

# Appendix A

## Currents in Silicon Homojunction and Silicon-Organic Heterojunction Diodes

### A.1 Introduction

In state-of-the-art silicon solar cells made on high-quality wafers, surface recombination is the dominant loss mechanism. Typically, p-p<sup>+</sup> (high-low) junctions are used in these devices to reduce surface recombination. However, the performance of these high-low junctions is limited and their cost of fabrication is high.

We are interested in the use of silicon/organic heterojunction to reduce carrier recombination at the Si/metal contacts. In this chapter, analytical expressions for the pre-exponential constant for the forward-bias current in a Si/organic heterojunction,  $J_0$ , are derived. Using these expressions, the effectiveness of the heterojunction in reducing the minority carrier recombination can be gaged.

## A.2 Basic equations and nomenclature

A review of the important equations and nomenclature that is followed in this document.

- Using Boltzmann distribution, hole ( $p$ ) and electron ( $n$ ) concentrations in terms of quasi-Fermi levels ( $E_{fp}$  &  $E_{fn}$ ) are expressed as

$$p(x) = N_V \exp\left(\frac{E_V(x) - E_{fp}(x)}{kT}\right) = n_i \exp\left(\frac{E_i(x) - E_{fp}(x)}{kT}\right) \quad (\text{A.1})$$

$$n(x) = N_C \exp\left(\frac{E_{fn}(x) - E_C(x)}{kT}\right) = n_i \exp\left(\frac{E_{fn}(x) - E_i(x)}{kT}\right) \quad (\text{A.2})$$

At equilibrium the two quasi-Fermi levels are equal to the Fermi level  $E_f$ .

- Continuity equation for holes and electrons in one dimension

$$\frac{dp(x)}{dt} = -\frac{1}{q} \frac{dJ_p(x)}{dx} + G_p(x) - R_p(x) \quad (\text{A.3})$$

$$\frac{dn(x)}{dt} = +\frac{1}{q} \frac{dJ_n(x)}{dx} + G_n(x) - R_n(x) \quad (\text{A.4})$$

where  $G$  and  $R$  are generation and recombination and  $J$  is the current density.

The subscript  $p$  or  $n$  indicate whether the carriers are holes or electrons.

- Hole and electron currents ( $J_p$  &  $J_n$ , respectively) can be further expressed in terms of drift and diffusion components as

$$J_p(x) = q\mu_p p(x)\mathcal{E}(x) - qD_p \frac{dp(x)}{dx} \quad (\text{A.5})$$

$$J_n(x) = q\mu_n n(x)\mathcal{E}(x) + qD_n \frac{dn(x)}{dx} \quad (\text{A.6})$$

where  $\mathcal{E}(x)$  is the electric-field at distance  $x$ ,  $\mu_p$  &  $\mu_n$  are the hole and electron mobility, respectively, and  $D_p$  &  $D_n$  are diffusion coefficient for holes and

electrons, respectively. The currents can also be expressed in terms of the quasi-Fermi levels

$$J_p(x) = \mu_p p(x) \frac{dE_{fp}(x)}{dx} \quad (\text{A.7})$$

$$J_n(x) = \mu_n n(x) \frac{dE_{fn}(x)}{dx} \quad (\text{A.8})$$

- Using the drift-diffusion equations, (A.5) and (A.6), we can simplify the continuity equation, (A.3) and (A.4), to

$$\frac{dp(x)}{dt} = -\mu_p p(x) \frac{d\mathcal{E}(x)}{dx} - \mu_p \mathcal{E}(x) \frac{dp(x)}{dx} + D_p \frac{d^2 p(x)}{dx^2} + G_p(x) - R_p(x) \quad (\text{A.9})$$

$$\frac{dn(x)}{dt} = +\mu_n n(x) \frac{d\mathcal{E}(x)}{dx} + \mu_p \mathcal{E}(x) \frac{dn(x)}{dx} + D_n \frac{d^2 n(x)}{dx^2} + G_n(x) - R_n(x) \quad (\text{A.10})$$

- According to SRH theory, the net rate of recombination of carriers ( $U$ ) due to midgap traps at energy  $E_t$  is given by

$$U = R - G = \frac{(pn - n_i^2)}{\left[ p + n + 2n_i \cosh\left(\frac{E_t - E_i}{kT}\right) \right] \tau} \quad (\text{A.11})$$

where the carrier recombination lifetime ( $\tau$ ) is given by

$$\tau = \frac{1}{N_t v_{th} \rho_0} \quad (\text{A.12})$$

Here  $v_{th}$  is the thermal velocity of carriers and  $N_t$  is the density of midgap defects. The equation assumes equal hole and electron capture cross-sections ( $\rho_0$ ). As long as

$$2n_i \cosh\left(\frac{E_t - E_i}{kT}\right) \ll N_D, N_A$$

the hyperbolic cosine term drops out ( $N_D, N_A$  represent extrinsic doping levels of n and p-type semiconductor). For the n-doped semiconductor  $N_D \gg n_i, n_i^2/N_D$ . So at low-level minority carrier injection  $n \approx N_D$  and the expression

reduces to

$$U = R - G = \frac{(p - p_0)}{\tau} \quad (\text{A.13})$$

Where  $p_0$  is the hole concentration at equilibrium. Similarly for the p-doped semiconductors with equilibrium hole concentration of  $n_0$ , the net recombination rate is given by

$$U = R - G = \frac{(n - n_0)}{\tau} \quad (\text{A.14})$$

- According to the Thermionic-Emission theory, the current across an abrupt junction, where  $E_{C,2} > E_{C,1}$ , has two opposing components. One going from layer 1 to 2.

$$J_{1 \rightarrow 2} = -A_{1,2} T^2 \exp\left(-\frac{E_{C,2} - E_{fn,1}}{kT}\right)$$

And the other going from 2 to 1.

$$J_{2 \rightarrow 1} = -A_{1,2} T^2 \exp\left(-\frac{E_{C,2} - E_{fn,2}}{kT}\right)$$

Here  $A_{1,2}$  is the Richardson constant for the heterojunction between material 1 and material 2.

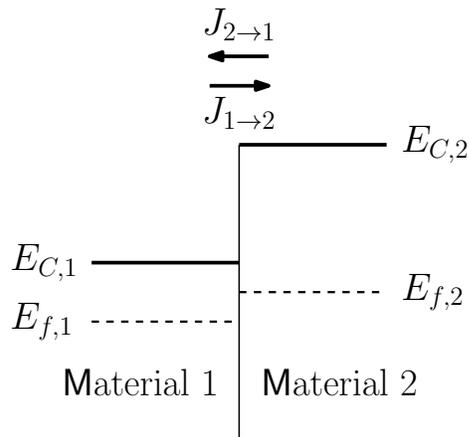


Figure A.1: Currents due to thermionic emission of electrons across a barrier due to an offset in the conduction band

### A.3 Current in a n-p Homojunction Diode

In this appendix we will consider only the electron current. The case for hole current can be derived in a similar way.

For a simple n-p junction diode, with uniform abrupt doping and infinite recombination velocity at the Si/metal interface, the current equations are well known. The current due to electron injection from the n into p-region is given by:

$$J_{n,n-p} = -q \frac{n_i^2}{N_{A,P}} \frac{D_{n,P}}{L_{n,P}} \coth \frac{W_P}{L_{n,P}} (e^{qV/kT} - 1) \quad (\text{A.15})$$

Where  $L_{n,P}$  is the diffusion length of electrons,  $D_{n,P}$  is the diffusion coefficient of electrons,  $N_{A,P}$  is the doping level, and  $W_P$  is the width of the p-layer. The subscript  $P$  refers to the fact that these values are for the p-doped layer of the p-n junction. For the case of a short base diode, when diffusion length  $L_{n,P} \gg W_P$  the junction depth, this further simplifies to

$$\begin{aligned} J_{n,n-p,SB} &= -q \left[ \frac{n_i^2}{N_{A,P}} \frac{D_{n,P}}{W_P} \right] (e^{qV/kT} - 1) \\ &= -q \frac{n_i^2 D_{n,P}}{G_P} (e^{qV/kT} - 1) \end{aligned} \quad (\text{A.16})$$

where  $G_P$  is the integrated base doping (in  $\text{cm}^{-2}$ ), also called the *Gummel number*. The equation represents the base case for a solar cell dominated by surface recombination.

For the case when the recombination velocity of the Si/metal interface is finite ( $S_{metal}$ ), the carrier concentration at the silicon metal junction,  $n(W_P)$ , is not pinned to zero. This changes one of the boundary conditions and relation for electron current changes to:

$$J_{n,n-p-metal} = -q \frac{n_i^2}{N_{A,P}} \frac{D_{n,P}}{L_{n,P}} \left[ \frac{1 + S_{metal} \frac{L_{n,P}}{D_{n,P}} \coth \frac{W_P}{L_{n,P}}}{\coth \frac{W_P}{L_{n,P}} + S_{metal} \frac{L_{n,P}}{D_{n,P}}} \right] (e^{qV/kT} - 1) \quad (\text{A.17})$$

In the limit of  $S_{metal} \rightarrow \infty$ , the relation reduces to (A.15). For the short base case when  $L_{n,P} \gg W_P$  the relation simplifies to

$$J_{n,n-p-metal} \approx -q \frac{n_i^2 D_{n,P}}{G_P} \left[ \frac{1}{1 + \frac{D_{n,P}}{W_P S_{metal}}} \right] (e^{qV/kT} - 1) \quad (\text{A.18})$$

## A.4 Current in a n-p-p<sup>+</sup> Homojunction Diode

Before analyzing the more complicated heterojunction, an analysis of the n-p-p<sup>+</sup> structure will be instructive. As before only expression for the electron current will be studied. We will refer to the n,p and p<sup>+</sup> regions as **N**, **P** and **P<sup>+</sup>** respectively. All variables will have one of these labels in the subscript to indicate the layer to which they refer to. For example, the doping and thickness of the **P** and **P<sup>+</sup>** layers are given by  $N_{A,P}$ ,  $W_P$  and  $N_{A,P+}$ ,  $W_{P+}$ , respectively. Fig.A.2 shows the band diagram of the structure.

