Cathodoluminescence measurement of grain boundary recombination velocity in vapour grown p-CdTe

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Abstract. A cathodoluminescence (CL) based method for measuring the minority carrier diffusion length ($L$) and reduced recombination velocity ($S_{\text{red}}$) of an individual grain boundary is presented. The technique is based on the van Roosbroeck model for the steady-state carrier distribution near a free surface in a semi-infinite solid. Values of $L = 0.55 \pm 0.03 \, \mu m$ and $S_{\text{red}} = 0.23 \pm 0.02$ are obtained for vapour grown p-type CdTe. The effect of the electron beam generation volume on the accuracy of measurement is also discussed. Intermediate beam voltages (e.g. 15 kV for CdTe) are likely to produce the most reliable results. The method can be used to characterise the electrical activity of grain boundaries in thin-film solar cells.

1. Introduction

Grain boundaries have an important effect on the electrical properties of thin-film solar cells, such as CdTe and Cu(In,Ga)Se$_2$. Charge is accumulated at the grain boundary due to the energy difference between the quasi-neutrality level of the boundary and Fermi level in the bulk semiconductor. The built-in potential leads to band bending (upward bending for $n$-type semiconductors and downward bending for $p$-type), such that majority carriers are repelled and minority carriers attracted towards the boundary, at a rate given by the recombination velocity, where they undergo recombination. Grain boundaries with a high recombination velocity are sinks for minority carriers, as well as strong barriers for majority carrier flow, and therefore reduce solar cell efficiency. The electrical activity depends on the nature of the grain boundary (e.g. coincident site lattice or random grain boundary).

Electron beam induced current (EBIC) has previously been used to measure the reduced recombination velocity (i.e. the recombination velocity divided by the bulk diffusion velocity for minority carriers) of individual grain boundaries in silicon [1-3]. The reduced recombination velocity is extracted from curve fitting of the raw data to non-analytic functions involving several material and experimental parameters. The electron beam generation volume is modeled using a simplified analytic function (e.g. a spherically symmetric Gaussian [3]). The present authors however have developed a cathodoluminescence (CL) method for measuring the reduced recombination velocity [4], based on the van Roosbroeck [7] model for steady-state carrier distribution near a free surface. The advantages of this method are that it does not need any electrical contacts (cf. EBIC) and the parameters of interest are extracted directly from the experimental data, without the need for curve fitting. However, the electron beam generation volume is assumed to be a uniform plane parallel to the boundary, which is unrealistic. In this paper the effect of the electron beam energy (and hence generation volume) on accuracy of the CL measurement is discussed. For completeness the theory behind the CL technique and experimental data on p-type CdTe are also presented, although a more detailed report on these aspects can be found in [5].
2. Background theory
The van Roosbroeck model [5] describes the steady-state carrier distribution in a semi-infinite solid containing a free surface. Time independent, uniform carrier generation in a plane parallel to and at a distance \(x_b\) from the free surface is assumed. If a grain boundary is substituted for the free surface the CL intensity, \(I(x_b)\), for an electron beam incident at position \(x_b\) is:

\[
I(x_b) = k \int_0^\infty \eta(x) \left[ \exp \left( -\frac{|x - x_b|}{L} \right) - \frac{S_{\text{red}} - 1}{S_{\text{red}} + 1} \exp \left( \frac{x + x_b}{L} \right) \right] dx
\]

where \(L\) is the minority carrier diffusion length, \(S_{\text{red}}\) the reduced recombination velocity, \(\eta\) the CL emission efficiency and \(k\) a constant relating to CL detection efficiency. The term within the square brackets is the van Roosbroeck steady-state carrier distribution [5], i.e. it is assumed that the CL intensity is directly proportional to the carrier density. This assumption may be invalid for strongly excitonic materials or at high injection levels, but was experimentally verified for CdTe by demonstrating a linear relationship between the CL intensity and electron beam current.

