

# Supplementary Information to Numerical Calculations of Space Charge Layer Effects in Nanocrystalline Ceia. Part I: Comparison with the Analytical Models and Derivation of Improved Analytical Solutions

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## S1 Poisson-Equation

In one dimension, the Poisson-equation can be derived as follows (please refer to Table 1 for the definition of the different quantities):

$$\frac{dE}{dx} = \frac{\rho}{\varepsilon_r \varepsilon_0} \quad \{\text{S-1}\}$$

$$E = -\frac{d\Phi}{dx} \quad \{\text{S-2}\}$$

$$\frac{d^2\Phi}{dx^2} = -\frac{\rho}{\varepsilon_r \varepsilon_0}. \quad \{\text{S-3}\}$$

The charge density  $\rho$  is a function of the charge carrier concentrations, which are determined by the concentrations of both the mobile and the immobile species (these concentrations depend on a number of different factors such as dopant concentration, temperature, oxygen partial pressure). For a material with  $N_M$  types of mobile and  $N_{IM}$  types of immobile charge carriers, one can write:

$$\rho = e \cdot \left( \sum_{i=1}^{N_M} (z_i c_i) + \sum_{j=1}^{N_{IM}} (z_{IM,j} c_{IM,j}) \right), \quad \{\text{S-4}\}$$

where, in the space charge layer (SCL)

$$c_i = c_{i,\infty} \cdot e^{-\frac{z_i e}{k_B T} \Phi} \quad \{\text{S-5}\}$$

holds. We can define the second term in the parenthesis as

$$\rho_{IM} = e \cdot \sum_{j=1}^{N_{IM}} (z_{IM,j} c_{IM,j}). \quad \{\text{S-6}\}$$

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Here, we assume the profile of the immobile charge carriers to be flat while it changes for the mobile charge carriers due to the electrical potential.

### S1.1 Analytical solutions

Eq. {S-3} to {S-6} result in the following differential equation:

$$\frac{d^2\Phi}{dx^2} = -\frac{e}{\epsilon_r\epsilon_0} \left( \sum_{i=1}^{N_M} \left( z_i c_{i,\infty} e^{-\frac{z_i e}{k_B T} \Phi} \right) + \rho_{IM} \right). \quad \{S-7\}$$

Notably, eq. {S-7} can be analytically solved for 2 ideal cases only.<sup>1</sup>

(1) In the first case (Mott-Schottky - MS), the defect chemistry is characterized by an immobile dopant charge carrier and a mobile charge carrier, which is depleted at the SCL. In such a situation, the charge density in the SCL is hence given by the dopant level  $\rho \approx \rho_{IM} = z_{IM} e c_{IM}$ .<sup>II,III</sup>

MS case

$$\frac{d^2\Phi}{dx^2} = -\frac{z_{IM} e c_{IM}}{\epsilon_r\epsilon_0}. \quad \{S-8\}$$

(2) In the second case (Gouy-Chapman - GC), all the charge carriers follow the potential and the SCL defect chemistry is dominated by the enrichment of one them:  $\rho \approx z_{maj} e c_{maj}$ .

GC case

$$\frac{d^2\Phi}{dx^2} = -\frac{z_{maj} e c_{maj,\infty}}{\epsilon_r\epsilon_0} e^{-\frac{z_{maj} e}{k_B T} \Phi}. \quad \{S-9\}$$

Here the index *maj* designates the enriched (majority) charge carrier. The index *depl* is used to designate the depleted charge carrier. Note that both cases are merely approximations for strong depletion and enrichment effects since only then the neglect of the further charge carriers is realistic, and this is the reason why we refer to them as ideal cases.

There is only one exception for which eq. {S-9} can be analytically solved for two charge carriers. This is the so-called symmetrical GC case, which is valid for two intrinsic charge carriers with  $z_{depl} = -z_{maj}$  and  $c_{depl,\infty} = c_{maj,\infty}$ :

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<sup>II</sup>  $z_{IM} (c_{IM})$  is in this case the charge number (bulk concentration) of the either acceptor (subscript  $A'$ ) or donor dopant (subscript  $D^\bullet$ ),  $z_{IM} c_{IM} \equiv z_{A'} c_{A'} + z_{D^\bullet} c_{D^\bullet}$ .