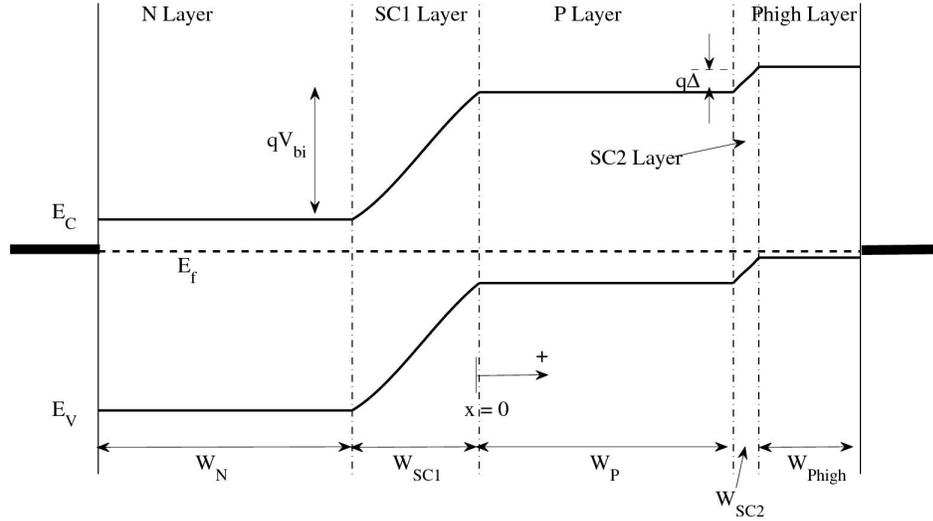


Figure A.2: Band diagram of a general n-p-p<sup>+</sup> homojunction, showing the three different layers: **N**, **P** and **P<sup>+</sup>**. Also shown is the

### A.4.1 General Solution

By definition,  $\mathcal{E}(x) = 0$  in the quasi neutral region in the P region (where the electrons get first injected from N region). Assuming a constant doping profile in the P region with an effective carrier lifetime of  $\tau_P$  and using and (A.14), the continuity equation (A.10) simplifies to

$$\frac{dn(x)}{dt} = 0 = D_{n_P} \frac{d^2n(x)}{dx^2} - \frac{(n(x) - n_{P,0})}{\tau_P} \quad (\text{A.19})$$

The solution to this differential equation, in terms of the excess minority carrier density  $n'(x) = n(x) - n_0$ , is

$$n'(x) = Ae^{-x/L_{n,P}} + Be^{x/L_{n,P}} \quad (\text{A.20})$$

Two boundary conditions are required to solve this second order equation. Once the expression of the excess minority carrier density ( $n'(x)$ ) is known, the expression for electron current can be easily found out using (A.6).

### A.4.2 Boundary Conditions

The boundary condition, at  $x = 0$ , is known

$$n'(0) = n_{P,0}(0)(e^{qV_{SC1}/kT} - 1) = \frac{n_i^2}{N_{A,P}}(e^{qV_{SC1}/kT}) \quad (\text{A.21})$$

where  $V_{SC1}$  is the voltage drop across the space charge region, SC1 (the depletion region of the p-n junction). Practically this value is very close to the applied external voltage  $V$ , i.e.  $V_{SC1} \approx V$ .

Unlike the boundary condition at  $x = 0$ , the boundary condition at  $x = W_P$  is more complicated due to the presence of the p-p<sup>+</sup> junction. To find the second boundary condition, we need to estimate the current across the p-p<sup>+</sup> interface ( $x =$

$W_P$ ). There are two components to the current across the p-p<sup>+</sup> interface a) the current due to injection of electrons from the quasi neutral P region into the P<sup>+</sup> region and b) the current due to recombination in the space-charge region of the p-p<sup>+</sup> junction (region SC2).

### A.4.3 Current across the p/p<sup>+</sup> junction

The current due to minority carriers injection into the P<sup>+</sup> region can be calculated from the continuity equation (A.10)

$$\frac{dn(x)}{dt} = 0 = D_{n_{P^+}} \frac{d^2n(x)}{dx^2} - \frac{(n(x) - n_{P^+,0})}{\tau_{P^+}} \quad (\text{A.22})$$

Assuming that the recombination velocity of the Si/metal interface is infinite, we can state that the excess minority carrier density at the Si/metal interface is zero, i.e.  $n'(W_P + W_{SC2} + W_{P^+}) = 0$ . Under this boundary condition, the electron injection current in the P<sup>+</sup> region comes out to be

$$J_{n,P^+} = -qn'(W_P + W_{SC2}) \frac{D_{n,P^+}}{L_{n,P^+}} \coth \frac{W_{P^+}}{L_{n,P^+}} \quad (\text{A.23})$$

Where,  $n'(W_P + W_{SC2})$  is the excess minority carrier density at  $x = (W_P + W_{SC2})$ . The negative sign signifies that the current flows in the negative x direction.

To solve for current due to recombination in the SC-2 region, apply the continuity equation

$$\begin{aligned} \frac{dn(x)}{dt} = 0 &= \frac{1}{q} \frac{dJ_n(x)}{dx} + G_{n,SC2}(x) - R_{n,SC2}(x) \\ \Rightarrow \int_{(J_{n,SC2} + J_{n,P^+})}^{J_{n,P^+}} dJ_n &= q \int_{W_P}^{W_P + W_{SC2}} -(G_{n,SC2}(x) - R_{n,SC2}(x)) dx \\ \Rightarrow J_{n,SC2} &= q \int_{W_P}^{W_P + W_{SC2}} (G_{n,SC2}(x) - R_{n,SC2}(x)) dx \end{aligned} \quad (\text{A.24})$$

Here the current  $J_{n,SC2}$  is the additional current due to recombination in the space charge region SC2. To estimate the integral, the recombination rate in the space charge region of the p-p<sup>+</sup> junction is required. Let's make the following assumptions

1. The potential drop across the region,  $\Delta$ , is constant even when external voltage is applied and given by the equation

$$\Delta = -\frac{kT}{q} \ln \left( \frac{N_{A,P^+}}{N_{A,P}} \right) \quad (\text{A.25})$$

The negative sign implies that the voltage *drops* across the p-p<sup>+</sup> junction.

2. The quasi Fermi levels are approximately flat in across the SC2 region

$$E_{fn}(x) = E_{fn}(W_P) = E_{fn}(W_P + W_{SC2})$$

$$E_{fp}(x) = E_{fp}(W_P) = E_{fp}(W_P + W_{SC2})$$

Using the Boltzmann statistics,(A.1) and (A.2), this translates to

$$\begin{aligned} n(W_P)N_{A,P} &= n(W_P + W_{SC2})N_{A,P^+} = n_i^2 \exp \frac{E_{fn}(W_P) - E_{fp}(W_P)}{kT} \\ \Rightarrow n(W_P + W_{SC2}) &= n(W_P) \frac{N_{A,P}}{N_{A,P^+}} \\ \Rightarrow n'(W_P + W_{SC2}) &= n'(W_P) \frac{N_{A,P}}{N_{A,P^+}} \end{aligned} \quad (\text{A.26})$$

3. The voltage,  $\phi(x)$ , in the region is a linear function in  $x$  i.e. for  $W_P \leq x \leq W_P + W_{SC2}$

$$\phi(x) = \frac{\Delta}{W_{SC2}} (x - W_P) \quad (\text{A.27})$$

And the the carrier concentrations vary exponentially, given by

$$p(x) = N_{A,P} \exp \left( -\frac{q\phi(x)}{kT} \right) \quad (\text{A.28})$$

$$n(x) = n(W_P) \exp\left(\frac{q\phi(x)}{kT}\right) \quad (\text{A.29})$$

Using the above expressions in SRH recombination equation (A.11), the net rate of recombination can be calculated

$$U = R - G = \frac{(pn - n_i^2)}{\left[p + n + 2n_i \cos\left(\frac{E_t - E_i}{kT}\right)\right] \tau_{SC2}} \approx \frac{(pn - n_i^2)}{p\tau_{SC2}} \quad (\text{A.30})$$

$$\begin{aligned} &= \frac{1}{\tau_{SC2}} \left(n(W_P) - \frac{n_i^2}{N_{A,P}}\right) \exp\left(\frac{q\phi(x)}{kT}\right) \\ &= \frac{1}{\tau_{SC2}} \left(n(W_P) - n_{P,0}\right) \exp\left(\frac{q\phi(x)}{kT}\right) \end{aligned} \quad (\text{A.31})$$

Putting this relation into (A.24) we can estimate the space charge region current  $J_{n,SC2}$

$$\begin{aligned} J_{n,SC2} &= -\frac{q(n(W_P) - n_{P,0})}{\tau_{SC2}} \int_{W_P}^{W_P+W_{SC2}} \exp\left(\frac{q\phi(x)}{kT}\right) dx \\ &= -\frac{qn'(W_P) kT W_{SC2}}{\tau_{SC2} q \Delta} \left(\exp\left(\frac{q\Delta}{kT}\right) - 1\right) \\ &= -q \frac{W_{SC2} kT}{\tau_{SC2} q \Delta} n'(W_P) \left(\frac{N_{A,P}}{N_{A,P+}} - 1\right) \\ &\approx +q \frac{W_{SC2} kT}{\tau_{SC2} q \Delta} n'(W_P) \\ &= -q \frac{W_{SC2} kT}{\tau_{SC2} q |\Delta|} n'(W_P) \end{aligned} \quad (\text{A.32})$$

Please note is that since  $\Delta$  is negative so the absolute value of the current is also negative. Now that both the components of current at the interface  $x = W_P$  have been calculated, the second boundary condition can be derived.