If \(\eta\) is assumed to be independent of position \(x\), equation (1) simplifies as:

\[
\ln[\Delta I(x_b)] = \ln \left( \frac{S_{\text{red}}}{S_{\text{red}} + 1} \right) - \frac{x_b}{L}; \quad \Delta I(x_b) = -I(x_b) - I(x_b = \infty)
\]

A plot of \(\ln[\Delta I(x_b)]\) vs \(x_b\) should therefore be a straight line. The gradient of the straight line gives the diffusion length \(L\) and the intercept gives the reduced recombination velocity \(S_{\text{red}}\).

3. Experimental procedure
Panchromatic CL images were obtained from a ~70 µm thick, \(p\)-type CdTe thin-film vapour grown on a Ge substrate. A Hitachi SU-70 scanning electron microscope (SEM) operating at 15 keV and 1.6 nA beam current was used together with a Gatan MonoCL system for CL detection. The pixel dwell time for the panchromatic CL image was 300 µs, i.e. significantly longer than the electron minority carrier lifetime (\(\tau\)) of 20 ns [6], thus ensuring steady-state conditions.

2D Monte-Carlo simulations of the electron beam generation ‘volume’ were carried out using screened Rutherford cross-sections, and from this the steady-state minority carrier distribution in bulk \(p\)-type CdTe was determined by solving the continuity equation using finite difference methods. In this paper we refer to this carrier distribution as the ‘steady-state source distribution’. The simulation parameters are \(L = 500 \text{ nm}\) (section 4.1), \(\tau = 20 \text{ ns}\) [6] and 1.6 nA electron beam current. A free surface recombination velocity of \(5 \times 10^5 \text{ cm/s}\) [7] was applied as the boundary condition.

4. Results and Discussion
4.1. Experimental data
Figure 1(a) shows a panchromatic CL image of a near end-on grain boundary in \(p\)-CdTe. The intensity normal to the grain boundary is extracted from the box region in figure 1(a), and is shown in figure 1(b). The intensity profile is used to plot a \(\ln[\Delta I(x_b)]\) vs \(x_b\) graph (figure 1(c)), which shows overall linear behavior except for data points closer to the grain boundary. The deviation from linearity could be due to variations in the CL emission parameter \(\eta\) at the grain boundary compared to the bulk (see [6] for a more detailed discussion on the effects of \(\eta\)). A straight line was least squares fitted to figure 1(c), ignoring the first four data points closest to the grain boundary, and values of \(L = 0.55 \pm 0.03 \text{ µm}\), \(S_{\text{red}} = 0.23 \pm 0.02\) extracted from the gradient and intercept respectively. The diffusion length \(L\) is similar to values reported in the literature [9]. Using \(\tau = 20 \text{ ns}\) [6], the measured values of \(L\) and \(S_{\text{red}}\) give a recombination velocity of \(\sim 630 \text{ cm/s}\). This is small compared to a \(5 \times 10^5 \text{ cm/s}\) recombination velocity for a free surface in \(p\)-CdTe [7] or a value of \(\sim 10^7 \text{ cm/s}\) for grain boundaries in Si [1-2]. However, our observations as well as previous reports [8] indicate that vapour grown CdTe contains low misorientation, sub-grain boundaries, which could explain the small recombination velocity.
4.2. Numerical simulations

Although a near-linear relationship was observed between \( \ln[\Delta I(x_b)] \) and \( x_b \) (figure 1(c)), carrier generation by the electron beam needs to be analysed in more detail. In the time independent van Roosbroeck model uniform carrier generation in an infinite plane parallel to the grain boundary is assumed. Since the CL data are acquired under steady-state conditions, the steady-state source distribution (section 3) effectively provides the excess carriers. Simulated steady-state source distributions for 5, 15 and 25 keV beam energies in \( p\)-CdTe are shown in figure 2. The spatial extent of the steady-state source distribution increases with beam energy.