<sup>III</sup> Note that not for all experimental conditions the dopant is immobile. The assumption  $\rho_{IM} = z_{IM} e c_{IM}$  is specifically made for the MS case.

$$\text{symmetrical GC case} \quad \frac{d^2\Phi}{dx^2} = -\frac{e}{\varepsilon_r \varepsilon_0} \left( z_{maj} c_{maj,\infty} e^{-\frac{z_{maj} e}{k_B T} \Phi} - z_{maj} c_{maj,\infty} e^{\frac{z_{maj} e}{k_B T} \Phi} \right). \quad \{S-10\}$$

The solutions of eq. {S-8} to {S-10} are:<sup>IV 1, 2</sup>

$$(1) \text{ MS case:} \quad \Phi = -\frac{z_{IM} e c_{IM}}{2 \varepsilon_r \varepsilon_0} (x - \lambda^*)^2, \quad \lambda^* = \sqrt{-\frac{2 \varepsilon_r \varepsilon_0 \Phi_0}{z_{IM} e c_{IM}}}, \quad x < \lambda^* \quad \{S-11\}$$

$$(2) \text{ GC case:} \quad \Phi = \Phi_0 + \frac{2 k_B T}{z_{maj} e} \ln \left( 1 + \frac{x}{2 \lambda} e^{-\frac{z_{maj} e}{2 k_B T} \Phi_0} \right), \quad \lambda = \sqrt{\frac{\varepsilon_r \varepsilon_0 k_B T}{2 z_{maj}^2 e^2 c_{maj,\infty}}}, \quad x < 2 \lambda \quad \{S-12\}$$

$$(3) \text{ symmetrical GC case:} \quad \Phi = -\frac{2 k_B T}{z_i e} \ln \left( \frac{1 + g_i \cdot e^{-\frac{x}{\lambda}}}{1 - g_i \cdot e^{-\frac{x}{\lambda}}} \right), \quad g_i = \frac{e^{-\frac{z_i e}{2 k_B T} \Phi_0} - 1}{e^{-\frac{z_i e}{2 k_B T} \Phi_0} + 1} \quad \{S-13\}^V$$

The concentration profiles are obtained by inserting eq. {S-11}-{S-13} in eq. {S-5}. While the SCL profiles are continuous and have no fixed length, the quantities  $\lambda^*$  (screening length in the MS case) and  $2\lambda$  ( $\lambda$  is the Debye length) roughly correspond to the extent of the SCL. This means that at  $x = \lambda^*$  (or  $x = 2\lambda$ ) the potential becomes equal to zero (or extremely small). Both cases (MS and GC) have in common that the extent of the SCL decreases with increasing bulk concentrations. However, the shape of the SCL varies considerably between the MS and GC case.

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<sup>IV</sup> Under the boundary conditions  $\Phi_{x=\lambda^*} = 0$  for the MS case,  $\lim_{x \rightarrow +\infty} (\Phi) = \Phi_\infty = 0$  for the symmetrical GC case and  $\Phi_{x=0} = \Phi_0$  for all cases

<sup>V</sup>  $g_i$ : degree of influence of an arbitrary CC  $i$  (symmetrical GC case)

## S2 Numerical Solutions

For the numerical solution of the Poisson-equation it is necessary to determine the strength of the electric field  $E$ . This can be done by integrating eq. {S-3} with semi-infinite boundary conditions from an arbitrary coordinate  $x_k$  to  $+\infty$ , an approach also used in semiconductor physics:<sup>3</sup>

$$\frac{d(E^2)}{dx} = \frac{d\left(\left(\frac{d\Phi}{dx}\right)^2\right)}{dx} = 2 \frac{d\Phi}{dx} \frac{d^2\Phi}{dx^2} = -\frac{2\rho}{\varepsilon_r \varepsilon_0} \frac{d\Phi}{dx} \quad \text{{S-14}}$$

$$\lim_{x \rightarrow +\infty} (E^2) - E_{x_k}^2 = \frac{-2}{\varepsilon_r \varepsilon_0} \int_{x_k}^{+\infty} \rho \cdot \frac{d\Phi}{dx} dx = \frac{-2}{\varepsilon_r \varepsilon_0} \int_{\Phi_{x_k}}^{\lim_{x \rightarrow +\infty} \Phi} \rho \cdot d\Phi \quad \text{{S-15}}$$

