Electronic Supplementary Information

Recombination kinetics in silicon solar cell under low-concentration: Electroanalytical characterization of space-charge and quasi-neutral regions

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THEORETICAL CONSIDERATION

The n⁺- p junction located at $x_j$ denoted by region 1 (see Fig. 1 of manuscript) have a total width of $w_j$ where, $w_j$ represents the total width of SCR. The acceptor and donor concentration of emitter and base depends on the depletion region width $w_n$ and $w_p$ respectively through the following equations (Eq. (1) & Eq. (2)):

$$w_n = \frac{N_a w_j}{N_a + N_d} \quad (1)$$

$$w_p = \frac{N_d w_j}{N_a + N_d} \quad (2)$$

Where $N_a$ and $N_d$ are the acceptor and donor concentrations, respectively. For n⁺ emitters ($N_d \gg N_a$), $w_n \ll w_p \approx w$.

The built-in potential ($V_{bi}$) at n⁺- p junction depends on acceptor ($N_a$), donor ($N_d$) and intrinsic carrier concentration ($n_i$); where, $n_i = \left( N_an_p0 \right)^{1/2} = \left( N_dp_n0 \right)^{1/2} n_p0$ and $p_n0$ denoting the minority carrier concentration in the base and emitter region, respectively [1, 2]. The built-in potential is given by Eq. (3):
\[ V_{bi} = (k_B T/|e|) \ln \left( \frac{N_a N_d / n_i^2}{N_a^+ / N_a} \right) \]  \hspace{1cm} (3)

where, \( k_B \) and \( T \) represent the Boltzmann constant and cell temperature, respectively; \( e \) is the electron charge.

The hole-accumulation and hole-depletion at p-p\(^+\) junction, located at \( x_0^+ \) sets up a back surface built-in voltage and is denoted by region 2 in Fig. 1 of manuscript. The magnitude of the built-in voltage is given as:

\[ V_{b0} = (k_B T/|e|) \ln \left( \frac{N_a^+ / N_a}{N_d^+ / N_d} \right) \]  \hspace{1cm} (4)

An electric field associated with p-p\(^+\) junction acts as a potential energy barrier to the minority electrons. This electric field repels electron back towards n\(^+\)-p region reducing the surface recombination and increasing the cells efficiency. The same polarity of \( V_{bi} \) and \( V_{b0} \) indicates that emitter-base and p-p\(^+\) junction both are in series. The above discussed regions (region 1 and 2) along with a leaky Schottky barrier formed at the back contact of aluminum [3, 4] are incorporated in the single diode model of a mono-crystalline Si solar cell (Fig. S1) [4-7].

Assuming that electrons are effectively repelled by back surface field associated with p-p\(^+\) junction, the resistance \( R_{SH} \) in Fig. S1 describes the main leakage path for electrons [8] across the n\(^+\)-p junction of the cell.

\( I_{PH}, I \) and \( I_{SH} \) are the light generated current, net output current and current flowing through \( R_{SH} \) of the cell respectively. The net output current \( (I) \), \( =I_{PH} - I_{d}' \). The current flowing through the p-p\(^+\) junction, \( I_{d}' = I_d + I_{SH} \), where \( I_d \) is the diode current through n\(^+\)-p junction.
Fig. S1 The standard single diode model of a mono-crystalline silicon solar cell

Generally, for Si solar cells $I_{PH} \gg I_{SH}$, so in Eq. 1 (manuscript), the small diode and ground-leakage currents can be ignored under zero-terminal voltage. Therefore the short-circuit current is approximately equal to the photocurrent. The temperature and illumination dependent expression for $I_{PH}$ is given by Eq. (5):

$$I_{PH} = [I_{SC} + K_l(T_C - T_{Ref})] \lambda$$

(5)

The saturation current of a solar cell varies with the cell temperature, which is described by Eq. (6):

$$I_0 = I_{RS} \left( \frac{T_C}{T_{Ref}} \right)^3 e^{\frac{q(E_{F_n} - E_{F_p}) (\frac{1}{T_{Ref}} - \frac{1}{T_C})}{mk_B}}$$

(6)
For the case of \( q(E_{Fn} - E_{Fp}) \approx V_{OC} \) in Eq. (6), the conditions for QNR prevail and under these conditions, the ideality factor, \( m = 1 \), otherwise, for the case of \( q(E_{Fn} - E_{Fp}) > V_{OC} \) the conditions of SCR prevail, that results in the ideality factor, \( m = 2 \). Reverse saturation current of the cell at reference temperature depends on the open-circuit voltage (\( V_{OC} \)) and can be approximately obtained by following equation as given by Tsai et al. [9]:

\[
I_{RS} = I_{SC}/\left[ \exp\left(\frac{qV_{OC}}{N_S k_B T C} \right) - 1 \right]
\] (7)

The maximum power output of LCPV cell is related to the \( I_{SC} \) and \( V_{OC} \) by following equation:

\[
P_{MAX} = FF \times V_{OC} \times I_{SC}
\] (8)

The values of \( I_{SC}, V_{OC} \) and \( FF \) can be determined from the I-V characteristics. The efficiency of the solar cell in relation with the \( P_{MAX} \) is given by following equation:

\[
\eta = P_{MAX}/(A \times \lambda)
\] (9)

\( A \) is the area of the solar cell and \( \lambda \) is the incident solar radiation (kW/m²).