#### A.4.4 Final Expressions

Using (A.23), (A.32) and (A.26) the boundary condition at the  $x = W_P$  is

$$\begin{aligned}
 J_n(W_P) &= (J_{n,P^+} + J_{n,SC2}) \\
 \Rightarrow qD_{n,P} \frac{dn(x)}{dx} \Big|_{x=W_P} &= -n'(W_P) \left( q \frac{N_{A,P}}{N_{A,P^+}} \frac{D_{n,P^+}}{L_{n,P^+}} \coth \frac{W_{P^+}}{L_{n,P^+}} + q \frac{W_{SC2}}{\tau_{SC2}} \frac{kT}{q|\Delta|} \right) \\
 \Rightarrow \frac{dn'(x)}{dx} \Big|_{x=W_P} &+ \alpha \frac{n'(W_P)}{L_{n,P}} = 0
 \end{aligned} \tag{A.33}$$

where

$$\alpha = \frac{\frac{D_{n,P^+}}{L_{n,P^+}} \frac{N_{A,P}}{N_{A,P^+}} \coth \frac{W_{P^+}}{L_{n,P^+}} + \frac{W_{SC2}}{\tau_{SC2}} \frac{kT}{q|\Delta|}}{\frac{D_{n,P}}{L_{n,P}}} \tag{A.34}$$

Using the two boundary conditions, (A.21) and (A.33), we can solve the constants in the general solution, (A.20), to get

$$n'(x) = n'(0) \left[ \frac{\cosh \left( \frac{W_P - x}{L_{n,P}} \right) + \alpha \sinh \left( \frac{W_P - x}{L_{n,P}} \right)}{\cosh \left( \frac{W_P}{L_{n,P}} \right) + \alpha \sinh \left( \frac{W_P}{L_{n,P}} \right)} \right] \tag{A.35}$$

Using (A.6) the electron current is

$$J_{n,n-p-p^+}(x) = -qn'(0) \frac{D_{n,P}}{L_{n,P}} \left[ \frac{\sinh \left( \frac{W_P - x}{L_{n,P}} \right) + \alpha \cosh \left( \frac{W_P - x}{L_{n,P}} \right)}{\cosh \left( \frac{W_P}{L_{n,P}} \right) + \alpha \sinh \left( \frac{W_P}{L_{n,P}} \right)} \right]$$

at  $x = 0$  we get the value of total electron current

$$J_{n,n-p-p^+} = -qn'(0) \frac{D_{n,P}}{L_{n,P}} \left[ \frac{1 + \alpha \coth \left( \frac{W_P}{L_{n,P}} \right)}{\coth \left( \frac{W_P}{L_{n,P}} \right) + \alpha} \right] \tag{A.36}$$

At a value of  $\alpha = 1$  the equation reduces to long base diode case. So  $\alpha$  tells us

whether the p-p<sup>+</sup> junction *reduces* ( $\alpha < 1$ ) or *increases* ( $\alpha > 1$ ) the current w.r.t the equivalent long base diode with only the lightly doped P region.

Another interesting interpretation of  $\alpha$  can be in terms of the recombination velocity. The surface recombination velocity (SRV),  $s$ , of a interface is defined as

$$U = R - G = sn'$$

Looking from the P region toward the p/p<sup>+</sup> junction, we observe a rate at which minority carrier recombine at the p/p<sup>+</sup> junction. For purposes of comparison, one can characterize this recombination in terms of an *effective* SRV of the p/p<sup>+</sup> interface,  $s_{p,p^+,eff}$ , which is given by

$$U = s_{p,p^+,eff}n(W_P)$$

This rate of recombination must be equal to the electron current flowing across the interface  $x = W_P$ . Thus

$$\begin{aligned} U(W_P) &= -D_{n,P} \left. \frac{dn'(x)}{dx} \right|_{x=W_P} \\ \Rightarrow s_{p,p^+,eff}n(W_P) &= n'(0) \frac{D_{n,P}}{L_{n,P}} \left[ \frac{\alpha}{\cosh\left(\frac{W_P}{L_{n,P^+}}\right) + \alpha \sinh\left(\frac{W_P}{L_{n,P^+}}\right)} \right] \\ \Rightarrow s_{p,p^+,eff} &= \frac{D_{n,P}}{L_{n,P}} \alpha = \frac{D_{n,P^+}}{L_{n,P^+}} \frac{N_{A,P}}{N_{A,P^+}} \coth \frac{W_{P^+}}{L_{n,P^+}} + \frac{W_{SC2}}{\tau_{SC2}} \frac{kT}{q|\Delta|} \end{aligned} \quad (\text{A.37})$$

#### A.4.5 Interpretation

For the purposes of this study we are interested in the special case when surface recombination dominates bulk recombination. We will now examine the expressions for current and effective surface recombination velocity in the case  $L_{n,P}, L_{n,P^+} \gg W_P, W_{P^+}$ , i.e. diodes are in the short-base condition. The expression for  $\alpha$  and electron current in this limit reduces to (subscript *SB* refers to the short-base condition).

$$\alpha_{SB} = \frac{\frac{D_{n,P^+}}{W_{P^+}} \frac{N_{A,P}}{N_{A,P^+}}}{\frac{D_{n,P}}{L_{n,P}}} \quad (\text{A.38})$$

$$\begin{aligned} J_{n,n-p-p^+,SB} &= -qn'(0) \frac{D_{n,P}}{L_{n,P}} \left[ \frac{\left( \frac{W_P}{L_{n,P}} \right) + \alpha}{1 + \alpha \left( \frac{W_P}{L_{n,P}} \right)} \right] \\ &= -q \frac{n_i^2}{G_P/D_{n,P} + G_{P^+}/D_{n,P^+}} (e^{qV/kT} - 1) \end{aligned} \quad (\text{A.39})$$

where  $G_P$  and  $G_{P^+}$  are the Gummel numbers for the  $P$  and  $P^+$  layer respectively. Compared to the simple n-p junction short base diode given by (A.16) the currents are reduced by a factor of

$$\frac{J_{n,n-p-p^+,SB}}{J_{n,n-p,SB}} = \frac{1}{1 + \frac{G_{P^+} D_{n,P}}{D_{n,P^+} G_P}} \quad (\text{A.40})$$

Using (A.38) the effective SRV expression will be

$$s_{p,p^+,eff,SB} = \frac{D_{n,P}}{L_{n,P}} \alpha = \frac{D_{n,P^+}}{W_{P^+}} \frac{N_{A,P}}{N_{A,P^+}} = \frac{D_{n,P^+} N_{A,P}}{G_{P^+}} \quad (\text{A.41})$$

For a typical p/p<sup>+</sup> junction in a solar cell, 1 $\mu$ m thick 10<sup>19</sup> cm<sup>-3</sup> doped p<sup>+</sup> layer and a 10<sup>16</sup> cm<sup>-3</sup> doped p-layer, this number comes out to be,

$$s_{p,p^+,eff} \approx \frac{2}{10^{-4}} \frac{10^{16}}{10^{19}} \text{ cm/s} = 20 \text{ cm/s} \quad (\text{A.42})$$

Similar values of  $s_{p,p^+,eff}$  were calculated in Fig. 2.6a.

## A.5 Current in the n-p-organic Heterojunction Diode

### A.5.1 The Silicon/Organic Heterojunction

Next, the highly doped layer is replaced by a wide bandgap material, say an organic semiconductor. The resulting band diagram is shown in Fig. A.3. We will refer to the n,p and organic regions as **N**, **P** and **Organic** respectively. All variables will have one of these labels in the subscript to indicate the layer to which the variable refers to. We start with the following assumptions.

1. The organic has a larger bandgap than silicon, i.e.  $E_{G,org} > E_{G,Si}$ .
2. The organic layer is so thin that there is no band-bending in it, i.e. in the organic layer  $\mathcal{E} = 0$ . Here we are also ignoring any voltage drop across the organic due series resistance. In terms of mathematics this means that the drift component of current in the organic is zero and current flows only due to diffusion.
3. The offset in the VB is zero so all the difference is at the CB i.e.  $\Delta E_V = 0$  and  $\Delta E_C = (E_{G,org} - E_{G,Si})$ .
4. The current across the heterojunction follows the thermionic emission theory.

### A.5.2 Boundary Conditions

The approach to the problem remains the same as in the case of n-p-p<sup>+</sup> Homojunction Diode (Section A.4). Two boundary conditions are needed to solve the second order equation (A.20). One of them, at  $x = 0$ , is given by (A.21). The other, at  $x = W_P$ , has to be calculated by estimating the current flowing across the heterojunction.

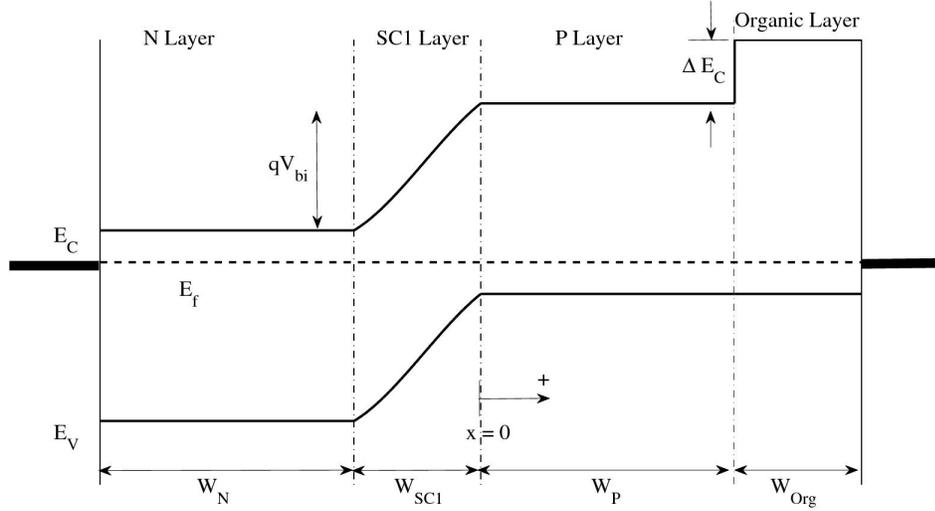


Figure A.3: Band diagram of a general n-p-organic heterojunction.

### A.5.3 Current Across the Si/Organic Heterojunction

At Si/organic interface ( $x = W_P$ ) the minority carrier current is composed of two components a) the current due to surface recombination at the Si/organic interface, characterized by the recombination velocity,  $S_{si,org}$  and b) the current due to electron injection into the organic layer. The current due to the recombination at the interface is given by

$$J_{n,SRV} = -qn(W_{P,Si})S_{si,org} \quad (\text{A.43})$$

where  $n'(W_{P,Si})$  is the excess minority carrier concentration in the silicon region at the Si/organic interface.