The upper integration limit of  $+\infty$  means that the integration is continued until it reaches the bulk of the material<sup>VI</sup>. In the bulk the electric field and potential vanishes:

$$\lim_{x \rightarrow +\infty} (E^2) = 0, \quad \lim_{x \rightarrow +\infty} (\Phi) = 0 \quad \text{{S-16}}$$

$$E_{x_k} = \text{sgn}(\Phi_{x_k}) \cdot \sqrt{\frac{2k_B T}{\varepsilon_r \varepsilon_0} \left( \sum_{i=1}^{N_M} (c_{i,x_k} - c_{i,\infty}) - \frac{\rho_{IM}}{k_B T} \Phi_{x_k} \right)}. \quad \text{{S-17}}^{\text{VII}}$$

The last relationship (eq. {S-17}) is of great importance. Firstly, it is valid for arbitrary  $x$  coordinates and thus for every position within the SCL. Secondly, for  $x_0 = 0$  it gives a direct analytical relationship between the space charge potential at the boundary  $\Phi_0$ , the corresponding electric field  $E_0$ , and hence the accumulated 2-dimensional charge density of the SCL  $\Sigma_{SCL}$ :

$$E_0 = \text{sgn}(\Phi_0) \cdot \sqrt{\frac{2k_B T}{\varepsilon_r \varepsilon_0} \left( \sum_{i=1}^{N_M} (c_{i,0} - c_{i,\infty}) - \frac{\rho_{IM}}{k_B T} \Phi_0 \right)} \quad \text{{S-18}}$$

$$\Sigma_{SCL} = \int_0^{+\infty} \rho \cdot dx = -\varepsilon_r \varepsilon_0 E_0. \quad \text{{S-19}}$$

The key aspect here is that eq. {S-18} is deduced without making use of any approximation (such as for example the restriction of considering only large accumulation or depletion effects), which instead is assumed for the determination of the usual analytical solutions of the SCL profile (e.g. see section 1.1 and ref. 4). Notably, in some cases, eq. {S-18} and {S-19} allow for the calculation of conductivity

<sup>VI</sup> This is valid for the case considered here, namely a grain size significantly larger than the extension of the SCL.

<sup>VII</sup>  $\text{sgn}(\Phi_0) = -1$  for  $\Phi_0 < 0$  and  $\text{sgn}(\Phi_0) = +1$  for  $\Phi_0 > 0$ .

changes analytically (i.e. without using the numerical solution discussed in the following), without being restricted to large effects and without the necessity to solve the SCL profile<sup>VIII</sup>.

The numerical calculation of the SCL profile is then performed using the following input parameters: the charge carrier bulk concentrations  $c_{i,\infty}$ , their charge numbers  $z_i$ , the relative permittivity  $\epsilon_r$ , the temperature  $T$ , the space charge potential  $\Phi_0$ <sup>IX</sup> and the number of calculation steps  $N_{steps}$ <sup>X</sup>.

At  $x_0 = 0$ , the concentrations  $c_{i,0}$ , the charge density  $\rho_0$ , and the electric field  $E_0$  are calculated using eq. {S-5}, {S-4} and {S-18} respectively. Subsequently, the  $x$  coordinate is increased by a certain value  $\Delta x$ :

$$x_k = x_{k-1} + \Delta x_k \quad \text{XI} \quad \{S-20\}$$

The potential at the new  $x + \Delta x$  coordinate is calculated according to a Taylor approximation of degree three (see. eq. {S-2} and {S-3}):

$$\Phi_{x_k} \approx \Phi_{x_{k-1}} + \Delta x_k \frac{d\Phi}{dx} + \frac{\Delta x_k^2}{2} \frac{d^2\Phi}{dx^2} + \frac{\Delta x_k^3}{6} \frac{d^3\Phi}{dx^3} \quad \{S-21\}$$

$$\Delta \rho \equiv \rho_{x_{k-1}} - \rho_{x_{k-2}} \approx \frac{d\rho}{dx} \cdot \Delta x_k = -\epsilon_r \epsilon_0 \frac{d^3\Phi}{dx^3} \cdot \Delta x_k \quad \{S-22\}^{XII}$$

