

MEASUREMENT OF AMBIPOLAR MOBILITY-LIFETIME PRODUCT AND ITS SIGNIFICANCE FOR AMORPHOUS SILICON SOLAR CELLS

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ABSTRACT

In order to evaluate correctly the ambipolar diffusion length (L_{amb}) or the ambipolar drift length (L_e) from a Steady State Photocurrent Grating (SSPG) diffusion or drift measurement, the condition of charge quasi-neutrality has to be maintained everywhere in the material (ambipolarity condition). This is shown theoretically, by calculating the experimentally accessible parameter (β) without assuming a priori that the ambipolarity condition holds. The effect of non-ambipolar behavior on the experimental plots, both for diffusion and drift is derived. Thereafter, measured SSPG plots for undoped a-Si:H are given, illustrating both ambipolar and non-ambipolar cases.

INTRODUCTION

Several transport measurements methods have been developed to evaluate the quality of semiconductors for photovoltaic and other device applications. In the past years, various researchers have tried to apply the measurement methods originally developed for crystalline silicon to the case of amorphous hydrogenated silicon (a-Si:H) and especially to that of undoped a-Si:H. This approach has been successful in evaluating electron transport properties. However, when attempting to evaluate the mobility of holes and their mobility-lifetime product, these "classical" semiconductor measurement techniques have led to major problems: i.e. they give unprecise values (as in the case of the Surface Photo Voltage (SPV) measurement where the Schottky barrier used affects the measurement in an unpredictable way (7)), they lead to controversial results (as in the case of Steady-State Hecht Plot where the distinction between holes and electrons is controversial (5,6)), or they lead to measurement difficulties (as in the case of the Photo Magnetic Effect (PME)(9)). On the other hand, transient measurement techniques like Time of Flight (TOF) (10) have allowed a clear determination of the electron- and hole- $(\mu\tau)$ products, but there is no evidence that values of the transient mobility and of the $(\mu\tau)$ -product measured thereby can be applied to the steady-state operation of a solar cell. Whatever may be the limiting carrier for collection in a-Si:H solar cells (this is, in fact, a controversial issue (5,6,8)), holes definitely have a key role to play in assuring the uniformity of the electric field within the $\langle i \rangle$ layer of a p-i-n a-Si:H solar cell. Thus, it remains important to find a method for the steady-state measurement of hole transport properties in the intrinsic a-Si:H layer.

The Steady State Photocurrent Grating (SSPG) measurement method has been recently proposed (3,4) as a reliable means to measure both the ambipolar diffusion length (L_{amb}) by performing the SSPG measurement with a negligible external electric field (E_{ext}); as well as the ambipolar drift length (L_e), by performing the SSPG measurement with a high E_{ext} . In ambipolar transport theory (see e.g. (1, 2)), the carrier with the lowest drift mobility will dominate transport. In intrinsic a-Si:H, holes have a lower drift mobility than electrons, due to the effect of fixed charges, i.e. of trapping. Therefore, L_{amb} and L_e as measured by SSPG, are predominately influenced by the transport properties of the holes. Note that in (1-4, 12) only the effect of trapping in bandtails has been taken into account. However the fixed charge due to dangling bonds is of at least equal importance. Revised calculations are under way and will be published later.

However, for solar cell design and analysis, it is not the value of L_{amb} that counts, but that of the hole steady-state drift mobility (μ_p^d) and of the $(\mu_p^d \tau_0)$ -product of holes (τ_0 is the small-signal lifetime, that can, in principle, be measured independently on the same sample). The value of μ_p^d is of particular importance, as it directly determines the uniformity of the inner electric field in a p-i-n solar cell (5,6). The expression for L_{amb} involves the steady-state drift mobilities μ_n^d and μ_p^d and τ_0 as well as the trapping coefficients $\gamma_{n,p}$ for electrons and for holes ($\gamma_{n,p}$ as defined in (1)):