The expression for diffusion current in the organic layer is also relatively simple. Assuming the continuity condition is valid, we get a similar equation for the minority carriers current as obtained in (A.23).

$$J_{n,org} = -qn'(W_{P,org})\frac{D_{n,org}}{L_{n,org}} \coth \frac{W_{org}}{L_{n,org}} \quad (\text{A.44})$$

where  $n'(W_{P,org})$  is the excess minority carrier concentration in the organic region at the Si/organic interface. For complete description of the second boundary condition, we only need to relate the minority concentrations at the two sides of the Si/organic interface,  $n'(W_{P,Si})$  and  $n'(W_{P,org})$ .

According to Boltzmann distribution (A.2), the minority carrier concentration across the Si/organic interface should satisfy

$$\begin{aligned} \frac{n(W_{P,Si})}{n(W_{P,org})} &= \frac{N_{C,P}}{N_{C,org}} \exp\left(\frac{E_{fn,P} - E_{fn,org}}{kT}\right) \exp\left(\frac{\Delta E_C}{kT}\right) \\ \Rightarrow \frac{n'(W_{P,Si})}{n'(W_{P,org})} &= \frac{N_{C,P}}{N_{C,org}} \exp\left(\frac{E_{fn,P} - E_{fn,org}}{kT}\right) \exp\left(\frac{\Delta E_C}{kT}\right) \end{aligned} \quad (\text{A.45})$$

Here we assume  $n'(W_{P,Si}) = n(W_{P,Si})$  and  $n'(W_{P,org}) = n(W_{P,org})$ . Unlike homojunctions, where quasi-fermi levels are always continuous, the quasi fermi-levels are not required to be continuous across a heterojunction. To calculate the change in the quasi fermi-levels across the Si/organic interface we need to use Thermionic Emission theory.

At the Silicon-organic interface net current flow of current across the interface ( $J_{n,P\leftrightarrow org}$ ) due to Thermionic Emission is given by

$$\begin{aligned} J_{n,P\leftrightarrow org} &= J_{Si\rightarrow org} - J_{org\rightarrow Si} \\ &= -A_{Si,org} T^2 \left[ \exp\left(-\frac{E_{C,org} - E_{fn,P}}{kT}\right) \right. \\ &\quad \left. - \exp\left(-\frac{E_{C,org} - E_{fn,org}}{kT}\right) \right] \\ &= -A_{Si,org} T^2 \frac{n(W_{P,org})}{N_{C,org}} \left[ \exp\left(\frac{E_{fn,P} - E_{fn,org}}{kT}\right) - 1 \right] \end{aligned} \quad (\text{A.46})$$

The injected minority carrier (electron) current given by (A.44) has to be equal to

the current predicted by the Thermionic theory, given by (A.46). So

$$\begin{aligned}
-A_{Si,org} T^2 \frac{n(W_{P,org})}{N_{C,org}} \left[ \exp\left(\frac{E_{fn,P} - E_{fn,org}}{kT}\right) - 1 \right] &= -qn'(W_{P,org}) \frac{D_{n,org}}{L_{n,org}} \coth \frac{W_{org}}{L_{n,org}} \\
\Rightarrow \exp\left(\frac{E_{fn,P} - E_{fn,org}}{kT}\right) &= 1 + q \frac{D_{n,org}}{L_{n,org}} \frac{N_{C,org}}{A_{n,2} T^2} \coth \frac{W_{org}}{L_{n,org}}
\end{aligned} \tag{A.47}$$

Plugging this value back into the Boltzmann relation given by (A.45), we get the relation between the minority carrier concentration on the two sides of the Si/organic interface.

$$n(W_{P,org}) = n(W_{P,Si}) \frac{N_{C,org}}{N_{C,P}} \frac{1}{1 + q \frac{D_{n,org}}{L_{n,org}} \frac{N_{C,org}}{A_{n,2} T^2} \coth \frac{W_{org}}{L_{n,org}}} \exp\left(-\frac{\Delta E_C}{kT}\right) \tag{A.48}$$

Plugging the values of  $n(W_{P,org})$  in (A.44), we get the final expression for the electron diffusion current in the organic layer

$$J_{n,org} = -qn'(W_{P,Si}) \frac{D_{n,org}}{L_{n,org}} \coth \frac{W_{org}}{L_{n,org}} \left( \frac{N_{C,org}}{N_{C,P}} \frac{1}{1 + q \frac{D_{n,org}}{L_{n,org}} \frac{N_{C,org}}{A_{n,2} T^2} \coth \frac{W_{org}}{L_{n,org}}} e\left(-\frac{\Delta E_C}{kT}\right) \right)$$

Typical values of  $D_{n,org}$ ,  $L_{n,org}$ ,  $N_{C,org}$ ,  $A_{Si,org}$ , and  $T$  are expected to be  $10^{-5}$  cm<sup>2</sup>/s, 10 nm,  $10^{19}$  cm<sup>-3</sup>, 120 A/cm<sup>2</sup>K<sup>2</sup>, and 300 K. So,

$$q \frac{D_{n,org}}{L_{n,org}} \frac{N_{C,org}}{A_{n,2} T^2} \coth \frac{W_{org}}{L_{n,org}} \approx 10^{-4} \ll 1$$

and hence the expression simplifies to

$$J_{n,org} = -qn'(W_{P,Si}) \frac{D_{n,org}}{L_{n,org}} \coth \frac{W_{org}}{L_{n,org}} \left( \frac{N_{C,org}}{N_{C,P}} e\left(-\frac{\Delta E_C}{kT}\right) \right) \tag{A.49}$$

### A.5.4 Final expressions

Using the expression for the two current components at the Si/organic interface  $x = W_P$ , the second boundary condition can be derived

$$\begin{aligned}
J_n(W_{P,Si}) &= q\mu_n n(W_{P,Si})\mathcal{E}(W_{P,Si}) + qD_{n,P} \left. \frac{dn(x)}{dx} \right|_{x=W_{P,Si}} = (J_{n,SRV} + J_{n,org}) \\
\Rightarrow qD_{n,P} \left. \frac{dn(x)}{dx} \right|_{x=W_{P,Si}} &+ qn(W_{P,Si}) \frac{D_{n,org}}{L_{n,org}} \frac{N_{C,org}}{N_{C,P}} e^{\left(-\frac{\Delta E_C}{kT}\right)} \coth \frac{W_{org}}{L_{n,org}} \\
&+ qn(W_{P,Si})S_{Si,org} = 0 \\
\Rightarrow \left. \frac{dn'(x)}{dx} \right|_{x=W_{P,Si}} &+ \beta \frac{n'(W_{P,Si})}{L_{n,P}} = 0
\end{aligned} \tag{A.50}$$

where

$$\beta = \frac{\frac{D_{n,org}}{L_{n,org}} \frac{N_{C,org}}{N_{C,P}} \exp\left(-\frac{\Delta E_C}{kT}\right) \coth \frac{W_{org}}{L_{n,org}} + S_{Si,org}}{\frac{D_{n,P}}{L_{n,P}}} \tag{A.51}$$

This is the same boundary condition that we derived in p/p<sup>+</sup> homojunction diodes, except for the fact that parameter  $\alpha$  is substituted with  $\beta$  in (A.36). Thus the final expression of electron current in the heterojunction diode is

$$J_{n,n-p-org} = -qn'(0) \frac{D_{n,P}}{L_{n,P}} \left[ \frac{1 + \beta \coth\left(\frac{W_P}{L_{n,P}}\right)}{\coth\left(\frac{W_P}{L_{n,P}}\right) + \beta} \right] \tag{A.52}$$

In the previous section on p/p<sup>+</sup> homojunction we calculated the effective surface recombination velocity of a p/p<sup>+</sup> back-surface field from the value of  $\alpha$ .  $\beta$  can also be interpreted in similar way. Looking from the P region, the *effective* recombination

velocity of the Si/organic heterojunction,  $S_{Si,org,eff}$ , is

$$\begin{aligned} S_{Si,org,eff} &= \frac{D_{n,P}}{L_{n,P}} \beta \\ &= \frac{D_{n,org}}{L_{n,org}} \frac{N_{C,org}}{N_{C,P}} \exp\left(-\frac{\Delta E_C}{kT}\right) \coth \frac{W_{org}}{L_{n,org}} + S_{Si,org} \end{aligned} \quad (\text{A.53})$$

### A.5.5 Interpretation

For the case when lifetimes are long and the diode is in the short-base condition, i.e.  $L_{n,P}, L_{n,P^+} \gg W_P, W_{P^+}$ , the expressions for electron current and  $\beta$  are given by (subscript SB refers to the short-base condition):

$$\begin{aligned} J_{n,n-p-org,SB} &= -qn'(0) \frac{D_{n,P}}{L_{n,P}} \left[ \frac{1 + \beta \left( \frac{L_{n,P}}{W_P} \right)}{\left( \frac{L_{n,P}}{W_P} \right) + \beta} \right] \\ &= -qn'(0) \frac{D_{n,P}}{L_{n,P}} \left[ \frac{\beta \left( \frac{L_{n,P}}{W_P} \right)}{\left( \frac{L_{n,P}}{W_P} \right) + \beta} \right] \\ &\approx -q \frac{n_i^2}{G_P} \left[ \frac{1}{1 + \frac{L_{n,P}}{\beta W_P}} \right] (e^{qV/kT} - 1) \end{aligned} \quad (\text{A.54})$$

where

$$\beta \approx \frac{\frac{D_{n,org}}{W_{org}} \frac{N_{C,org}}{N_{C,P}} \exp\left(-\frac{\Delta E_C}{kT}\right) + S_{Si,org}}{\frac{D_{n,P}}{L_{n,P}}} \quad (\text{A.55})$$

Looking closely at two terms in the numerator of  $\beta$ , we can see that for a practical Si/organic heterojunction with a  $S_{Si,org} > 1$  cm/s and a band-offset ( $\Delta E_C$ ) of  $>0.5$

eV, the exponential term is inconsequential.

$$\begin{aligned} \frac{D_{n,org}}{W_{org}} \frac{N_{C,org}}{N_{C,P}} \exp\left(-\frac{\Delta E_C}{kT}\right) &\approx \frac{10^{-5}}{10^{-6}} \frac{cm/s 10^{19}}{10^{19}} 10^{-9} \\ &= 10^{-8} \\ &\ll S_{p,org} \end{aligned} \quad (\text{A.56})$$

