

## Supplementary Material

### Impedance Analysis of Semiconductor Electrodes in the Accumulation Region

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## 1. Glossary of Symbols

$C_{meas}$	= experimental capacitance (F/cm <sup>2</sup> )
$C_{HH}$	= differential capacitance on solution side of interface (F/cm <sup>2</sup> )
$C_{SC}$	= differential space charge capacitance (F/cm <sup>2</sup> )
$D(E_c)$	= density of states of conduction band
$E_C$	= conduction band energy
$E_F$	= Fermi energy
$E_V$	= valence band energy
$N_D$	= doping density for electrons (#/cc)
$F_{1/2}(\eta)$	= Fermi-Dirac integral of order 1/2
$\eta$	= $(E_C - E_F)/kT$
$V_{appl}$	= applied potential (volts)
$y$	= band bending (in units of $e/kT$ )
$y_s$	= band bending at the surface (in units of $e/kT$ )
$\phi_0$	= electrostatic potential in bulk of solid
$\phi_e$	= electrostatic potential of electrons at surface
$\phi_h$	= electrostatic potential of holes at surface
$N$	= electron quasi-fermi level – unitless as $e(\phi_e - \phi_0)/kT$
$P$	= hole quasi-fermi level– unitless as $e(\phi_h - \phi_0)/kT$
$E_i$	= $(E_C - E_V)/2$
$L_D$	= Debye length
$w_{A,B}$	= energy difference of levels A and B, $(E_A - E_B)/kT$
$u_b$	= $(E_C - E_i)/kT$ in bulk
$u_s$	= $(E_C - E_i)/kT$ at surface

## 2. Derivation of eqn (1)

The expression for capacitance in eqn (1) resulted from early semiconductor physics research by Shockley and Garrett and Brattain in the 1950s. This work derived mathematical expressions describing the charge and electric field of a semiconductor space charge region and made it possible to calculate the electric field in the space charge region of a semiconductor. Their integration of the total charge over the space charge region from surface to bulk yielded the analytical expression:

$$F(y, \lambda, P, N) = \pm \left[ \frac{\lambda e^P (e^{-y} - 1) + \lambda^{-1} e^{-N} (e^y - 1)}{(\lambda + \lambda^{-1})y} \right]_{1/2} \quad \text{eqn S1}$$

where  $\lambda = p_0/n_i = n_i/n_0$ ,  $p_0$  and  $n_0$  being the bulk hole and electron densities of the semiconductor,  $y$  is the band bending in units of  $kT/e$ , and  $n_i$  is the intrinsic charge carrier density.  $P$  and  $N$

represent the concentration of free holes and free electrons in the space charge region in the form of the quasi-fermi levels:

$$P = \frac{e}{kT}(\varphi_p - \varphi_0) \quad \text{eqn S2}$$

and

$$N = \frac{e}{kT}(\varphi_n - \varphi_0) \quad \text{eqn S3}$$

where  $\varphi_p$  and  $\varphi_n$  are the quasi fermi level for holes and electrons owing to the free charge concentrations and  $\varphi_0$  is the dark equilibrium fermi level without external charge. P and N can be changed by dark events such as charge injection from redox agents or photoexcitation. Implicit in the derivation of eqn (1s) this is the assumption that P and N are constant throughout the space charge region, as would be the case for carriers with a diffusion length greater than the depth of band bending.<sup>7</sup> Any circumstance that considers a functional, position dependent recombination dependence of electrons with holes inserts cross products of the electron and hole concentrations into solutions of the equations above and would require a numerical solution equivalent to eqn (1s).