The capacitive components of Si solar cell are represented by emitter capacitance (\( C_{de} \)), transition capacitance (\( C_T \)) and the base capacitance (\( C_{db} \)). The resistive and capacitive components at p-p⁺ interface are represented by \( R_{pp⁺} \) and \( C_{pp⁺} \) respectively. The total junction resistance at n⁺-p junction (see Fig. 1 of manuscript) is given by Eq. (10).

\[
R_j = \frac{R_d R_{SH}}{R_d + R_{SH}}
\] (10)

where \( R_d \) is the diffusion resistance of n⁺-p junction. Analytical expression for diffusion resistance (\( R_d \)) is obtained by parallel combination of the resistances offered by emitter and base junction as given by Eq. (11).
\[ R_d = \frac{R_{db}R_{de}}{R_{db} + R_{de}} \]  

Recombination properties of a solar cell can be explored by observing the variation of \( R_d \) with voltage or by comparing different solar cells having different morphology or energy band gaps. At low forward bias condition, \( R_j \) saturates to a value that might be due to the dominating shunt resistance \( (R_{SH}) \) as a consequence of unavoidable leakage currents. Under strong forward bias or in quasi-neutral region (QNR), the last term of the denominator in Eq. 4 (manuscript) can be neglected and the total D.C. resistance reduces to Eq. (12):

\[
R_{dc} = \frac{\left( R_d + R_s + R_{pp}^+ \right)}{\left[ 1 + I\left( \frac{dR_{pp}^+}{dV} \right) \right]}
\]

(12)

The net capacitance \( (C_j) \) for n\(^+\)-p junction is given by Eq. (13):

\[ C_j = (C_T + C_d) \]

(13)

where, \( C_d \) represent the diffusion capacitance of n\(^+\)-p junction. The relation between \( C_d \) and diffusive component of base \( (C_{db}) \) and emitter \( (C_{de}) \) region (see Fig. 1 of manuscript) is given by Eq. (15):

\[ C_d = (C_{db} + C_{de}) \]

(14)

\[
C_d = \frac{e^2 n_i^2}{m_k B T} \left( \frac{L_p}{N_d} + \frac{L_n}{N_a} \right) \exp \left( \frac{|e|V_j}{m_k B T} \right)
\]

(15)

where \( L_p \) and \( L_n \) represent the diffusion length of holes and electrons respectively.
In general, diffusion capacitance (also known as chemical capacitance, $C_\mu$) is governed by excess carriers and related to the change in electron occupancy of density of states \( C_\mu = q^2 L g_n(V_F) \) where L is the active thickness of Si solar cell. At higher forward bias, the electron occupancy of density of states progresses leading to an increase in the value of $C_d$. The transition capacitance, $C_T$ (also known as depletion-region capacitance, shown in Fig. 1 of manuscript) decreases or remains constant with increasing reverse bias which is expected since the separation of charges increase with applied bias. The voltage dependence of $C_T$ is utilized for the extraction of built-in potential and doping density of n$^+$-p junction. By measuring the junction capacitance ($C_j$) and junction resistance ($R_j$) over a voltage range, the values of $C_T$, and $C_d$ as well as $R_{Sil}$ and $R_d$ can be determined. The transition capacitance is given by Eq. (16) [10]:

$$C_T = \left( \frac{2(e|e|N_a)}{V_b - V_j} \right)^{1/2} \tag{16}$$

By combining these identities the minority carrier lifetime in emitter and base region of n$^+$-p junction is determined. The effective carrier lifetime $\tau_j$ can be given by Eq. (17):

$$\tau_j = 2 R_j C_j \tag{17}$$

The net impedance ($Z$) of the equivalent circuit shown in Fig. 1 (manuscript) is a series combination of the impedances, $Z_j$ and $Z_{pp+}$ of the n$^+$-p and the p-p$^+$ junctions, respectively. The $R_{pp+} + C_{pp+}$ loop will remain undetected in EIS as long as the following conditions are satisfied: (i) $Z'_j \gg Z'_{pp+}$, and (ii) $|Z''_j| \gg |Z''_{pp+}|$, where the primed and double primed terms represent real and imaginary impedance components respectively. Considering the individual impedance elements of Fig. 1 (manuscript), these two conditions can be written as follows [11]:
\[
\frac{R_j}{1 + \left(\frac{\omega}{\omega_j}\right)^2} \gg \frac{R_{pp} +}{1 + \left(\frac{\omega}{\omega_p}\right)^2} \\
\frac{(R_j^2C_j)}{1 + \left(\frac{\omega}{\omega_j}\right)^2} \gg \frac{(R_{pp} + )^2C_{pp}}{1 + \left(\frac{\omega}{\omega_p}\right)^2}
\] (18)

\[
\omega_j = \frac{1}{2R_jC_j} \text{ (for } \omega_j \tau \ll 1 \text{)} \text{ is the rate constant of recombination and equivalent to the reciprocal of the electron lifetime, } \omega \text{ is the angular frequency and } i = (-1)^{1/2}. \text{ The carrier collection efficiency is governed by a key parameter known as diffusion length, } L_n. \text{ The diffusion length is related to recombination characteristic angular frequency (i.e. } \omega_j = \frac{D_n}{L_n^2}).
\]

REFERENCES