$L_{amb}^2 = (kT/e) \tau_0 (\gamma_n^{-1} + \gamma_p^{-1}) (\mu_n^d \mu_p^d) / (\mu_n^d + \mu_p^d)$. (Note: if $\mu_n^d \gg \mu_p^d$, then $(\mu_n^d \mu_p^d) / (\mu_n^d + \mu_p^d) \approx \mu_p^d$). The apparition of the unknown factors $\gamma_{n,p}$ in the expression of L_{amb} implies that the measurement of L_{amb} alone is insufficient in order to evaluate the $(\mu_p^d \tau_0)$ -product. The measurement of L_e is thus needed in order to get more information about $\gamma_{n,p}$. L_e , that had been called L_{amb}^e in (2), can be expressed as:

$L_e = \tau_0 (\gamma_n^{-1} - \gamma_p^{-1}) E_{ext} (\mu_n^d \mu_p^d) / (\mu_n^d + \mu_p^d) = -\mu_{amb} \tau_0 E_{ext}$
where $\mu_{amb} = (\gamma_p^{-1} - \gamma_n^{-1}) (\mu_n^d \mu_p^d) / (\mu_n^d + \mu_p^d)$. Note here that if $\gamma_n = \gamma_p$ then $L_e = 0$. The "effective" Einstein relation applies here: $L_e / L_{amb}^2 E_{ext} = e/kT (\gamma_n - \gamma_p) / (\gamma_n + \gamma_p)$ (2); and it will give us the value of $r = (\gamma_n - \gamma_p) / (\gamma_n + \gamma_p)$. The value of r will help us to assess the magnitude of the factors $\gamma_{n,p}$. Unfortunately it is not possible even with both L_{amb} and L_e measurements to evaluate the two factors γ_n and γ_p . A model relating e.g. trapping to the Density of States (DOS) is needed here in order to evaluate $\gamma_{n,p}$ (see (12, 4, 1) for a model that takes only bandtails into account).

Furthermore, even for the SSPG method, particular care has to be taken with regards to the measurement conditions: as mentioned in (2) and (4), one has to fulfill the ambipolarity condition in order that an SSPG measurement renders the correct values for L_{amb} or L_e . This condition can be attained

only if *a*) the material fullfills the so-called lifetime criterion: the ratio τ_0/T_d (where $T_d = \epsilon/\sigma_B$ is the dielectric relaxation time, ϵ is the dielectric constant and σ_B the photoconductivity due to the bias light) is large as compared to a certain threshold Γ (the value of Γ depends on the ratio of the drift mobilities and will be different for the drift and diffusion cases (see(2))) and if *b*) the experimental excitation conditions insure that charge neutrality is maintained everywhere in the material. (Note here that the ambipolarity condition is more restrictive than the lifetime criterion: in a lifetime material, local space charge can persist due to the particular excitation conditions. Furthermore, our general calculations for the SSPG case show that it is impossible to perform ambipolar transport measurements in a non-lifetime material).

Practically, for the SSPG diffusion measurement, Balberg et al. (7) have proposed to determine L_{amb} from the experimentally accessible parameter β by plotting a particular function: $\Lambda^{-2} = f[(2/(1-\beta))^{0.5}]$, where Λ is the grating period and β is defined as described in the experimental part of this article. Assuming a priori that the ambipolar condition is fulfilled, they calculate this plot to be a straight line. From the intercept of this straight line with the Λ^{-2} axis, L_{amb} can be evaluated. Similarly, if one performs SSPG drift measurements, and again assumes ambipolarity condition to hold, one can evaluate L_e from the slope of another plot; as can be calculated from (3), the function applicable now is: $\Lambda^{-2} = f[2/(1-\beta)]$, and this plot will again become a straight line.

In the present paper we will first show theoretically how the particular plots for drift and diffusion are modified when the lifetime criterion or the ambipolarity condition are not fulfilled. We will then give experimental evidence for different a-Si:H samples, of behaviors both fulfilling and not fulfilling the ambipolarity condition.