In the dark at equilibrium without redox couples in solution,  $e^P$  and  $e^{-N}$  are unity and eqn (1s) has been used to derive:<sup>1,2</sup>

$$C_{SC} = \left( \frac{n_i \epsilon \epsilon_0 kT}{8\pi e} \right)^{1/2} \left\{ \left( \frac{p_o}{n_i} (1 - e^{-y_s}) + \frac{n_o}{n_i} (e^{y_s} - 1) \right) / F(Y, \lambda, P, N) \right\} \quad \text{eqn S4}$$

Here  $y_s$  is the band bending at the surface in units of kT. For an n-type semiconductor, this can be rewritten:<sup>2</sup>

$$C_{s.c.} = \left( \frac{e^2 N_D \epsilon \epsilon_0}{2kT} \right)^{1/2} \frac{|e^{y_s} - 1|}{(e^{y_s} - y_s - 1)^{1/2}} \quad \text{eqn S5}$$

When a semiconductor electrode is biased in the depletion region where  $y_s < 0$ , this leads to eqn (1) of the text.

There are two immediate observations from this overview that are little appreciated. The first concerns the phrase “flatband” potential intercept  $V_{fb}$  which eqn (4) shows is kT away from the potential at which the band bending  $y_s = 0$  and has a net charge in the space charge region of zero. As eqn (1s) shows, the bands are only flat when P and N are zero in the measurement – there is no redox couple in solution and no illumination. Following eqn (1), Mott-Schottky analyses in the presence of redox couples in solution or at the surface can yield an intercept with the potential axis, but it is not necessarily where  $y_s = 0$ , but rather the potential where the sum of all charges from electrons, holes, and ionized dopant atoms equals zero. It is a potential where there is zero net charge in the space charge region. The bands are not necessarily flat. A second

observation derives from eqn (5s) as  $y_s$  goes to zero and the exponential terms can be expanded into a series approximation. In this case, at  $y_s = 0$ , we have the expression in the test:

$$C_{s.c.} = \sqrt{2} \left( \frac{e^2 N_D \epsilon \epsilon_0}{2kT} \right)^{1/2} \quad (2)$$

If one extracts  $V_{fb}$  for a semiconductor electrode through eqn (1), the observed value of  $C_{SC}$  at the potential where  $y_s = 0$  should be given by eqn (2), assuming that any potential drop of the applied potential across the Helmholtz layer can be neglected.

### 3. Expressions for the two models – ionized vs. general

It is possible to compare the form of the capacitance expressions for the fully ionized model and the general models. The former was given in eqn (5s) for an n-type material:

$$C_{s.c.} = \left( \frac{e^2 N_D \epsilon \epsilon_0}{2kT} \right)^{1/2} \frac{|e^Y - 1|}{(e^Y - Y - 1)^{1/2}} \quad \text{eqn S5}$$

With the relation between  $N_D$  and  $u_b$  being defined by the neutrality condition of eqn (6), it is possible to express the general model for capacitance as:

$$C_{SC} = \left( \frac{e^2 N_D \epsilon \epsilon_0}{2kT} \right)^{1/2} \left\{ \left[ \frac{-1}{1 + 2 \exp(u_s - w_{D,I})} \right] + \frac{1}{(1 + 2 \exp(u_b - w_{D,I})) F_{1/2}(u_b - w_{C,I})} F_{1/2}(u_s - w_{C,I}) \right\} / F_a$$

eqn S6

where the term  $F_a$  is now written:

$$F_a = \ln \left[ \frac{1 + \frac{1}{2} \exp(w_{D,I} - u_s)}{1 + \frac{1}{2} \exp(w_{D,I} - u_B)} \right] + \frac{1}{((1 + 2 \exp(u_b - w_{D,I})) F_{1/2}(u_b - w_{C,I}))} \left[ \frac{2}{3} F_{3/2}(u_s - w_{C,I}) - \frac{2}{3} F_{3/2}(u_B - w_{C,I}) \right]$$

### 4. Data Analysis of Mott-Schottky measurements

The Mott-Schottky analyses used in this work to determine  $V_{fb}$  included a self-consistency check with eqn 2. The slope of the Mott-Schottky plot provided a prediction of  $C_{SC}$  at  $y_s = 0$  from eqn

(5s). The data was used in this work only if  $V_{fb}$  extracted from Mott-Schottky analyses was within  $2kT$  of this predicted result.

