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Degradation of photovoltaic devices at high concentration by space charge limited currents

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ABSTRACT

High-injection mobility reduction is examined by theory, modeling, and experimental data acquired by resonance-coupled photoconductive decay (RCPCD). The ambipolar mobility is shown to reduce to zero when the constituent injection-dependent carrier mobilities are taken into account. Modeling of the photoconductivity incorporating the transient, injection-dependent, ambipolar mobility confirms experimental reduction in signal at increasing carrier-generation rates. The onset of the reduction of mobility occurs at approximately 10 times the background carrier density; thus devices that utilize lightly doped materials are susceptible to anomalous injection-based behavior. For photovoltaic applications, high-injection device-performance degradation would result from mobility reduction due to reduced diffusion length.

With the increasing popularity of concentrated photovoltaics (PV), the behavior of the PV material at high optical injection level is critical. One of the key issues in silicon-based devices is the dominance of Auger recombination at high injection levels. An additional issue that we address in this work is a decrease in the mobility of all PV materials because of space-charge effects. Here we have measured the ambipolar mobility at high injection by combining transient photoconductive decay (PCD) and transient free-carrier absorption (FCA) at identical injection levels. As the PCD signal is proportional to $\Delta n\mu$ and the FCA varies as $\Delta n/\mu$, the mobility can be extracted from the ratio of the measurements.

Prior work has shown high-injection behavior including surface recombination velocities [1–4] and minority-carrier lifetimes [5] that influence solar-cell performance. With the increasing popularity of concentrator technology, high-injection effects must be considered during both device design and characterization. Rein [6] and others [2] have investigated injection-dependent lifetime phenomena where increasing intensities led to increased bulk lifetime. There are many factors that can reduce carrier lifetime at high injection, including Auger recombination [7] and carrier–carrier scattering [8], while an important factor for traditional semiconductors and organic solar cells, high-injection mobility reduction has largely been overlooked as an aspect of conventional photovoltaic device physics.

When an optical excitation produces excess electrons and holes, the resulting excess carrier behavior is controlled by the recombination processes (band-to-band, Shockley–Read–Hall, Surface, and Auger) [9]. The transient excess carrier concentration and recombination processes can be accurately described by the photoconductive decay. Photoconductive measurements measure the minority-carrier lifetime from the slope of the transient decay, which depends on the recombination behavior of the excess carriers. The various recombination processes have a wide range of time constants that can be extracted at different points along the waveform. A single exponential decay is typical for bulk materials at low-injection. Photoconductive decay can be described in the equation

$$\Delta\sigma(t) = q(\Delta n(t)\mu_n + \Delta p(t)\mu_p), \tag{1}$$

where $\Delta\sigma(t)$ is the transient photoconductivity, q is the fundamental charge of an electron, $\Delta n(t)$ and $\Delta p(t)$ are the transient excess carrier concentrations of electrons and holes, and μ_n and μ_p are the electron and hole mobilities, respectively. Currently, for all photoconductive decay measurements, the electron and hole mobilities are often assumed constant or invariant with time and injection through all excitation ranges.

This approximation works for low-injection conditions when the excess free-carrier concentration is much less than the background-carrier concentration of the sample. In the low-injection regime, the minority-carrier capture controls the lifetime. At higher injection however, the recombination becomes a complex function of the injection level, and electron and hole capture cross section.

The derivation of the ambipolar mobility may be found in many semiconductor textbooks but most notably by Smith [10]. The

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derivation accounts for high-injection effects when the excess carrier concentration exceeds the dopant concentration. The ambipolar transport equation is composed of the recombination, diffusion, and drift of carriers. Combining the drift-diffusion equations with Poisson's equation, one gets

$$\frac{\partial \Delta p}{\partial t} = -\frac{\Delta p}{\tau_p} + D_a \frac{\partial^2 \Delta p}{\partial x^2} - \mu_a E \frac{\partial \Delta p}{\partial x}, \tag{2}$$

where τ_p is the carrier lifetime, D_a is the ambipolar diffusion coefficient, μ_a is the ambipolar mobility, and E is the electric field. The ambipolar diffusion coefficient is a function of the specific conductivity (σ_n and σ_p) and diffusion coefficient (D_n and D_p) of each carrier:

$$D_a = \frac{\sigma_n D_p + \sigma_p D_n}{\sigma_n + \sigma_p} = \frac{n\mu_n D_p + p\mu_p D_n}{n\mu_n + p\mu_p}. \tag{3}$$

By use of the Einstein relation ($D = \mu kT/q$), this can be reduced to

$$D_a = \frac{n+p}{\frac{n}{D_p} + \frac{p}{D_n}}. \tag{4}$$

Additionally, we can solve for the ambipolar mobility and apply the Einstein relation for simplification as well

$$\mu_a = \frac{\sigma_n \mu_p - \sigma_p \mu_n}{\sigma_n + \sigma_p} = \frac{n-p}{\frac{n}{\mu_p} + \frac{p}{\mu_n}} = \frac{p_0}{\frac{n}{\mu_p} + \frac{p}{\mu_n}} \tag{5}$$

It is obvious to see from Eq. (5) that the ambipolar mobility approaches 0 as the ratio of the background carrier density to the total carrier concentration decreases with higher injection levels. Returning to the ambipolar transport equation in Eq. (2), for continuity to occur, when the mobility approaches zero, the electric field must increase in magnitude. This can be explained by the increased density of free-carriers which creates a space charge plasma, where the internal electric field of the optically generated electron–hole plasma exceeds the built-in electric field of the dopant concentration. Therefore, within the plasma region the mobility is reduced until recombination reduces the carrier density.