CALCULATION OF THE GENERAL SSPG SOLUTION FOR DIFFUSION.

This calculation is an application of the theory developed by the authors in (1). If the applied electric field E_{ext} used for the SSPG measurements is negligible, only the diffusion of carriers will be responsible for the measured effect. We have derived in (1) the critical electric field E_c above which drift also begins to influence the measured effect. Neglecting the effect of the factors $\gamma_{n,p}$, E_c becomes $E_c = (kT/e) \cdot (1/L_{amb})$. E_c will be larger if one considers the effect of $\gamma_{n,p}$ (1). Therefore E_c , as defined above, is the minimal critical electric field. Note here that E_c decreases when L_{amb} increases, i.e. drift effects will affect the measurement even at low electric fields for samples where L_{amb} is large.

We have solved the system of transport equations for the small-signal sinusoidal excitation of the SSPG experiment without assuming that the ambipolarity condition holds. We have used the argumentation of (4) to calculate β (defined as in (4)), using our general solution for the distribution of the carriers. We find the following general expression, not restricted to the lifetime and ambipolar case:

$$\sqrt{\frac{2}{1-\beta}} = C \frac{[1+(2\pi L_-/\Lambda)^2] [1+(2\pi L_+/\Lambda)^2]}{A + B (2\pi/\Lambda)^2} \quad [1]$$

where $A = (\mu_n^d/\gamma_n + \mu_p^d/\gamma_p) / (\mu_n^d + \mu_p^d) = 1$
 $B = 2 (kT/e) T_d (\mu_n^d \mu_p^d) / (\gamma_n \gamma_p (\mu_n^d + \mu_p^d))$
 $C = \tau_B / \tau_0 \approx 1$
 τ_B is the bias carrier recombination time (1),
 L_+, L_- are the general diffusion characteristic lengths (1).

The "pure" diffusion plot: $\Lambda^{-2} = f[(2/(1-\beta))^{0.5}]$ gives a straight line if and only if *a*) the material is in the lifetime regime: $L_- = L_{amb} \gg L_+ = L_{die}$ and *b*) the term $B \cdot (2\pi/\Lambda)^2$ is negligible compared with A (i.e. if Λ is large enough: ambipolarity condition). Note here that lifetime behavior depends on material parameters as defined under bias light, and that the ambipolarity condition depends on excitation (i.e on Λ in this case and, in general, also on the boundary conditions).

If, for example, Λ is comparable to L_{die} , space charge will be present in a lifetime material (non-ambipolar case), and the $\Lambda^{-2} = f[(2/(1-\beta))^{0.5}]$ plot will no longer be a straight line. If the material does not fulfill the lifetime criterion, (i.e. either if $L_- = L_+$, or if $L_- = L_1 \gg L_+ = L_2$ (relaxation case (1)), then the term $B(2\pi/\Lambda)^2$ is not negligible compared with A , and we can see from [1], that the plot of $\Lambda^{-2} = f[(2/(1-\beta))^{0.5}]$ is no longer a straight line. For both the non-ambipolar case and for the relaxation regime, the second derivative of the function $\Lambda^{-2} = f[(2/(1-\beta))^{0.5}]$ is positive, corresponding to a concave curve. Such a concave curve is therefore the signature of the presence of space charge in the material. In this case, the value of the characteristic lengths cannot be easily deduced from the $\Lambda^{-2} = f[(2/(1-\beta))^{0.5}]$ plot.