- a. **Fig. S1 - Data for pSi of Fig. 3 at 100 mM TBAPF<sub>6</sub>**
- b. **Fig. S1a - Data for pSi of Fig. 3 at 100 mM TBAPF<sub>6</sub> in deep depletion**
- c. **Fig. S2 - Data for nSi of Fig. 4 at 100 mM TBAPF<sub>6</sub>**
- d. **Fig. S3 - Data for nInP of Fig. 5 at 100 mM TBAPF<sub>6</sub>**

**a. Data for pSi of Fig. 3 at 100 mM TBAPF<sub>6</sub>**

The Mott-Schottky analysis yields for following:

$$V_{fb} = -.61 \text{ V vs. ferrocene}$$

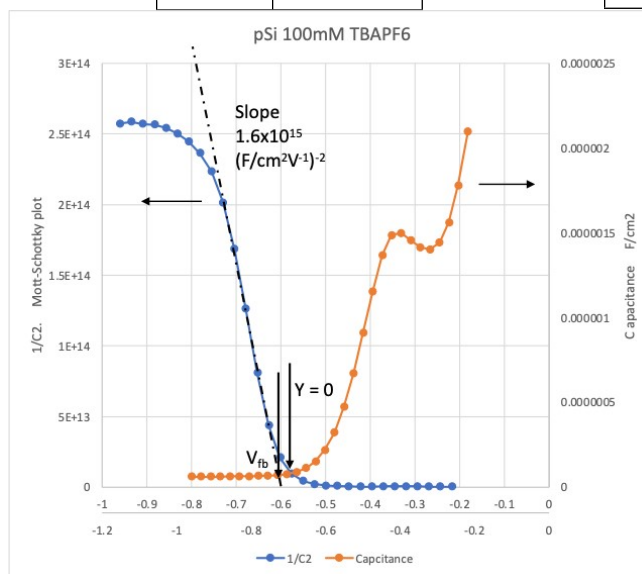
$$N_A = 7 \times 10^{15} / \text{cc}$$

In this experiment, the slope of the  $1/C^2$  plot can be inserted into eqn 2 to obtain  $C_{SC}$  at  $y_s = 0$ , or  $2.2 \times 10^{-7}$ . From eqn 1 it is known that  $y_s = 0$  is found at  $V_{fb} + kT$ , or  $-.57$ , designated in red in the following data table. The closest value of  $C$  to  $2.2 \times 10^{-7}$  is found within  $kT$  of  $y_s = 0$ .

pSi Data:

Pot (V)	C (F/cm <sup>2</sup> )
-0.218	2.10E-06
-0.244	1.78E-06
-0.269	1.56E-06
-0.295	1.44E-06
-0.320	1.40E-06
-0.346	1.41E-06
-0.372	1.46E-06
-0.397	1.50E-06
-0.423	1.49E-06
-0.448	1.37E-06
-0.474	1.15E-06
-0.500	9.08E-07
-0.525	6.73E-07
-0.551	4.73E-07

-0.576	3.21E-07
-0.602	2.18E-07
-0.628	1.51E-07
-0.653	1.11E-07
-0.679	8.91E-08
-0.704	7.70E-08
-0.730	7.04E-08
-0.756	6.69E-08
-0.781	6.50E-08
-0.807	6.39E-08
-0.832	6.32E-08
-0.858	6.27E-08
-0.884	6.24E-08
-0.909	6.24E-08
-0.935	6.22E-08
-0.960	6.23E-08



**Fig. S1**

**b. Fig. S1a - Data for pSi of Fig. 3 at 100 mM TBAPF<sub>6</sub> in deep depletion**

Capacitance measurements and Mott-Schottky plots that extend into a deep depletion bias of a p-type Si electrode. The bias scans here from positive of flatband to negative of the conduction band.