This calculation assumes  $D_{n,org}=10^{-5}$  cm<sup>2</sup>/s,  $W_{org}=10$  nm,  $N_{C,org}=N_{C,P}=10^{19}$  cm<sup>-3</sup>, and  $L_{n,org} \gg W_{org}$ . The expression for  $\beta$  then simplifies to

$$\beta \approx S_{Si,org} \frac{L_{n,P}}{D_{n,P}} \quad (\text{A.57})$$

and the expression for current simplifies to

$$J_{n,n-p-org,SB} \approx -q \frac{n_i^2}{G_P} \left[ \frac{1}{1 + \frac{D_{n,P}}{S_{Si,org} W_P}} \right] (e^{qV/kT} - 1) \quad (\text{A.58})$$

This is exactly the same expression as (A.18), which we derived for a finite recombination velocity silicon-metal contact, except for  $S_{metal}$  has been substituted by  $S_{Si,org}$ . The fact that  $S_{Si,org}$  is more important for calculating the current than  $\Delta E_C$  was also shown in Fig. 2.6a, where the electron-current of a n<sup>+</sup>-p Si diode with a non-ideal heterojunction BSF ( $S_{p,org} \neq 0$ ) had a very weak dependence on the conduction-band offset ( $\Delta E_C$ ). To a first-order the current was set by the value of  $S_{p,org}$ , irrespective of  $\Delta E_C$ .

Another interesting question is - how big a band-offset if large enough for the heterojunction to function as a BSF? Compared to the simple n-p junction short-

base diode given by (A.16), the SOH back-surface field does better by a ratio of:

$$\frac{J_{n,n-p-org,SB}}{J_{n,n-p,SB}} = \left[ \frac{1}{1 + \frac{D_{n,P}}{S_{Si,org}W_P}} \right] \quad (\text{A.59})$$

Since the ration is always less than 1, one can always expect to get a reduction in current in a short-base diode by the use of a heterojunction.

A more interesting analysis would be to compare the performance of a p/p<sup>+</sup> BSF against a heterojunction BSF. Using the expressions for current in the two case of a homojunction and heterojunction BSF ((A.39) and (A.58), respectively), we get:

$$\frac{J_{n,n-p-org,SB}}{J_{n,n-p-p^+,SB}} = \frac{1 + \frac{G_{P^+}D_{n,P}}{D_{n,P^+}G_P}}{1 + \frac{D_{n,P}}{S_{Si,org}W_P}} \quad (\text{A.60})$$

To outperform the homojunction the  $S_{Si,org}$  of the heterojunction should satisfy

$$\begin{aligned} \frac{J_{n,n-p-org,SB}}{J_{n,n-p-p^+,SB}} &= \frac{1 + \frac{G_{P^+}D_{n,P}}{D_{n,P^+}G_P}}{1 + \frac{D_{n,P}}{S_{Si,org}W_P}} < 1 \\ &\Rightarrow \frac{G_{P^+}D_{n,P}}{D_{n,P^+}G_P} < \frac{D_{n,P}}{S_{Si,org}W_P} \\ &\Rightarrow S_{Si,org}W_P > \frac{D_{n,P}}{W_P} \frac{D_{n,P^+}G_P}{G_{P^+}D_{n,P}} \\ &= \frac{D_{n,P^+}N_{A,P}}{G_{P^+}} \\ &= \frac{2 \times 10^{16}}{10^{19} \times 10^{-4}} \text{ cm/s} \Rightarrow S_{Si,org}W_P = 20 \text{ cm/s} \end{aligned} \quad (\text{A.61})$$

Thus, to outperform a typical homojunction, the heterojunction should be able to reduce  $S_{Si,org}$  to less than 20 cm/s. The calculation assumes a 200 $\mu$ m thick p-type substrate, with a 1  $\mu$ m thick 10<sup>19</sup> cm<sup>-3</sup> doped p<sup>+</sup> homojunction BSF layer.

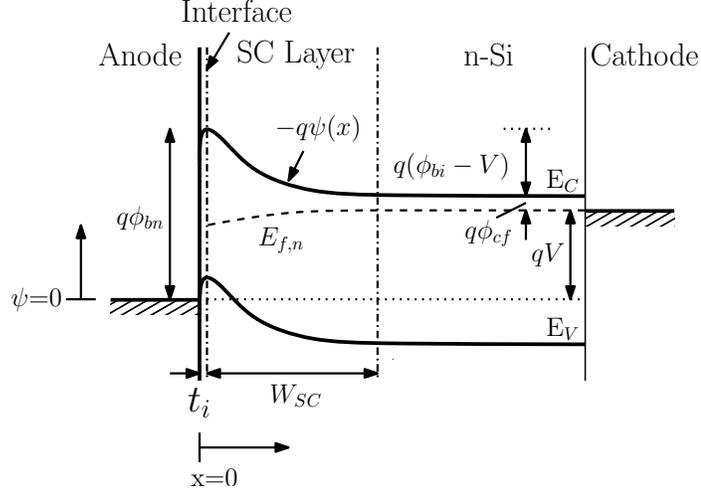


Figure A.4: A Si/metal Schottky junction diode at forward bias.

## A.6 Current in the n-Silicon/Metal Schottky Diode

Currents in Schottky diodes are mostly due to majority carriers. The two well-known approaches to derive current expression are: a) Thermionic emission theory and b) the isothermal diffusion theory [166].

Assuming that there are no electron collisions in the depletion region of silicon, i.e. there is no diffusion of electrons in depletion region of silicon, the currents are limited only by the Si/metal interface.

$$J_{n,si-metal} = A_{n,si} T^2 \left[ \exp \left( -\frac{q\phi_{bn}}{kT} \right) \right] (e^{qV/kT} - 1) \quad (\text{A.62})$$

However, if we assume electron collisions are important, the diffusion currents cannot be ignored and at quasi-equilibrium

$$J_{n,si-metal} = \frac{q^2 D_{n,si} N_{c,si}}{kT} \left[ \frac{2q N_{D,si} (\phi_{bn} - V)}{\epsilon_{si}} \right]^{1/2} \left[ \exp \left( -\frac{q\phi_{bn}}{kT} \right) \right] (e^{qV/kT} - 1) \quad (\text{A.63})$$

The two approaches were combined into a single theory by Cromwell and Sze

[32]. This new model takes into account both mechanism of current conduction - Thermionic emission and electron diffusion.

$$J_{n,si-metal} = \frac{qN_{C,si}s_{metal}}{1 + \frac{s_{metal}}{s_{depSi}}} \left[ \exp\left(-\frac{q\phi_{bn}}{kT}\right) \right] (e^{qV/kT} - 1) \quad (\text{A.64})$$

$s_{depSi}$  and  $s_{metal}$  are two parameters, with units of surface recombination velocity (cm/s), that serve as the measures of current due to the two competing current mechanisms - electron diffusion and thermionic emission, respectively. If  $s_{depSi} \ll s_{metal}$ , current is limited by the ability of electron to diffuse over the potential barrier and (A.64) reduces to (A.63). On the other hand, if  $s_{depSi} \gg s_{metal}$ , current is limited by the ability of electrons to cross the Si/metal interface and (A.64) reduces to (A.62).

$s_{depSi}$  is an effective diffusion velocity (similar to a surface recombination velocity) associated with the transport of electrons from the edge of depletion region (neutral n-type region) in silicon ( $x = W_{SC}$ ) to the potential energy maximum (at  $x = t_i$ ).

$$s_{depSi} = \left[ \int_{t_i}^{W_{SC}} \frac{q}{\mu kT} \exp\left(-\frac{q}{kT}(\phi_{bn} + \psi(x))\right) dx \right]^{-1} \quad (\text{A.65})$$

where,  $\phi(x)$  is the electrostatic potential in the silicon region as a function of distance  $x$  from the Si/metal interface (assuming the metal is at defined to be at zero potential).

If  $s_{metal} \gg s_{depSi}$ , the diffusion process dominates and ignoring image charges,

$$s_{depSi} = \epsilon_{si}\mathcal{E}(t_i) \quad (\text{A.66})$$

where  $\mathcal{E}(t_i)$  is electric field in Si at the interface. The current expression in this case, approximates the diffusion current expression (A.63). For a diode at 0.5 V forward

bias, fabricated on  $5 \times 10^{14}$  doped wafer,

$$s_{depSi} = 9 \times 10^6 \text{ cm/s} \quad (\text{A.67})$$

On the other hand,  $s_{metal}$  is the surface recombination velocity of the Si/metal interface( $x = t_i$ ):

$$J_{interface} = qs_{metal}(n(t_i) - n_0(t_i)) \quad (\text{A.68})$$

where  $n$  and  $n_0$  are the electron density in semiconductor at bias  $V$  and equilibrium, respectively, and

$$\begin{aligned} n(t_i) &= N_{C,si} \exp\left(\frac{E_{F,n}(t_i) - q\phi_{bn}}{kT}\right) \\ n_0(t_i) &= N_{C,si} \exp\left(-\frac{q\phi_{bn}}{kT}\right) \end{aligned} \quad (\text{A.69})$$

So

$$J_{interface} = qs_{metal}N_{C,si} \exp\left(-\frac{q\phi_{bn}}{kT}\right) \left(\exp\left(\frac{E_{F,n}(t_i)}{kT}\right) - 1\right) \quad (\text{A.70})$$

Since  $s_{metal}$  is a measure of the current due to thermionic emission over the Si/metal barrier, so using the Thermionic emission theory the net current at the Si/metal interface is given by

$$\begin{aligned} J_{interface} &= J_{Si \rightarrow M} - J_{M \rightarrow Si} \\ &= A_{n,si}T^2 \exp\left(-\frac{q\phi_{bn}}{kT}\right) \left[\exp\left(\frac{E_{F,n}(t_i)}{kT}\right) - 1\right] \end{aligned} \quad (\text{A.71})$$

Eliminating  $J_{interface}$  from (A.70), (A.69), and (A.71), we derive the expression for  $s_{metal}$

$$s_{metal} = \frac{A^*T^2}{qN_C} \quad (\text{A.72})$$

Substituting this value of  $s_{metal}$  into (A.64) and assuming  $s_{depSi} \gg s_{metal}$ , we re-

discover the expression for current due to the Thermionic theory, (A.62). At 300°K typical values of  $A$  are  $\approx 120 \text{ A/cm}^2\text{K}^2$ , so

$$s_{metal} \approx 2 \times 10^6 \text{ cm/s.} \quad (\text{A.73})$$

# Appendix B

## Generalized Quasi-Steady-State Lifetime Measurement

### B.1 Introduction

Minority carrier recombination is a powerful tool to characterize electrical quality of semiconductor surfaces. In this project, minority carrier recombination lifetimes were measured using WCT-120 from Sinton Consulting, an instrument based on the Quasi-static photoconductance decay (QSSPCD) method [79].