CALCULATION OF THE GENERAL SSPG SOLUTION FOR DRIFT

When $E_{ext} \gg E_c$, drift will predominantly affect the carrier distribution, i.e diffusion will be negligible. The intermediate case, when both diffusion and drift affect the carrier distribution, has already been studied, provided the ambipolarity condition holds, by Ritter et. al. (3). They could show that here the effect of diffusion simply adds to the effect of drift. One can however show that if the ambipolarity condition does not hold, one can no more simply add these two effects. Therefore the non-ambipolar (drift - diffusion) intermediate case is more complicated, and we restrict our analysis to the case $E_{ext} \gg E_c$ (drift only). We obtain then:

$$\sqrt{2/(1-\beta)} = \frac{\sqrt{1+(2\pi L_-/\Lambda)^2} \sqrt{1+(2\pi L_+/\Lambda)^2}}{\mu_n^d \sqrt{1+(2\pi T_d E_{ext} \mu_p^d/\Lambda)^2} + \mu_p^d \sqrt{1+(2\pi T_d E_{ext} \mu_n^d/\Lambda)^2}} \tau_B \tau_0 \quad [2]$$

where L_{\pm} are the general drift lengths:
 $L_{\pm} = 2 T_d \mu_n^d \mu_p^d E_{ext} / \{\mu_{\sim} \pm (\mu_{\sim}^2 + 4\mu_n^d \mu_p^d T_d / \tau_0)^{0.5}\}$, where $\mu_n^d, \mu_p^d, \mu_{\sim}$ are as defined in (1).
 If the material fullfills the lifetime criterion, then $L_- = L_e$ and $L_+ = L_{die}^{drift} \ll L_e$.

If the ambipolarity condition is fulfilled, our expression reduces to the usual one for large electric fields (3). In a SSPG "pure" drift experiment ($E_{ext} \gg E_c$), the plot of $\Lambda^{-2} = f[2/(1-\beta)]$ will give a straight line only and only when ambipolar condition is fulfilled. In this case, the value of $(\gamma_n^{-1} - \gamma_p^{-1})(\mu_p^d \tau_0)$ can be deduced from the slope of the plot of L_e as a function of E_{ext} . Note that the values of β measured in an ambipolar "pure" drift measurement will give a parabolic curve when plotted on a "pure" diffusion plot: $\Lambda^{-2} = f[(2/(1-\beta))^{0.5}]$. Therefore, the observation of a curvature on a diffusion plot can be due either to the effect of a relatively large E_{ext} (comparable to E_c), or to non-ambipolar behavior in a "pure" diffusion case. Note also here that the ambipolarity condition is more difficult to establish in the case of a SSPG drift measurement as compared to a SSPG diffusion measurement. First, because the presence of an

external electric field renders the lifetime criterion more difficult to fulfill, and secondly because by increasing L_{ext} , L_e and L_{diel}^{drift} also increase. As the range of Λ is limited by the laser wavelength used, one tends thus to reach the non-ambipolar case where $L_e \gg \Lambda = L_{diel}^{drift}$.

EXPERIMENTAL

In the SSPG measurement, a He-Ne (10 mW) polarised laser beam is split into two beams of different intensities F_1 and F_2 ($F_1/F_2 = 35$ in our case). These two beams interfere in the sample, producing *a*) an interference grating when they are polarised parallel to each other, or *b*) an uniform illumination when one of them is polarised perpendicularly to the other. In case *a*), the HeNe light interference pattern photogenerates a carrier grating. The measurement of the photoconductivity perpendicular to the grating depends on the average amplitude of the carrier distribution; its value $\sigma_{grating}$ is different from the value $\sigma_{no\ grating}$ obtained under uniform illumination. In the SSPG method, L_{amb} is determined from the variation of the experimental ratio $\beta = \sigma_{grating}/\sigma_{no\ grating}$ with the grating period Λ . Λ is varied by changing the angle of incidence of the two laser beams on the sample. Diffusion measurements are performed with a negligible E_{ext} , whereas drift measurements are performed with E_{ext} high compared to E_c . We will present the results obtained for two a-Si:H samples in the degraded state. The electro-optical characteristics of sample 1 and of sample 2 are given in Table 1. Two parallel Chromium contacts, separated by a 0.5mm gap, were evaporated on the surface of the samples. The measurements were performed at an illumination intensity of about 10 mW/cm² for the bias light (HeNe laser). The photoconductivity σ_B was measured with the bias light.

