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# Diffusion length variation in photovoltaic cells with Bridgman-grown $CuInSe_2$ substrates

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**Abstract**

In a group of $CuInSe_2$-CdS-ZnO photovoltaic cells, where the absorber was a layer cut from Bridgman-grown p-type $CuInSe_2$ ingots, electron diffusion lengths at room temperature ($L_n$) were estimated by the photocurrent–capacitance method. Dark capacitance measurements were also made on the same cells against reverse bias and from Mott-Schottky plots, slope concentrations $p_{MS}$ were determined at a reverse bias of 1.5 V. In a plot of $L_n$ against $p_{MS}$, it was found that, despite much scatter in the experimental points, there was an apparent trend of $L_n$ decreasing by about an order of magnitude with increase of $p_{MS}$ from $10^{16}$ to $10^{17}$ $cm^{-3}$. Detailed proposals were then made to explain this trend. These were reduction of lifetime via Shockley-Read trapping with mobility decrease by impurity scattering, shunt resistance lowering by light and optical penetration depth reduction at shorter illumination wavelengths.


*Keywords:* Copper–indium-diselenide; Diffusion length; Solar-cell; Photocurrent–capacitance-method; Mott-Schottky-plot

## 1. Introduction

A convenient nondestructive way of estimating the minority diffusion length, $L_n$ in the p-type absorber layer of a photovoltaic cell, when this quantity is of the order of micrometers, is the photocurrent–capacitance method. It has been used on different cells over many years [1,2] and is based on the increase of photocurrent arising from the widening of the depletion width ($W$) with increasing reverse bias in a cell illuminated with penetrating light. If this long wavelength light has an optical absorption coefficient of $\alpha$, then the method requires that the optical penetration depth $1/\alpha$ should be much larger than $W$, that is $\alpha W \ll 1$. If the depletion approximation applies, the junction capacitance $C_p$ is given by $C_p=\epsilon_o\epsilon_r A/W$, where $\epsilon_r$ is the relative dielectric constant of the absorber, $\epsilon_o$ is the permittivity of a vacuum and $A$ is the cell area. Then the illuminated current $I_L$ to dark current $I_D$ change $\Delta I=I_L-I_D$, can be shown to be given by $\Delta I=K(W+L_n)$, where $K$ is a quantity independent of reverse bias, $V_R$. Hence, this can now be written as $\Delta I=K(\epsilon_r\epsilon_o A/C_p+L_n)$, so that if $\Delta I$ is plotted against $1/C_p$ with the increase of reverse bias, it will ideally yield a straight line from which extrapolation can be made to the abscissa, cutting it at the negative value $-1/C_i$. The diffusion length is then given by $L_n=-\epsilon_r\epsilon_o A/C_i$.

This method has been used in this laboratory to estimate diffusion lengths in Se photovoltaic cells and $CuInSe_2$-based cells [3–5]. Most of the latter cells, were laboratory fabricated layer structures of the form $CuInSe_2$-CdS-ZnO, where the $CuInSe_2$ absorber was a wafer of Bridgman-grown p-type material, the CdS film was deposited from a chemical bath and the ZnO layer by r.f. sputtering. These measurements yielded $L_n$-estimates over the range 0.2 to 3 μm, with a variability of ±25%, taking $\epsilon_r=10$ for $CuInSe_2$. In a study on a group of cells fabricated in a similar way, Mott-Schottky plots were also measured, from which slope concentrations, $p_{MS}$ were determined at a reverse bias of 1.5 V. It was found that if the $L_n$-estimates on these cells were plotted against $p_{MS}$ [5], despite much scatter in the points, there was an apparent correlation between the quantities, with $L_n$ apparently decreasing with increasing $p_{MS}$.

In the present paper, this trend is again reported with more complete results, but, in addition, possible explanations of its cause are presented. These include, not only possible fundamental changes of lifetime and mobility but also the effect of deviation from ideality in the cells and in the experimental measurement conditions.

## 2. Experimental results

Details of the experimental technique used have been given previously [6]. However, some brief information is as follows.

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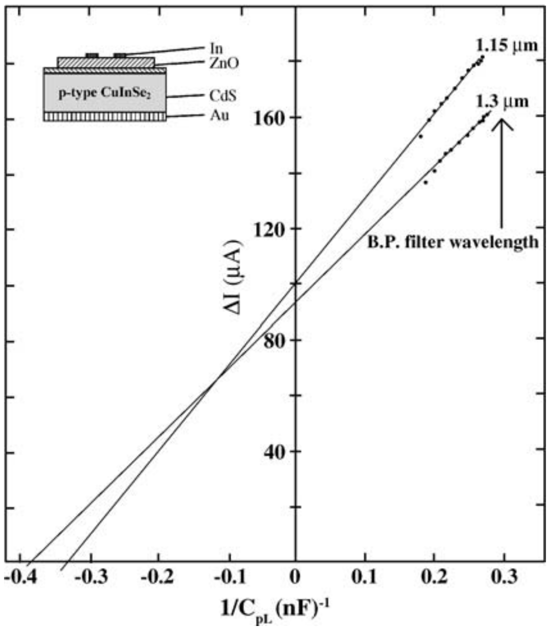


Fig. 1. Plot of illuminated-to-dark photocurrent change $\Delta I$ against reciprocal capacitance $1/C_{pL}$ for a $CuInSe_2$-CdS-ZnO cell (No. 35), measured under illumination via 2 optical band pass filters.

The monochromatic illuminating source mostly used was a quartz-halogen lamp with optical filters at band pass wavelengths of 1.1, 1.15, 1.2 and 1.3 μm. The junction capacitances $C_{pL}$ on the cells were measured in the parallel mode under the same illumination at a frequency of 10 kHz with a signal level of 20 mV.