The van Roosbroeck criterion of an infinite carrier generation plane clearly cannot be satisfied. A more reasonable criterion is that the dimensions of the steady-state source distribution must be at least \( 2L \). The full width at half maximum (FWHM) of the steady-state source distribution along a given direction is arbitrarily defined as being the characteristic dimension along that direction. Hence the plots in figure 2 must have a FWHM of at least \( 2L \) along the vertical and horizontal axes. For the 15 keV beam the FWHM is 820 and 1070 nm along the vertical and horizontal axes respectively (the FWHM was calculated through the most intense region of the steady-state source distribution using a linear scale for the excess carriers). Since \( L\sim 500 \text{ nm} \) (section 4.1), the steady-state source distribution size is satisfactory for the 15 keV beam. Beam energies below 15 keV (e.g. 5 keV) have steady-state source distributions that are more point-like and are therefore unsuitable, and vice-versa for beam energies above 15 keV (e.g. 25 keV).

The symmetry of the plots in figure 2 about the vertical beam direction means that if the steady-state source distribution is uniformly broadened by \( 2\delta \) (\( \delta \geq L \)) along the horizontal axis, then the plane of excess carriers in the van Roosbroeck model must be replaced by a uniform slab of thickness \( 2\delta \). If the slab is centred at the incident beam position \( x_b \) the steady-state carrier distribution, \( c'(x) \), at distance \( x \) from the boundary is obtained from superposition of the van Roosbroeck result over the entire slab thickness, i.e.:
where \( c(x) \) is the van Roosbroeck distribution for an excess carrier plane at position \( x_b \) (i.e. \( c(x) \) is equal to the integrand in equation (3)). The \( 1/(2\delta) \) pre-integral factor is a normalisation constant. Equation (3) indicates that a uniform slab of excess carriers does not change the shape of the steady-state carrier distribution from the van Roosbroeck model, but simply increases its magnitude by a constant factor. This has no effect on the extracted values of \( L \) and \( S_{red} \) or the linear relationship between \( \ln[\Delta f(x_b)] \) and \( x_b \). It must be noted however that this is only an approximation, since the true steady-state source distribution is more complicated than a uniform slab of constant thickness.

Figure 3 shows the steady-state carrier distribution for a 15 keV electron beam incident at a distance of \( 0.5L \), or 250 nm, away from a grain boundary, which is at the arbitrary position of 0 nm. It is assumed that carrier generation by the electron beam is not significantly modified at the grain boundary. In figure 3(a) the grain boundary recombination velocity is 630 cm/s (value obtained in this study), while in figure 3(b) it is \( 10^4 \) cm/s (value for a high angle grain boundary in Si [1-2]). It is clear that excess carriers can be present on either side of the grain boundary, even if the recombination velocity is relatively large. The van Roosbroeck model however is for a free surface and hence excess carriers can only be present on one side of the boundary, meaning that the \( \ln[\Delta f(x_b)] \) vs \( x_b \) plot will deviate from linearity for electron beam positions close to the grain boundary. Since the steady-state source distribution size increases monotonically with beam energy, higher beam energies give rise to larger deviations from linear behaviour. Note that the CL emission parameter \( \eta \) could also vary close to the grain boundary and is a further reason for non-linear behaviour.

Figure 3. steady-state carrier distribution for a 15 keV electron beam incident 250 nm away from a grain boundary (broken line in the figure), which is at the arbitrary position of 0 nm. In (a) the grain boundary recombination velocity is 630 cm/s, while in (b) it is \( 10^4 \) cm/s.

5. Conclusions

A CL method, based on the van Roosbroeck model, for measuring the reduced recombination velocity of a single grain boundary is described and applied to \( p \)-type CdTe. The role of electron beam energy on the accuracy of the measurement has also been investigated. Low beam energies are unsuitable as the steady-state source distribution is more similar to a point-source, rather than a plane of excess carriers. High beam energies however generate carriers on either side of the grain boundary, while in the model it is assumed that the carriers are only present on one side. Hence an intermediate beam energy (e.g. 15 keV for CdTe) is likely to give the most reliable results. Further experiments are required to confirm this. Furthermore a comparison with Donolato’s EBIC method [1], applied to the same grain boundary, is necessary in order to determine the accuracy of the reduced recombination velocity measured using the CL technique.

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