Sample	d/ μm	σ_B/S	E_0/meV	N_s/cm^{-3}	$L_{amb}/\mu\text{m}$	E_c/Vcm^{-1}	b
1	2.4	$2 \cdot 10^{-7}$	61	$7 \cdot 10^{16}$	0.08	3260	7
2	2.5	$7 \cdot 10^{-7}$	61	$2.5 \cdot 10^{16}$	0.135	1911	20

Table 1: Electro-optical properties of samples 1 and 2. E_0 and N_s are the Urbach parameter and total defect density, respectively, measured by PDS, $E_c = kT L_{amb}/c$ is the minimum critical electric field (see text), $b = \mu_n^d/\mu_p^d$ is estimated according to (4). The two samples were deposited by VHF-GD at 70 MHz. Sample 1 was deposited at $T_d = 150$ °C, and sample 2 at $T_d = 300$ °C (see (11) for details of the deposition parameters). The experimental results are given in Fig.1 and Fig.2.

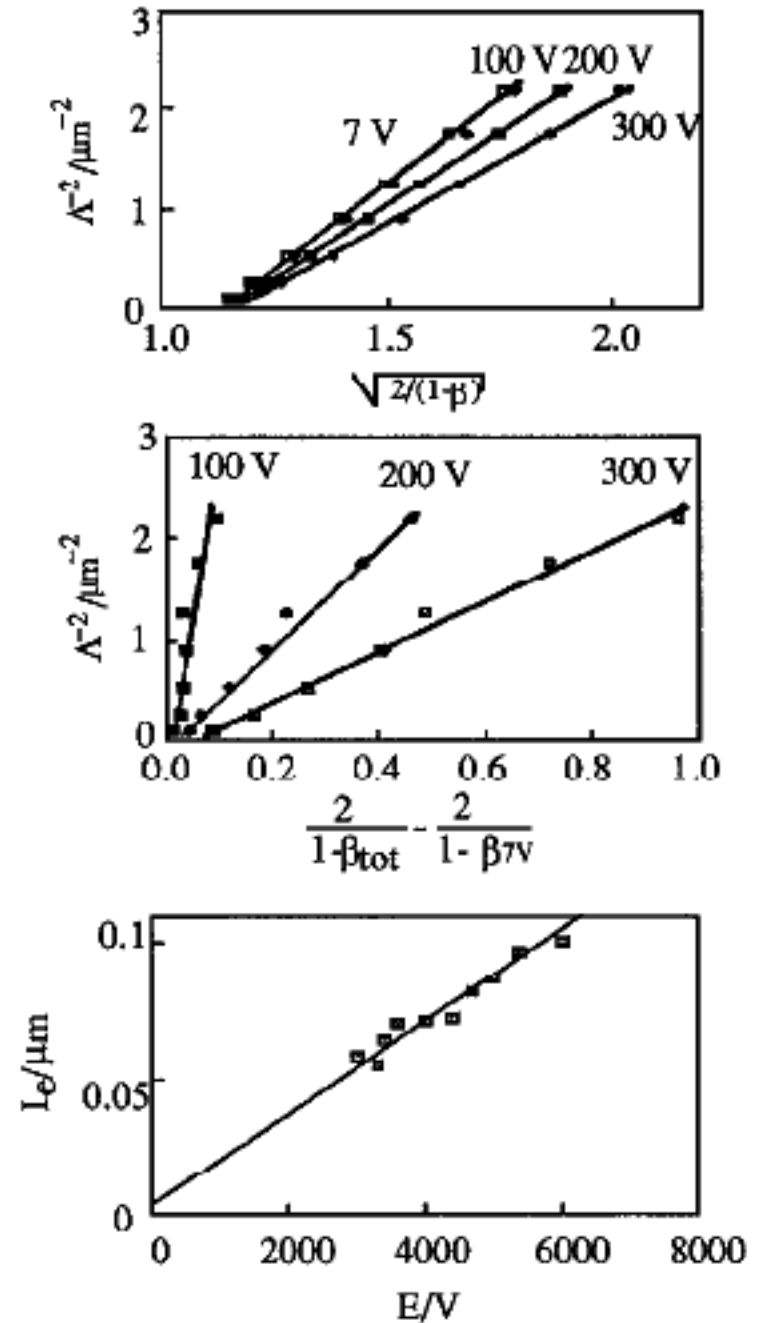


Fig.1: Measured SSPG curves, at different voltages for sample 1. From the $\Lambda^{-2} = f[(2/(1-\beta))^{0.5}]$ plot at a voltage $V=7\text{V}$, the value $L_{amb}=0.08\mu\text{m}$ was deduced. We did not measure, on any of our degraded samples, a non-ambipolar behavior in the diffusion case. The critical voltage $V_c = E_c/0.05\text{cm} = 163$ V. According to (3), the plot of $2/(1-\beta_{tot}) - 2/(1-\beta_{7V})$ gives a straight line in the ambipolar drift-diffusion intermediate case. The slope of this straight line gives L_e . From a $L_e=f(E)$ plot, we can evaluate $\mu_{amb}\tau_0 = (\gamma_p^{-1} - \gamma_n^{-1})(\mu_p^d\tau_0) = 1.67 \cdot 10^{-9} \text{cm}^2\text{V}^{-1}\text{s}^{-1}$ in the mixed drift and diffusion regime (i.e when $L_e \approx L_{amb}$, where both diffusion and drift play a role). The "effective" Einstein relation is found to be $1.55 kT/e$. From this measured value we obtain $\gamma_n = 5\gamma_p$. Such a large difference between γ_n and γ_p shows that the approximation $\mu_{amb}\tau_0 = \mu_p^d\tau_0$ would certainly not be valid for this sample. As V_c was high, it was experimentally not possible to reach the regime where drift is the predominant effect.