This chapter details the derivations and assumptions made in the extraction of minority carrier lifetime and surface recombination velocity from the raw QSSPCD data.

### B.2 Basics

Surface defects can act as minority carrier recombination centers with recombination rate  $U$  (in  $\text{cm}^{-2}\text{s}^{-1}$ )

$$U = S n'_{\text{minority}} \tag{B.1}$$

where  $n'_{minority}$  is the minority carrier density at the surface and  $S$  is the surface recombination velocity (SRV in cm/s). For a neutral surface. SRV relates to the surface defects density  $N_t$

$$S = N_t v_{th} \sigma \quad (\text{B.2})$$

where,  $v_{th}$  is the electron thermal velocity, and  $\sigma$  is the capture cross-section of the surface defects.

The continuity equations for the excess minority carriers in a semiconductor are

$$\frac{\partial n}{\partial t} = G_n - U_n + \frac{1}{q} \nabla J_n \quad (\text{B.3})$$

$$\frac{\partial p}{\partial t} = G_n - U_p - \frac{1}{q} \nabla J_p \quad (\text{B.4})$$

For the case of low-injection and negligible band-bending, the equations simplify to

$$\frac{\partial \Delta n(x, t)}{\partial t} = G(x, t) - \frac{\Delta n(x, t)}{\tau_{bulk}} + D_n \frac{\partial^2 \Delta n(x, t)}{\partial x^2} \quad (\text{B.5})$$

$$\frac{\partial \Delta p(x, t)}{\partial t} = G(x, t) - \frac{\Delta p(x, t)}{\tau_{bulk}} + D_p \frac{\partial^2 \Delta p(x, t)}{\partial x^2} \quad (\text{B.6})$$

Where  $\Delta n$  and  $\Delta p$  are the excess minority carrier densities. The loss of minority carriers due to surface recombination at the wafer of thickness  $W$  is given by the boundary conditions

$$D_n \left. \frac{\partial \Delta n(x, t)}{\partial x} \right|_{x=0} = S_{front} \Delta n(0, t) \quad \& \quad - D_n \left. \frac{\partial \Delta n(x, t)}{\partial x} \right|_{x=W} = S_{back} \Delta n(W, t) \quad (\text{B.7})$$

for p-type substrates and for n-type substrates

$$D_p \frac{\partial \Delta p(x, t)}{\partial x} \Big|_{x=0} = S_{front} \Delta p(0, t) \quad \& \quad - D_p \frac{\partial \Delta p(x, t)}{\partial x} \Big|_{x=W} = S_{back} \Delta p(W, t) \quad (\text{B.8})$$

### B.3 Relation between $\tau_{eff}$ and SRV

For a n-type wafer in dark ( $G = 0$ ) the continuity equation reduces to

$$\frac{\partial \Delta n(x, t)}{\partial t} = - \frac{\Delta n(x, t)}{\tau_{bulk}} + D_n \frac{\partial^2 \Delta n(x, t)}{\partial x^2} \quad (\text{B.9})$$

The general solution to this equation is of the form [167]

$$\Delta n(x, t) = e^{-t/\tau_{bulk}} \left[ A e^{-\beta^2 D_n t} \cos \beta x + B e^{-\beta^2 D_n t} \sin \beta x \right] \quad (\text{B.10})$$

where  $A$ ,  $B$ , and  $\beta$  are constants which must satisfy the boundary conditions (B.7).

Substituting the solution in (B.9)

$$\frac{\partial \Delta n(x, t)}{\partial t} = - \frac{\Delta n(x, t)}{\tau_{eff}} \quad (\text{B.11})$$

where,

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_{bulk}} + \frac{1}{\tau_{surface}} \quad (\text{B.12})$$

and

$$\tau_{surface} = \frac{1}{D_n \beta^2} \quad (\text{B.13})$$

Assume that  $S_{front} = s$  and  $S_{back} = 0$ . Solving for the boundary conditions

$$\tan(\beta W) = \frac{s}{\beta D_n} \quad (\text{B.14})$$

where  $W$  is the wafer thickness. In the limits of high and low surface recombination, the equation can be simplified to

$$\tau_{surface}|_{s \rightarrow \infty} = \frac{4W^2}{\pi^2 D_n} \quad \& \quad \tau_{surface}|_{s \rightarrow 0} = \frac{W}{s} \quad (\text{B.15})$$

For a silicon wafer with recombination on both sides of the wafer, boundary conditions change to  $S_{front} = S_{back} = s$ , and the the final expressions change to

$$\tan\left(\frac{\beta W}{2}\right) = \frac{s}{\beta D_n} \quad (\text{B.16})$$

$$\tau_{surface}|_{s \rightarrow \infty} = \frac{W^2}{\pi^2 D_n} \quad \& \quad \tau_{surface}|_{s \rightarrow 0} = \frac{W}{2s} \quad (\text{B.17})$$

## B.4 Quasi Steady-State Photoconductance Decay: Analysis

Integrating the equation (B.5) over the width of the wafer, we get

$$\begin{aligned} \int_0^W \frac{\partial \Delta n(x, t)}{\partial t} dx &= \int_0^W G(x, t) dx - \int_0^W \frac{\Delta n(x, t)}{\tau_{bulk}} dx + \int_0^W D_n \frac{\partial^2 \Delta n(x, t)}{\partial x^2} dx \\ \Rightarrow \frac{d}{dt} \int_0^W \Delta n(x, t) dx &= \int_0^W G(x, t) dx - \frac{1}{\tau_{bulk}} \int_0^W \Delta n(x, t) dx \\ &\quad + D_n \frac{\partial \Delta n(x, t)}{\partial x} \Big|_{x=W} - D_n \frac{\partial \Delta n(x, t)}{\partial x} \Big|_{x=0} \end{aligned} \quad (\text{B.18})$$

Dividing the whole equation by the wafer width  $W$ , and using the boundary conditions (B.7), the expression simplifies to

$$\Rightarrow \frac{d\Delta n_{av}(t)}{dt} = G_{av}(t) - \frac{\Delta n_{av}(t)}{\tau_{eff}(\Delta n_{av})} \quad (\text{B.19})$$

where,

$$\Delta n_{av}(t) = \frac{1}{W} \int_0^W \Delta n(x, t) dx \quad (\text{B.20})$$

$$G_{av}(t) = \frac{1}{W} \int_0^W G(x, t) dx \quad (\text{B.21})$$

$$\frac{\Delta n_{av}(t)}{\tau_{eff}(\Delta n_{av})} = \frac{\Delta n_{av}(t)}{\tau_{bulk}(\Delta n_{av})} + \frac{1}{W} S_{front} \Delta n(0, t) + \frac{1}{W} S_{back} \Delta n(W, t) \quad (\text{B.22})$$

The WCT-120 measures the incident power,  $G_{av}(t)$ , using a calibrated photodiode and measures the conductivity of the sample using an inductive coil. From the conductivity data, the control program then estimates the average value of excess minority carrier density,  $\Delta n_{av}(t)$ . Unfortunately, average values are not enough to rigorously extract the bulk lifetime ( $\tau_{bulk}$ ) and recombination velocities ( $S_{front}$  and  $S_{back}$ ) from (B.22). One also requires the exact values of the excess minority carrier at the surfaces, i.e.  $\Delta n(0, t)$  and  $\Delta n(W, t)$ .

### B.4.1 Need for Simulations

As mentioned in the previous section, to analytically find the bulk lifetime and values of recombination velocities, the exact profile of excess carrier density ( $\Delta n(x, t)$ ) is required. However the instrument only measures the average carrier density ( $\Delta n_{av}(t)$ ), so a simple analytical analysis is not enough.

To solve this inverse problem, we can run a MATLAB program to calculate a simulated  $\Delta n(x, t)$ , for a range of bulk lifetime and recombination velocities, using the continuity equation (B.3) or (B.4). The simulated profiles will be constrained to satisfy Eq. (B.20) & (B.21). From the simulated profile the average values of minority carrier density,  $\Delta n_{av}(t)$ , can then be calculated.

By comparing the simulated  $\Delta n_{av}(t)$  and measured  $\Delta n_{av}(t)$ , and obtaining the best fit, the values of bulk-lifetime and recombination velocity can be calculated.

## B.4.2 Generation Rate Profile

For simulating the minority carrier density profile in a wafer,  $\Delta n_{av}(t)$ , using the continuity equation (B.3) or (B.4), one needs the exact profile of generation rate inside the wafer, i.e.  $G(x, t)$ . Once again, what the instrument measured is the average value,  $G_{av}(t)$ . However, since the AM1.5 spectrum is known, one can calculate  $G(x, t)$ , from the average  $G_{av}(t)$ .

We know the incident light power,  $G_{av}(t)$  (in suns). Assume that the spectrum of the Xe lamp used in the measuring instrument is similar to AM 1.5 spectrum (Fig. 1.3). We also know the absorption depth ( $\alpha_\lambda$ ) of photon with a given wavelength ( $\lambda$ ). The exact generation rate  $G(x, t)$  will then simply be

$$G(x, t) = 0.7 \cdot N \cdot G_{av}(t) \sum_{\forall \lambda} \Phi(\lambda) \frac{e^{-\alpha_\lambda x} - e^{-\alpha_\lambda (x+\Delta x)}}{\Delta x} \quad (\text{B.23})$$

Where  $N$  is a normalization factor to set the optical intensity i.e. satisfy equation (B.21),  $\Phi(\lambda)$  is the photo-flux as a function of wavelength (Fig. 1.3(b)), and 0.7 accounts for the 30% reflectance of the silicon surface with no AR coating.