While this derivation accounts for high-injection conditions when n approaches p, it fails to account for the carrier-dependent mobility with respect to time. Additionally, we must consider the total carrier concentration, including the background carrier density and the optically generated excess carriers, as the dopant concentration provides a lower limit for conductivity. The total carrier concentration n is composed of the transient excess carrier concentration $\Delta n(t, \Delta n_0)$ and the background carrier density n_0:

$$n(t, \Delta n_0) = \Delta n(t, \Delta n_0) + n_0 \tag{6}$$

$$\Delta n(t, \Delta n_0) = \Delta n_0 e^{-t/\tau} \tag{7}$$

$$\Delta n_0 = \alpha I_0 e^{-\alpha x} \tag{8}$$

The excess carrier concentration is further defined by the volume generation Δn_0 and the carrier lifetime τ. The volume generation is composed of the incident energy I_0, the absorption coefficient α, and the thickness of the sample x. Similar equations may also be derived for holes, where $\Delta n(t, \Delta n_0) = \Delta p(t, \Delta p_0)$.

Mobility as a function of the dopant concentration has also been previously derived [11,12] with respect to carrier–carrier scattering and here we expand that model to include the total transient carrier concentration:

n−type Si

$$\mu_n(t, \Delta n_0) = 65 + \frac{1265}{1 + \left(\frac{n(t, \Delta n_0)}{8.5 \times 10^{16}}\right)^{0.72}}$$

$$\mu_p(t, \Delta n_0) = 130 + \frac{370}{1 + \left(\frac{p(t, \Delta n_0)}{8 \times 10^{17}}\right)^{1.25}} \tag{9}$$

p−type Si

$$\mu_n(t, \Delta n_0) = 232 + \frac{1180}{1 + \left(\frac{n(t, \Delta n_0)}{8 \times 10^{16}}\right)^{0.9}}$$

$$\mu_p(t, \Delta n_0) = 48 + \frac{447}{1 + \left(\frac{n(t, \Delta n_0)}{6.3 \times 10^{16}}\right)^{0.76}}. \tag{10}$$

Finally, we may insert the transient-carrier concentration-dependent mobility and transient total-carrier concentrations back into Eq. (5), garnering a transient, injection-dependent, ambipolar mobility:

$$\mu_a(t, \Delta n_0) = \frac{n(t, \Delta n_0) - p(t, \Delta n_0)}{\frac{n(t, \Delta n_0)}{\mu_p(t, \Delta n_0)} + \frac{p(t, \Delta n_0)}{\mu_n(t, \Delta n_0)}}. \tag{11}$$

Furthermore, using this new ambipolar mobility in the photoconductive decay equation, which accounts for total carrier concentration, allows for the demonstration of the injection dependence with respect to time,

$$\Delta\sigma(t, \Delta n_0) = q\mu_a(t, \Delta n_0)(n(t, \Delta n_0) + p(t, \Delta n_0)). \tag{12}$$

Photoconductivity data were acquired by the use of the resonance-coupled photoconductive decay [13] (RCPCD) technique on an unpassivated p-type (100) Si wafer. The RCPCD apparatus can be seen in Fig. 1a and is composed of an RF coil operating at approximately 500 MHz that magnetically induces eddy currents in the free-carriers of an illuminated sample. The photoconductive signal is acquired by measuring the transient impedance difference between the input coil signal and the mutual impedance of the sample. The impedance difference between the coil alone and an illuminated sample can be seen in Fig. 1b. The circuit operates at 50 Ω, so the frequency and phase are tuned at low intensity so that the phase component is nullified. This tuning allows the user to tune the signal so that there is a balance of maximum amplitude and best fits a single exponential decay. The exact details of RCPCD operation may be found elsewhere [14].

While this mobility reduction was seen experimentally in many Si substrates of varying doping concentration and polarity, this correlation of theory and results will focus on a single sample that is typical for solar cells. This p-type (100) silicon wafer is polished on one side, has a thickness of ~350 μm, and the wafer manufacturer listed 10–30 Ω cm resistivity. Capacitance–voltage (CV) measurements [15] were performed on this sample, and the dopant density was found to be $1.55 \times 10^{14}\,\mathrm{cm}^{-3}$. The low-injection RCPCD lifetime was measured and determined to be ~5 μs, based on the single exponential time constant.

For high-injection conditions, the RCPCD low-injection phase and frequency settings remained constant and the lamp voltage of the 1064 nm YAG laser was systematically increased. Instantaneous waveform data acquisition and beam-power measurements were taken to ensure accurate injection conditions for each data set. The 3 mm YAG beam was incident on a beam splitter, and the areal flux was measured with a thermopile detector. The beam was further expanded to an area of ~0.9 cm^2, the latter of which was incident on the sample. A combination of the computer-controlled lamp voltage and neutral density filters were used to produce a range of volume generation from $\sim 1 \times 10^{13}$ to $5 \times 10^{16}\,\mathrm{cm}^{-3}$. Carrier-volume generation density was then calculated based on the 350 μm sample thickness and the absorption coefficient for silicon at 1064 nm.