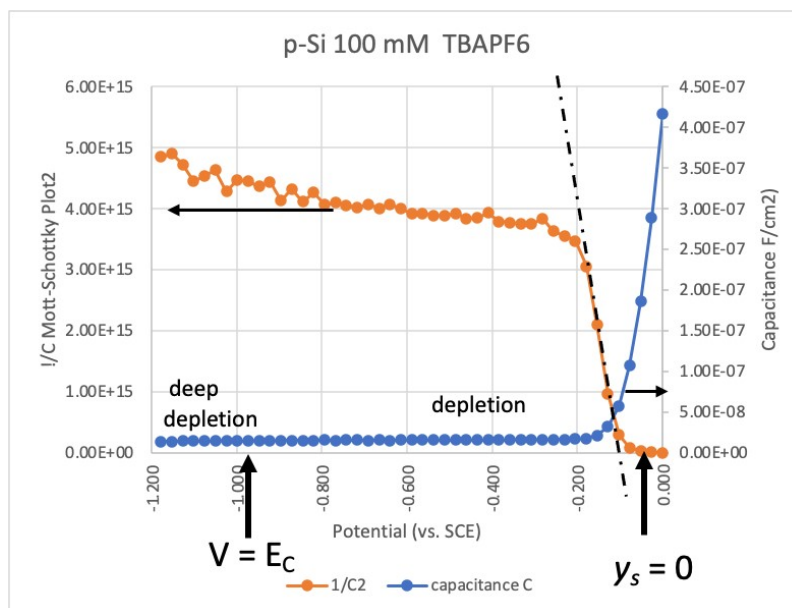


Fig. S1a

**c. Data for nSi of Fig. 4 at 100 mM TBAPF<sub>6</sub>**

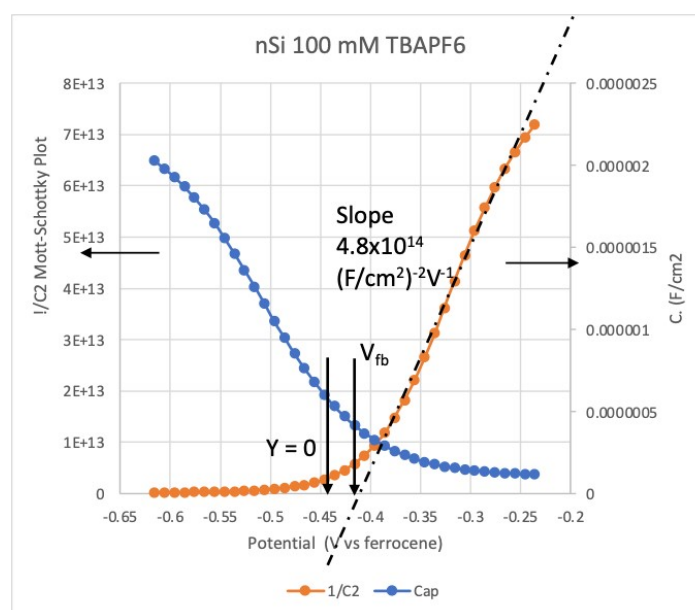
In a manner similar to above, a  $V_{fb}$  of  $-0.395$  V and an  $N_D$  of  $6 \times 10^{14}/\text{cc}$  leads to a  $y_s = 0$  potential of  $-0.42$ . This is within  $kT$  of the slope-derived  $C$  of  $4.0 \times 10^{-7}$  F/cm<sup>2</sup>.

nSi Data

Pot (V)	Cap (F/cm <sup>2</sup> )
-0.616	2.02718E-06
-0.606	1.98053E-06
-0.596	1.92778E-06
-0.586	1.86895E-06
-0.576	1.80334E-06
-0.566	1.72894E-06
-0.556	1.64755E-06
-0.546	1.55808E-06
-0.536	1.46222E-06

-0.526	1.36274E-06
-0.516	1.25928E-06
-0.506	1.15556E-06
-0.496	1.05106E-06
-0.486	9.50089E-07
-0.476	8.53109E-07
-0.466	7.624E-07
-0.456	6.78077E-07
-0.446	6.01588E-07
-0.436	5.32226E-07
-0.426	4.70176E-07
-0.416	4.15505E-07
-0.406	3.67756E-07
-0.396	3.26569E-07
-0.386	2.90865E-07