## B.4.3 Data Plots and Extracted Parameters

In a usual lifetime measurement, there are three samples: oxide-coated, unpassivated and PQ-passivated. There are 5 unknowns that need to be calculated to completely describe the set of devices under test: bulk lifetime ( $\tau_{bulk}$ ), the top surface oxide SRV ( $S_{front,ox}$ ), the bottom surface oxide SRV ( $S_{back,ox}$ ), the top surface native-oxide SRV ( $S_{front,no}$ ), and the top surface PQ SRV ( $S_{front,PQ}$ ). Let us call them the unknown parameters. To numerically find the optimum fit of the 5 parameters, we have 3 curves each with 50-80 points - the  $\Delta_{av}(t)$  for oxide, native-oxide and PQ-passivated silicon.

The measured data for the p-type wafers coated with thermal-oxide, native oxide,

and PQ,  $\Delta n_{av}$  and  $G_{av}$  as a function of time ( $t$ ), is plotted in Fig. B.1 (dotted line). The solid lines represent, the fit of the model with the optimized parameters. The optimized parameters that generated the best-fit are given in Table B.1. As seen, the model closely fits the measured data. Similar analysis for the n-type wafers is given in Fig. B.1 and Table B.1.

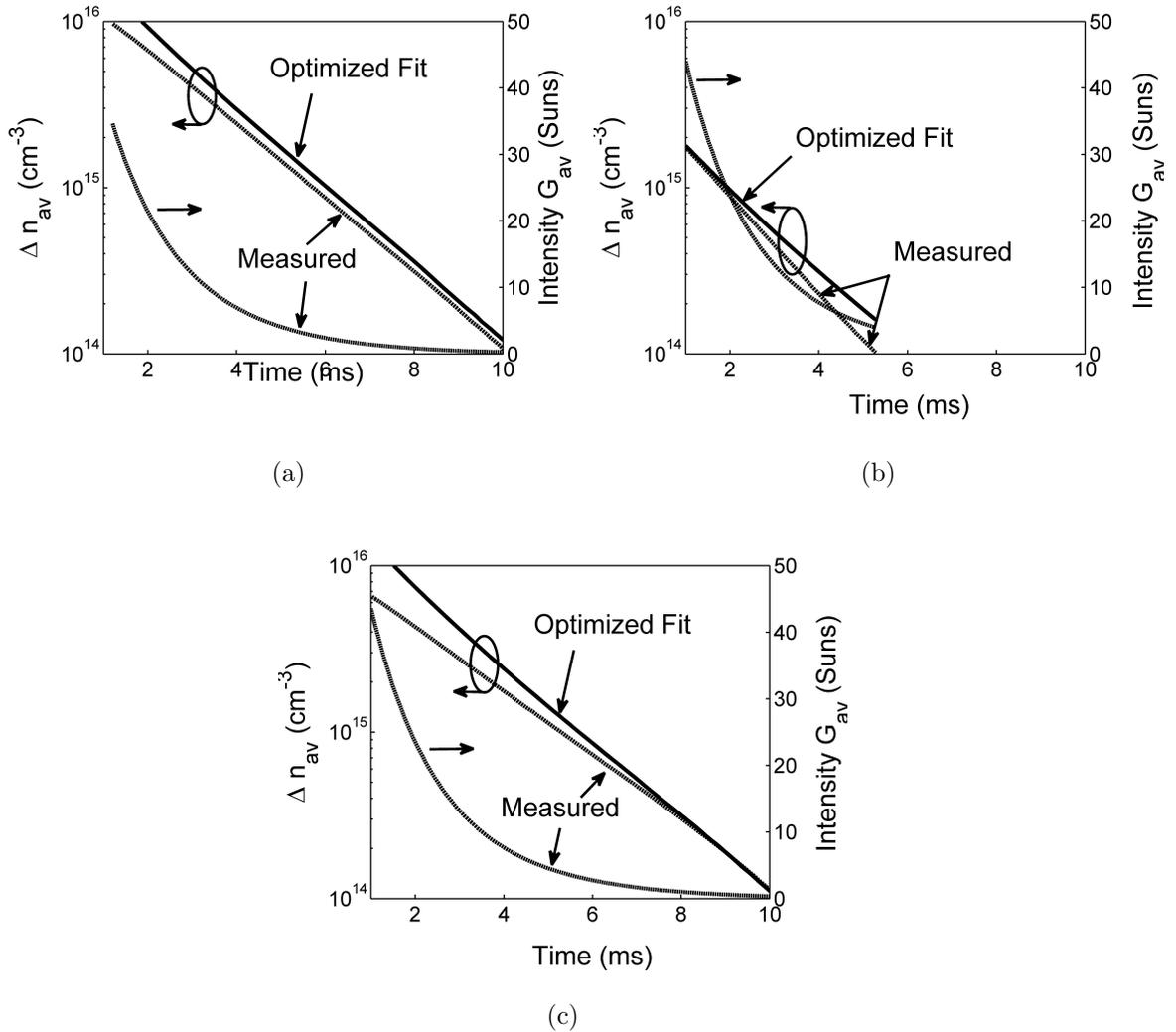


Figure B.1: QSSPCD data for p-type wafer coated with (a) thermal oxide, (b) native oxide, and (c) PQ. The dotted lines are actual data measured by the instrument and the solids line is the best fit using the generalized model derived above.

The extracted value of the optimized parameters, surface recombination velocity (SRV) for PQ-silicon interface for both p and n-type substrates. The three condi-

Table B.1: The optimized values of QSSPCD parameters that best fit the data of Fig. B.2 & B.1: bulk lifetime ( $\tau_{bulk}$ ), the top surface oxide SRV ( $S_{front,ox}$ ), the bottom surface oxide SRV ( $S_{back,ox}$ ), the top surface native-oxide SRV ( $S_{front,no}$ ), and the top surface PQ SRV ( $S_{front,PQ}$ ).

	Lifetime ( $\mu s$ )	SRV (cm/s)			
	$\tau_{bulk}$	$S_{front,ox}$	$S_{back,ox}$	$S_{front,no}$	$S_{front,PQ}$
p-type	122	9	33	4804	145
n-type	252	26	32	2014	133

tions represent different surface treatments; passivated with a high-quality thermal oxide, native oxide (unpassivated), and PQ-passivated.

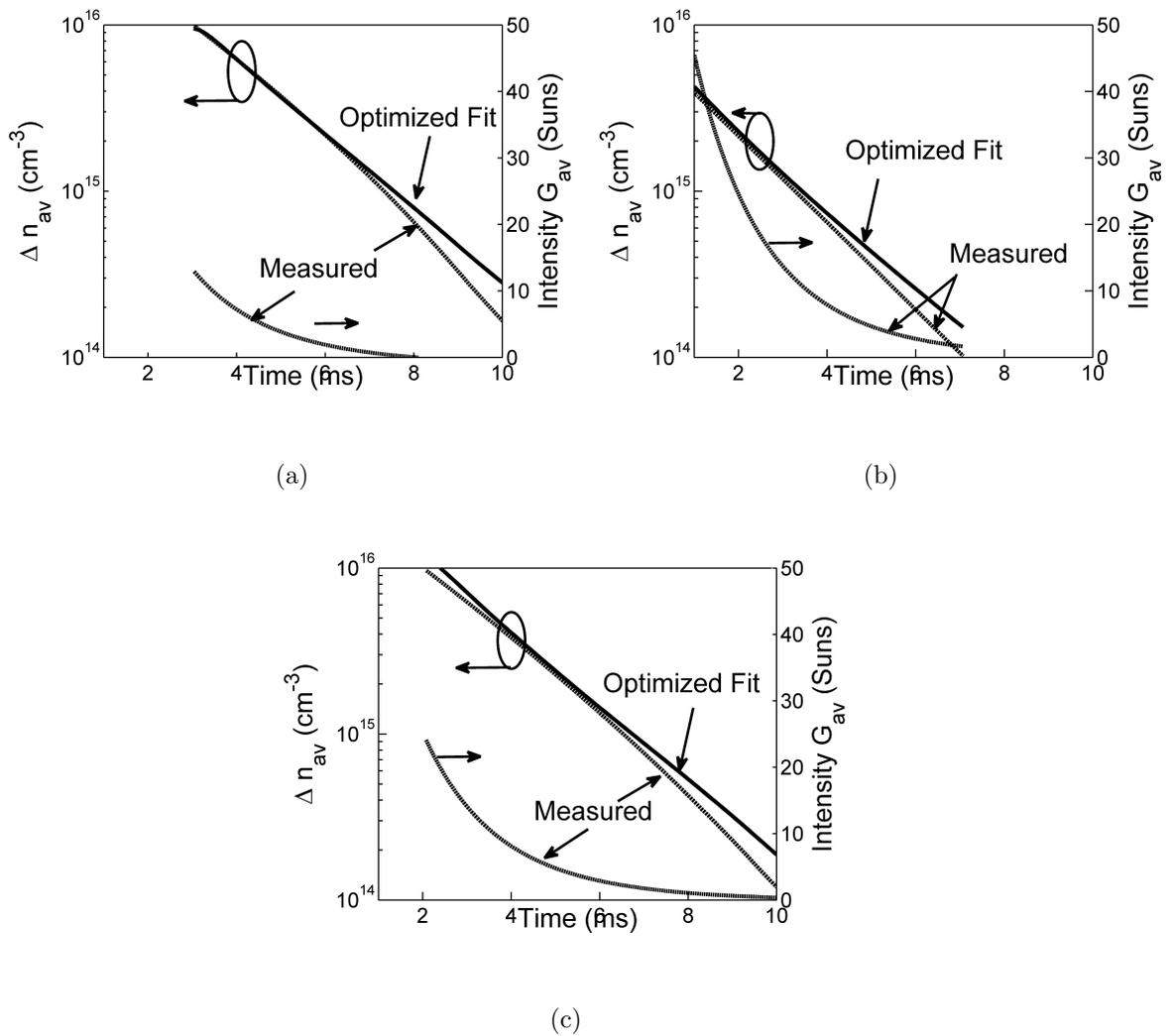


Figure B.2: QSSPCD data for n-type wafer coated with (a) thermal oxide, (b) native oxide, and (c) PQ. The dotted lines are actual data measured by the instrument and the solids line is the best fit using the generalized model derived above.

