, where all of the parameters are obtained

from the IPCE measurements and known optical constants.

As in Gärtner's model, we start with the photocurrent given by:⁷ $J=J_{DL}+J_{DIFF}$, where J_{DL} is the drift current density due to carriers generated inside the depletion layer and J_{DIFF} is the diffusion current density of minority carriers generated outside the depletion layer in the bulk of Cu₂O and diffusing into the depletion region.

$$J_{DL} = q \int_0^w G(x) dx, \quad (1)$$

where w is width of depletion layer, $G(x)$ is the generation rate of electrons, and $x=0$ is at the ZnO/Cu₂O interface. J_{DIFF} is determined by Eq. (2) for the excess concentration of electrons $n(x)$.

$$D_0 \frac{\partial^2 n(x)}{\partial x^2} - \frac{n(x)}{\tau_0} + G(x) = 0. \quad (2)$$

To solve Eq. (2), we chose boundary conditions $n(w)=0$ and $dn(d)/dx=0$ corresponding to a total carrier sweep and negligible electron current toward the anode, respectively.⁹ d is the thickness of Cu₂O layer. This last condition is used instead of Gärtner's $n(\infty)=0$, which is only appropriate for a bulk semiconductor and is not adequate for thin electrodeposited devices.

If φ is the flux of incident photons on the cell and α is the monochromatic absorption coefficient, $G(x)$ for gold and glass sides is approximated by,

$$G_{Au}(x) = \varphi T_{Au} \alpha e^{-\alpha(d-x)}, \quad (3)$$

$$G_{glass}(x) = \varphi T_{glass/ZnO} \alpha e^{-\alpha x}, \quad (4)$$

where T_{Au} and $T_{glass/ZnO}$ are the transmittance through gold and glass/ZnO to Cu₂O, respectively. They are measured independently by spectroscopic optical transmittance of the individual layers.

Solving Eq. (2) for back and front illuminations gives the electron concentration in the Cu₂O film. J_{DIFF} is proportional to the gradient of $n(x)$ at $x=w$. The IPCEs (J/φ) for gold and glass sides are given by,

$$IPCE_{gold} = e^{-d\alpha} \left[-1 + \frac{2e^{(d+w+dL\alpha)/L} L^2 \alpha^2 + e^{w(2/L+\alpha)} (-1+L\alpha) - e^{2d/L+w\alpha} (1+L\alpha)}{(e^{2d/L} + e^{2w/L}) (-1+L^2 \alpha^2)} \right] T_{Au}, \quad (5)$$

$$IPCE_{glass} = \left\{ 1 - e^{-w\alpha} + \frac{e^{-(d+w)\alpha} L \alpha [-2e^{(d+w+Lw\alpha)/L} L \alpha + e^{d(2/L+\alpha)} (-1+L\alpha) + e^{2w/L+d\alpha} (1+L\alpha)]}{(e^{2d/L} + e^{2w/L}) (-1+L^2 \alpha^2)} \right\} T_{glass/ZnO}, \quad (6)$$

where L is the diffusion length, ($L=\sqrt{D_0\tau_0}$). For long wavelengths (λ), where $\alpha(\lambda)$ is small (literature values⁶) and $\alpha L \ll 1$, one can obtain approximated expressions neglecting those small terms following the work of Lindquist *et al.*¹⁰ A useful feature of this limit is that one can obtain an estimate of the depletion layer width at short circuit conditions

$$\frac{w}{d} = \frac{IPCE_{glass}}{T_{glass/ZnO}} \left(\text{at } \lambda, \text{ where } \frac{IPCE_{gold}}{T_{Au}} \text{ is maximum} \right). \quad (7)$$

In our case, the $IPCE_{gold}/T_{Au}$ reaches its maximum at $\lambda=540$ nm (Fig. 2), where α is small⁶ and we can estimate

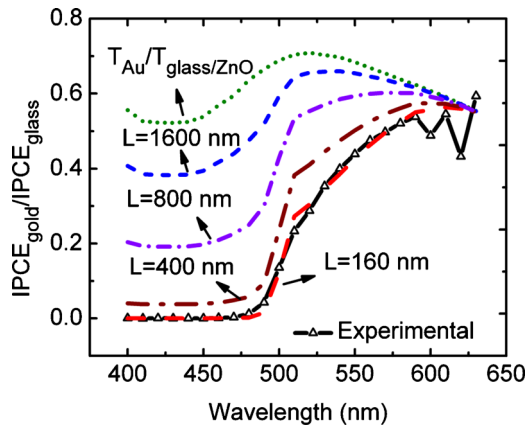


FIG. 3. (Color online) Experimental (open triangles) and simulated IPCE ratios with different proposed diffusion lengths ($L=160, 400, 800,$ and 1600 nm). Limit to IPCE ratio is set by the ratio of transmittances of gold to that of glass/ZnO.