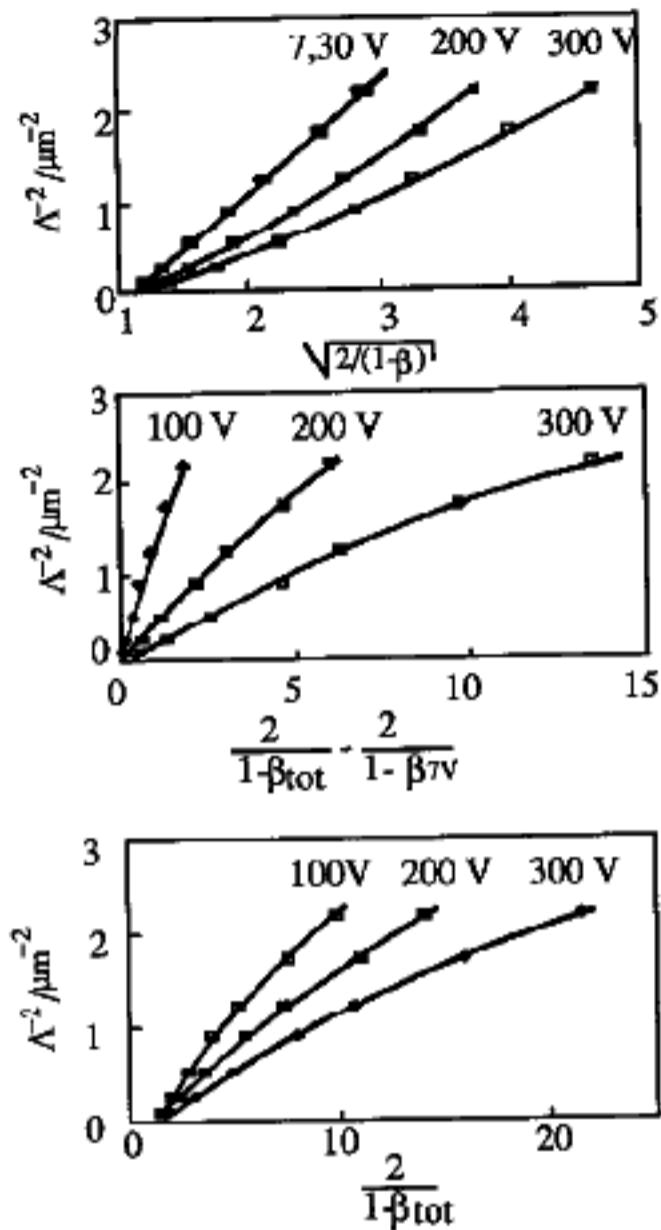


Fig.2: Measured SSPG curves at different voltages for sample 2. From the $\Lambda^{-2} = f[(2/(1-\beta))^{0.5}]$ diffusion plot and at voltage $V=7V$, the value $L_{amb}=0.135 \mu m$ was deduced. For this sample $V_c=96 V$. For samples with large L_{amb} , such as this one, the effect of drift manifests itself at low electric fields. Note that the representation of β measured at high applied voltage gives a curve on the diffusion plot: $\Lambda^{-2} = f[(2/(1-\beta))^{0.5}]$. For voltages $V=200V$ and above, we observe a deviation from the straight line on the $2/(1-\beta_{tot}) - 2/(1-\beta_{7V})$ plot. Such a convex curve is observed when non-ambipolar conditions prevails, for example if: $L_e \gg \Lambda = L_{diff}^{drift}$. In the non-ambipolar case, one cannot any longer determine L_e . For our samples, the value of E_{ext} at which ambipolarity condition is no longer fulfilled is reached at about $2E_c$. This shows that there is only a small region with mixed diffusion and drift where the necessary ambipolar condition holds.

CONCLUSIONS

The particular experimental curves for both the SSPG drift and diffusion measurements, i.e. $\Lambda^{-2} = f[2/(1-\beta)]$, and $\Lambda^{-2} = f[(2/(1-\beta))^{0.5}]$ respectively, are straight lines if and only if the ambipolarity condition is fulfilled. If this is the case, one can correctly evaluate L_{amb} and L_e . In a lifetime material, depending on excitation conditions (i.e. on the grating period), the ambipolarity condition may hold or not, whereas in a non-lifetime material, the ambipolarity condition cannot be fulfilled

in the SSPG measurement. All our measurements have shown non-ambipolar behavior when performing SSPG drift measurements at high E_{ext} ($E_{ext} > 2E_c$). It is therefore not legitimate to assume a priori that the ambipolarity condition holds. With our samples, we were only able to evaluate correctly the value of L_e (i.e. of the $(\mu_{amb} \tau_0)$ -product) in the case of mixed drift and diffusion.

The value of μ_{amb} is not useful per se for solar cells analysis: in a p-i-n solar cell, the ambipolarity condition certainly does not hold, because the electrons and holes are forcefully separated by the inner field. It is clearly the $(\mu_p^d \tau_0)$ -product value (and the drift mobility μ_p^d) that is important for solar cell design and analysis.

The measurement of both L_e and L_{amb} is generally necessary, as it allows one to get information about the ratio γ_n/γ_p . If this ratio is much larger than 1, it is not legitimate to pretend that the measured $(\mu_{amb} \tau_0)$ -product value is approximately equal to the $(\mu_p^d \tau_0)$ -product. It is therefore necessary to perform both L_{amb} and L_e measurements to check to what extent the factors $\gamma_{n,p}$ intervene in the determination of the $(\mu_p^d \tau_0)$ -product value. In order to evaluate precisely the value of the $(\mu_p^d \tau_0)$ -product, it is necessary to use a model based on the density of states for the evaluation of γ_n and of γ_p (see (12) for an attempt at such a model).

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