# Appendix C

## Control

## Metal-Oxide-Semiconductor

## Transistors

To serve as a control for the PQ-passivated MISFET device (Chapter 3), conventional MOS devices using the high-quality thermal-oxide were also fabricated. The devices used the same implanted and annealed silicon wafers, to define the source and drain, as the MISFET devices. The oxide was grown in Thermco furnace at 1000 °C in dry-oxygen ambient. The estimated thickness of the oxide layer was 25 nm. Source and drain contact holes were etched using photolithography. Metal was deposited by thermal evaporation.

The structure,  $I_{DS}-V_{GS}$ , and transconductance characteristics of the n-channel and p-channel devices are shown in Fig. C.1. Oxide capacitance value was measured to be 125 nF/cm<sup>2</sup> by a small-signal capacitance meter (20kHz). The W/L of the devices was 1/2.2 (Fig. 3.15(b)) extracted electron and hole mobility were 700 cm<sup>2</sup>/Vs and 225 cm<sup>2</sup>/Vs, respectively (Fig. 3.15(d) & (f)).

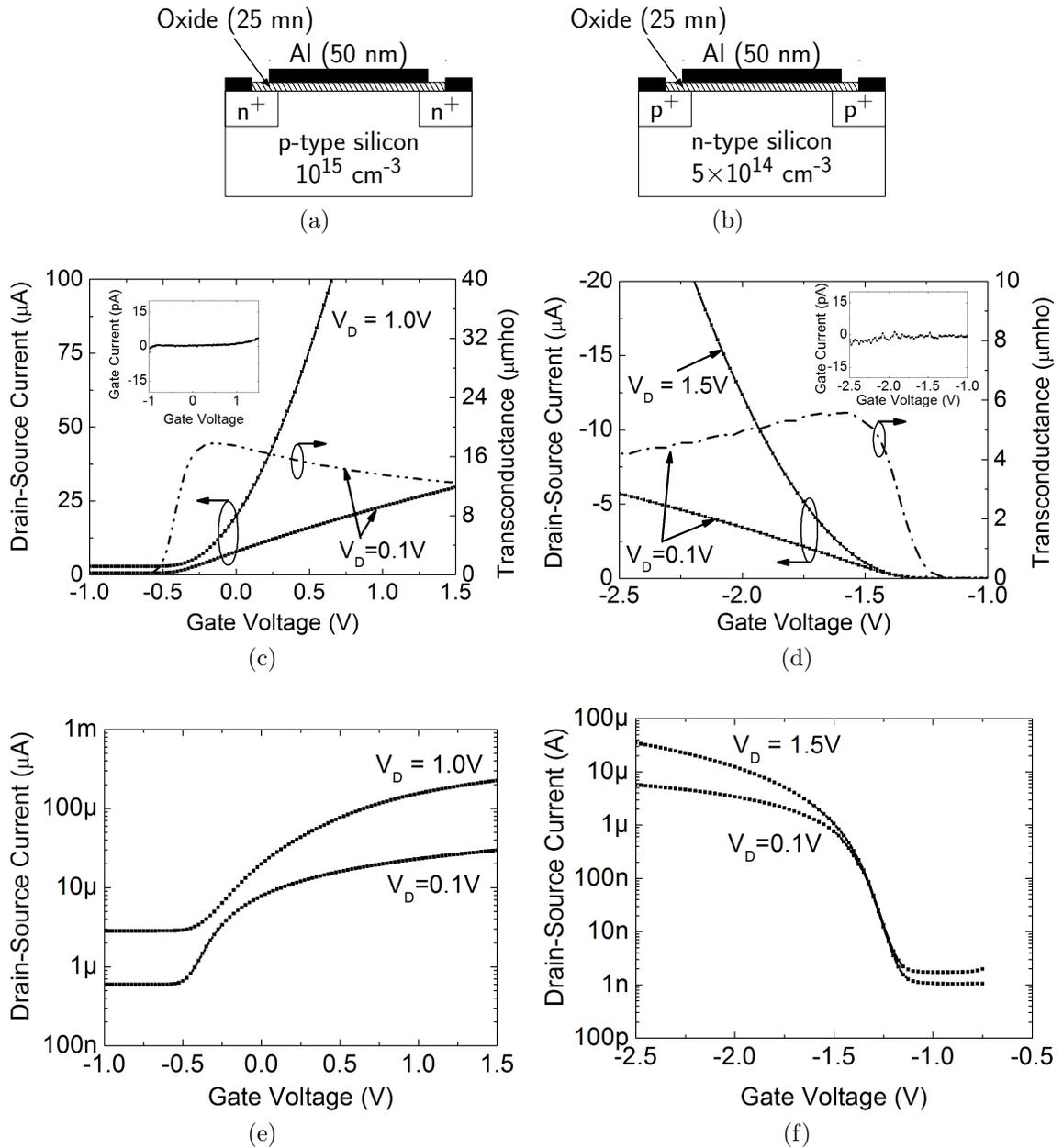


Figure C.1: Structure of the control metal-oxide-semiconductor field-effect (a) n-channel and (b) p-channel transistors. The L and W of the devices are 1 mm and 2.2 mm, respectively. Drain current and transconductance vs. gate voltage characteristics at low drain voltages in (c) n-channel and (d) p-channel devices. Drain current vs. gate voltage characteristics on a log scale at low drain voltages in (e) n-channel and (f) p-channel devices

# Appendix D

## Publications and Presentations

### D.1 Refereed journal articles

**Sushobhan Avasthi**, Stephanie Lee, Yueh-Lin Loo, and James C. Sturm, “Role of Majority and Minority Carrier Barriers Silicon/Organic Hybrid Heterojunction Solar Cells,” accepted for publication at *Advanced Materials* (September, 2011)

**Sushobhan Avasthi**, Yabing Qi, Grigory Vertelov, Jeffrey Schwartz, Antoine Kahn, and James C. Sturm, “Electronic structure and band alignment of 9,10-phenanthrenequinone passivated silicon surfaces,” *Surface Science* **605**, 1308 (2011)

**Sushobhan Avasthi**, Yabing Qi, Grigory Vertelov, Jeffrey Schwartz, Antoine Kahn, and James C. Sturm, “Silicon Surface Passivation by an Organic Overlayer of 9,10-phenanthrenequinone,” *Applied Physics Letters* **96**, 222109 (2010)

Shyam Shankar, Alexei M. Tyryshkin, **Sushobhan Avasthi**, Stephen A. Lyon, “Spin Resonance of 2D Electrons in a Large-area Silicon MOSFET,” *PHYSICA E*, March 2008.

## D.2 Published Proceedings

**Sushobhan Avasthi**, and James C. Sturm, “Charge Separation and Minority Carrier Injection in P3HT-Silicon Heterojunction Solar Cells,” in *Proceedings of 37<sup>th</sup> IEEE Photovoltaic Specialists Conference*, June 2011.

**Sushobhan Avasthi**, Grigory Vertelov, Jeffrey Schwartz and James C. Sturm, “Reduction of Minority Carrier Recombination at Silicon Surfaces and Contacts Using Organic Heterojunctions,” in *Proceedings of 34<sup>th</sup> IEEE Photovoltaic Specialists Conference*, June 2009.

## D.3 Conference Presentations

**Sushobhan Avasthi**, Stephanie Lee, Yueh-Lin Loo, and James C. Sturm, “P3HT-Silicon Organic-Silicon Heterojunction for Photovoltaic Applications,” presented at *2011 Materials Research Society Spring Meeting*, San Francisco, CA, April 2011.

**Sushobhan Avasthi**, Yabing Qi, Sieu Ha, Grigory Vertelov, Jeffrey Schwartz, Antoine Kahn, and James C. Sturm, “P3HT-Silicon Organic-Silicon Heterojunction for Photovoltaic Applications,” presented at *2010 Materials Research Society Fall Meeting*, Boston, MA, December 2010.

**Sushobhan Avasthi**, Yabing Qi, Grigory Vertelov, Jeffrey Schwartz, Antoine Kahn, and James C. Sturm, “Stability of Electrical Properties of Silicon (100) Surfaces Passivated with 9,10-phenanthrenequinone,” presented at *2009 Materials Research Society Fall Meeting*, Boston, MA, December 2009.

James C. Sturm, Bahman Hekmatshoar, Lin Han, **Sushobhan Avasthi**, Grigory Vertelov, Yabing Qi, Jeffrey Schwartz, Antoine Kahn and Sigurd Wagner, “Towards Organic-based Dielectrics for Low-Temperature Silicon-based Devices for Large-Area

Electronics,” presented at the *2009 Materials Research Society Fall Meeting*, Boston, MA, December 2009

**Sushobhan Avasthi**, Yabing Qi, Jeffrey Schwartz, Antoine Kahn, and James C. Sturm, “Electronic Passivation of Silicon (100) Surfaces by Organic Layer of 9,10-phenanthrenequinone,” presented at *51<sup>st</sup> Electronic Materials Conference*, College Park, PA, June 2009.

**Sushobhan Avasthi**, Grigory Vertelov, Jeffrey Schwartz and James C. Sturm, “Reduction of Minority Carrier Recombination at Silicon Surfaces and Contacts Using Organic Heterojunctions”, presented at *34<sup>th</sup> IEEE Photovoltaic Specialists Conference*, Philadelphia, PA, June 2009.

## D.4 Patents

**Sushobhan Avasthi**, Jeffrey Schwartz, and James C. Sturm, “Photovoltaic Device and Method of Making the Same,” Patent Application 13/113,606 (2011)

**Sushobhan Avasthi**, Jeffrey Schwartz, and James C. Sturm, “Reduction of Minority Carrier Recombination at Silicon Surfaces and Contacts Using Organic Heterojunctions,” Provisional Patent Application 61/347666 (2010)

**Sushobhan Avasthi**, and James C. Sturm, “Organic-Silicon Heterojunctions for Efficient Photovoltaic Devices,” Provisional Patent Application 61/416986 (2010)

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