$w \sim 269$ nm, using the film thickness (~ 1600 nm) obtained from SEM (Fig. 1) cross section. L can now be assessed from the ratio of the $\text{IPCE}_{\text{gold}}$ to the $\text{IPCE}_{\text{glass}}$.

In Fig. 3, we plot the experimental and simulated IPCE ratios with different proposed diffusion lengths. The features of the curves can be explained from the generation profile $G(x)$. Figure 2 shows $G(x)$ at 470 and 500 nm with illumination for both sides. As we can see, more electrons are generated close to where light enters the Cu_2O layer and the generation decays exponentially through the film. At short wavelength, α is large and the difference of generation profiles between the two illumination directions is huge. On average, only electrons within a distance $\leq L+w$ to the ZnO interface can be collected. For a relatively short L , at short wavelengths most electrons can reach the interface for front illumination. In contrast carriers generated from back illumination are too far away from the interface to be collected. At long wavelengths the difference in $G(x)$ becomes less significant as α gets smaller and the collection of electrons is almost independent of illumination direction. Therefore, the ratio of the IPCEs is small at short wavelengths and close to the ratio of incident light intensity on Cu_2O from the two illumination directions at long wavelengths. If one allows L to increase, the electron collection becomes more independent on the direction of illumination for all wavelengths, and the ratio of IPCEs is determined mainly by the ratio of transmittances.

From Fig. 3, we estimate that L is ~ 160 nm. The poorer fitting at longer wavelengths is independent of the parameter. It is due to the low IPCE values (near zero) that result in a noisy ratio in conjunction with possible light scattering losses from the sample roughness. As shown, our model provides a good fit to the IPCE ratio. The diffusion length found here is significantly shorter at least by one order of magni-

tude than the values reported previously.^{5,6} Moreover, when those values are applied with the classical Gärtner's model to the gold side illumination alone, they resulted in a negative $\text{IPCE}_{\text{gold}}$ at short wavelengths, which is not observed experimentally. One should note that those previous diffusion lengths were obtained from studying the IPCE of a $\text{Cu}/\text{Cu}_2\text{O}$ solar cell, which may have a different, and presumably better, crystalline structure. Nevertheless, such long L values would be in conflict with the low photocurrents obtained from electrodeposited Cu_2O . Furthermore, a qualitative inspection of the SEM cross section in Fig. 1, points to numerous microcrystalline defects that most likely should limit the free scattering path to submicron lengths.

In conclusion, we fabricated ZnO/ Cu_2O solar cell by PLD and electrodeposition. A value of ~ 160 nm for L is estimated from IPCE by a simple drift and diffusion model. For a 1600 nm thick absorption layer, only photogenerated carriers within the distance ~ 430 nm have a fair chance of being collected. Our result suggests a possible path to improve the J_{sc} performance of these devices. As proposed by Musselman *et al.*,³ a nanoscale structuring of the $\text{Cu}_2\text{O}/\text{ZnO}$ interface could be introduced to minimize electron transport lengths. However, this structure should be designed mindful of the transport length found in this letter, as a nanoscale scale less than this critical length will not bring additional benefits and could have a detrimental effect given the numerous potential interface defects that scale as the heterojunction contact area increases, in itself a big concern responsible for the less than expected V_{oc} . Finally, this approach could also be applied to study similar properties in other low cost photovoltaic and photoelectrochemical materials in which critical charge transport lengths are in conflict with optical absorption distances.

Support for this work is from NSF (Solar: Grant No. DMR-093433) and UNC-Chapel Hill Institute for the Environment (Carolina Energy Fellows Program).

¹M. Izaki, T. Shinagawa, K. T. Mizuno, Y. Ida, M. Inaba, and A. Tasaka, *J. Phys. D* **40**, 3326 (2007).

²J. J. Loferski, *J. Appl. Phys.* **27**, 777 (1956).

³K. P. Musselman, A. Wisnet, D. C. Iza, H. C. Hesse, C. Scheu, J. L. MacManus-Driscoll, and L. Schmidt-Mende, *Adv. Mater. (Weinheim, Ger.)* **22**, E254 (2010).

⁴J. Nelson, *Physics of Solar Cells* (Imperial College Press, London, 2003), p. 20.

⁵F. Biccari, C. Malerba, and A. Mittiga, *Sol. Energy Mater. Sol. Cells* **94**, 1947 (2010).

⁶L. C. Olsen, F. W. Addis, and W. Miller, *Sol. Cells* **7**, 247 (1982).

⁷W. Gärtner, *Phys. Rev.* **116**, 84 (1959).

⁸S. Soedergren, A. Hagfeldt, J. Olsson, and S. E. Lindquist, *J. Phys. Chem.* **98**, 5552 (1994).

⁹S. M. Sze, *Physics of Semiconductor Devices* (Wiley, New York, 1981), p. 802.

¹⁰S. E. Lindquist, B. Finnström, and L. Tegnér, *J. Electrochem. Soc.* **130**, 351 (1983).