-0.376	2.60147E-07
-0.366	2.34224E-07
-0.356	2.12571E-07
-0.346	1.94026E-07
-0.336	1.78854E-07
-0.326	1.6622E-07
-0.316	1.55424E-07
-0.306	1.46701E-07
-0.296	1.39664E-07
-0.286	1.34004E-07
-0.276	1.29323E-07
-0.266	1.25709E-07
-0.256	1.22624E-07
-0.246	1.20042E-07
-0.236	1.17971E-07



**Fig. S2**

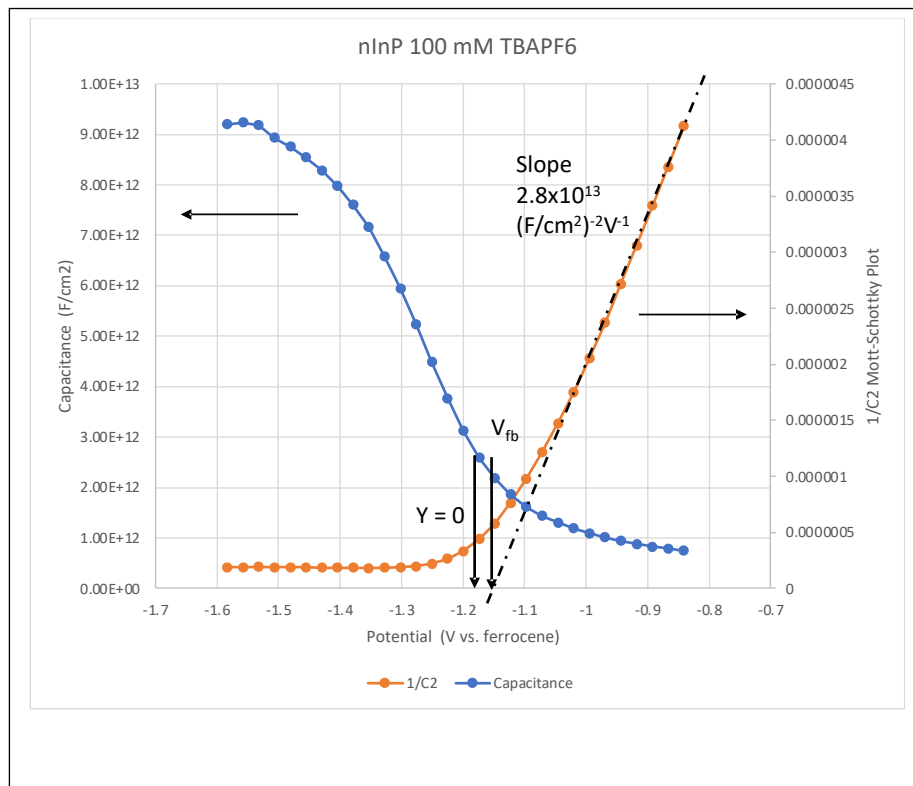


**d. Data for nInP of Fig. 5 at 100 mM TBAPF<sub>6</sub>**

In a manner similar to above, a  $V_{fb}$  of -1.17 V and an  $N_D$  of  $4 \times 10^{17}/\text{cc}$  leads to a  $y_s = 0$  potential of -1.20. This is within  $kT$  of the slope-derived  $C$  of  $6.64 \times 10^{-7} \text{ F/cm}^2$ .