Fig. 1 shows a plot of $\Delta I$ against $1/C_{pL}$ for one (No. 35) of a group of cells having the layer structure Au-$CuInSe_2$-CdS-ZnO-In (see insets in Figs. 1, 2 and 3). This particular device had an AMGlobal 1.5 solar conversion efficiency ($\eta$) of over 10%, without an antireflection coating. Extrapolation in Fig. 1 from the lower plotted points is seen to give intercepts of $-0.33$ and $-0.38$ $nF^{-1}$ for the 1.15 and 1.3 μm illuminating wavelengths respectively. Thus, taking an average intercept of $-0.36$ $nF^{-1}$, a total cell area of 0.138 $cm^2$ with $\epsilon_r = 10$, the $L_n$ value works out to be 0.44 μm. Measurements of $C_p$ versus reverse voltage, $V_R$, under darkness were made on the cells, yielding the Mott-Schottky plots of $(A/C_p)^2$ versus $V_R$, shown for 3 cells from the group in Fig. 2. From the curve for cell No. 35, a slope of $2 \times 10^{14}$ $cm^4$ $F^{-2}$ $V^{-1}$ was determined at $V_R = 1.5$ V, which corresponds to a slope concentration of $p_{MS} = [2/(e\epsilon_o\epsilon_r)]\{\Delta V_R/\Delta[(A/C_p)^2]\} = 7 \times 10^{16}$ $cm^{-3}$.

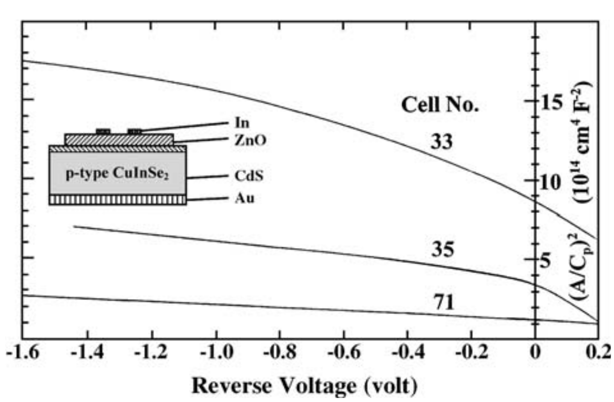


Fig. 2. Mott-Schottky plots of $(A/C_p)^2$ versus reverse voltage $V_R$ for 3 $CuInSe_2$-CdS-ZnO cells, where $A$ is the cell area and $C_p$ is the dark parallel capacitance, measured at 10 kHz.

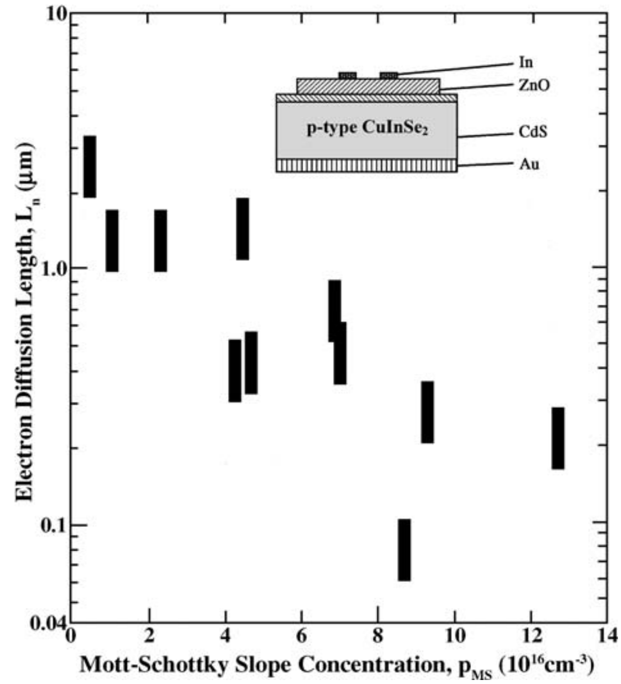


Fig. 3. Plot of diffusion length values $L_n$, obtained from $\Delta I - 1/C_{pL}$ plots, against Mott-Schottky slope concentrations $p_{MS}$, measured at $V_R = 1.5$ V, for a group of $CuInSe_2$-CdS-ZnO cells.

Fig. 3 shows a plot of $\Delta I$ against $p_{MS}$ for this group of similarly fabricated $CuInSe_2$-CdS-ZnO cells. This is a similar but revised plot to one shown previously [5]. Despite considerable scatter in the points, a trend of a general decrease of $L_n$ from about 2 to 0.2 μm with increasing $p_{MS}$ from $10^{16}$ to $10^{17}$ $cm^{-3}$ is apparent.

## 3. Trend interpretation possibilities

The following are possible explanations for the observed trend based on the assumption that the quantity $p_{MS}$ reflects the behaviour of the true hole concentration from shallow acceptors, even though it may not be exactly equal to it. Thus, to be explained is an order of magnitude decrease in the apparent $L_n$ value as the shallow acceptor concentration, and hence also the hole concentration, is increased from $10^{16}$ to $10^{17}$ $cm^{-3}$.

### *3.1. Lifetime and/or mobility decrease*

The first option to be examined assumes the method yields a true value for $L_n$, controlled via Shockley-Read trapping and/or mobility reduction from impurity scattering. This could occur through the relation $L_n = (D_n\tau_n)^{1/2}$, where $\tau_n$ is the electron lifetime and $D_n$ is the electron diffusion coefficient in the p-type material. From Shockley-Read theory [7], with a postulated trap level 0.1 eV above the valence band, this could lead to about a 5-fold decrease in $\tau_n$ with the supposed hole increase and