-0.816	1.26E-07
-0.841	1.33E-07
-0.867	1.40E-07
-0.892	1.47E-07
-0.918	1.56E-07
-0.944	1.67E-07
-0.969	1.80E-07
-0.995	1.94E-07
-1.020	2.11E-07
-1.046	2.31E-07
-1.072	2.56E-07
-1.353	1.27E-06
-1.379	1.35E-06
-1.404	1.41E-06
-1.430	1.47E-06

-1.097	2.87E-07
-1.123	3.30E-07
-1.148	3.86E-07
-1.174	4.60E-07
-1.200	5.55E-07
-1.225	6.68E-07
-1.251	7.95E-07
-1.276	9.27E-07
-1.302	1.05E-06
-1.328	1.17E-06

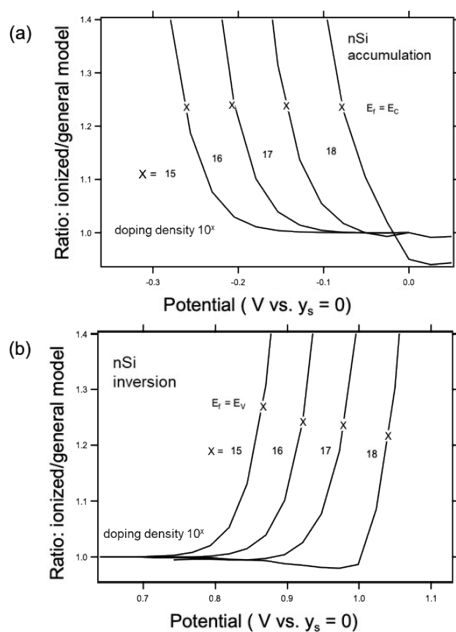


**Fig. S3**

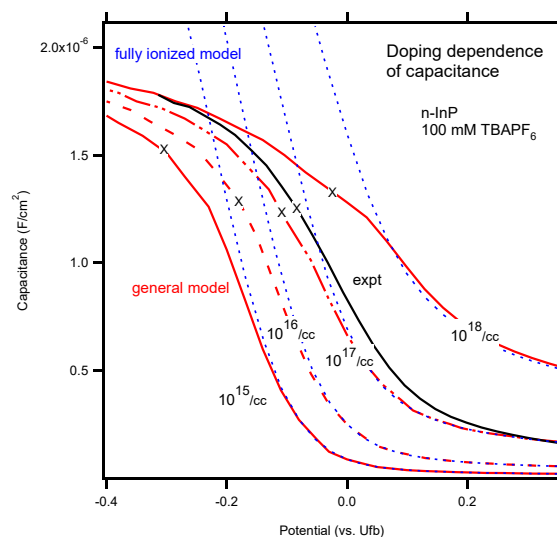
**5. Range of validity of fully ionized model**

It is of use to establish the potential range in accumulation where the fully ionized model ceases to be a good description of the space charge region and the general model must be employed. This is done for the outlined box area in Fig. 2 in the accumulation region of nSi and is shown in Fig. S4(a) as the ratio of eqn (5s) to eq (5), the fully ionized model to the general model. For each doping density in Fig. S4(a) from  $10^{15}/\text{cc}$  to  $10^{18}/\text{cc}$  the potential is marked where  $E_f = E_c$ . At this band bending the calculated ratio is 1.3 and from there the ratio continues its steep climb negative of this point and the fully ionized model of eqn (5s) fails to be a good description of the band bending in the semiconductor. It is evident from the data in Fig. 3, Fig. 4 and Fig. 5, that even a modest polarization of an electrode into the accumulation region from  $y_s = 0$  puts it into the transition region between the two models. With  $E_f$  passing through the donor energy levels at  $E_D$ , distortions in the ratio curves appear at appear at  $10^{18}/\text{cc}$  near  $y_s = 0$ . A similar plot of ratios is given in Fig. S4(b) for an electrode polarized in an inversion region. In Fig S5 the calculated curves from the fully ionized model are shown for the experimental curves of Fig. 5 in the text.

**Fig. S4**



**Fig. S5**



## 6. Debye length of Si and InP

An estimation of the Debye length uses the formula:

$$\lambda = \frac{h}{\sqrt{2\pi m^* kT}}$$

eqn S8

Where  $h$  is Planck's constant,  $m^*$  is the carrier effective mass. For Si with  $m^*$  near  $m_e$ , this results in 1.4 nm and for n-InP and an  $m^*$  of  $.08 m_e$  the length is 5 nm.