From this, it follows

$$\Phi_{x_k} \approx \Phi_{x_{k-1}} - \Delta x_k \cdot E_{x_{k-1}} - \frac{\Delta x_k^2}{2\epsilon_r \epsilon_0} \left( \rho_{x_{k-1}} + \frac{\Delta \rho}{3} \right). \quad \{S-23\}$$

At the end of this step the concentration, charge density and electric field values are calculated at  $x_k$ . For the following step,  $k$  is increased by one and the operation described above is repeated yielding the determination of (i)  $\Delta x_k$ ,  $x_k$  and  $\Phi_{x_k}$ , then (ii)  $c_{i,x_k}$ , and (iii)  $\rho_{x_k}$ , and finally (iv)  $E_{x_k}$ . This procedure is carried out until  $k$  reaches the total number of calculation steps  $N_{steps}$  defined at the beginning. To utilize the numerical algorithm described here, a home built software was developed using the C# programming language.

<sup>VIII</sup> As an example for a material with one mobile charge carrier (and one immobile charge carrier for charge compensation) that is enriched at the SCL the number of excess charge carriers and, hence, the conductivity increase at parallel boundaries can easily be computed with eq. {S-18} and {S-19} also for arbitrarily small potentials.

<sup>IX</sup> Instead of  $\Phi_0$  it is also possible to give  $\Sigma_{SCL}$  or  $E_0$  as start parameters. In this case  $\Phi_0$  can be calculated by numerically solving eq. {S-18} and {S-5}.

<sup>X</sup> For the simulations discussed here values for  $N_{steps}$  between  $10^3$  and  $10^7$  were used.

<sup>XI</sup>  $k$  being the calculation step, which ranges from 1 to  $N_{steps}$  and increases by unity at each step.

<sup>XII</sup> For the first step ( $k = 1$ )  $\Delta \rho$  is set zero.

**Table 1** Description of the constants and variables used here.

| Physical Constants         | Description                                                                                                          | First appearance in equation |
|----------------------------|----------------------------------------------------------------------------------------------------------------------|------------------------------|
| $\epsilon_0$               | vacuum permittivity ( $8.85418781762 \cdot 10^{-12}$ F/m)                                                            | {S-1}                        |
| $e$                        | elementary charge ( $1.60217648 \cdot 10^{-19}$ C)                                                                   | {S-4}                        |
| $k_B$                      | Boltzmann constant ( $1.380648 \cdot 10^{-23}$ J/K)                                                                  | {S-5}                        |
| <b>Variables</b>           |                                                                                                                      |                              |
| $b, b'$                    | coefficient of the reduction of $\phi$ in each calculation step (at the second half of the calculation)              | {S-27}                       |
| $c_A$                      | concentration of the immobile acceptor dopant                                                                        | Footnote II                  |
| $c_D$                      | concentration of the immobile donor dopant                                                                           | Footnote II                  |
| $c_{depl,\infty}$          | bulk concentration of the depleted charge carrier                                                                    | Section S1.1                 |
| $c_{end}/c_\infty$         | relative concentration of the charge carrier with $z_{\max}$ at the last calculation step (at $x_{N_{Steps}}$ )      | {S-26}                       |
| $c_{i,\infty}$             | bulk concentration of mobile charge carrier $i$                                                                      | {S-5}                        |
| $c_i, c_{i,x}$             | concentration of mobile charge carrier $i$ (at coordinate $x$ )                                                      | {S-4}                        |
| $c_{IM,j}$                 | bulk concentration of immobile charge carrier $j$                                                                    | {S-4}                        |
| $c_{maj,\infty}$           | bulk concentration of the majority charge carrier                                                                    | {S-9}                        |
| $d$                        | grain size                                                                                                           | {S-43}                       |
| $d_L$                      | individual layer thickness                                                                                           | {S-53}                       |
| $d_{TF}$                   | thin film thickness                                                                                                  | {S-57}                       |
| $E, E_x$                   | electric field (at coordinate $x$ )                                                                                  | {S-1}                        |
| $i$                        | counter variable for mobile charge carriers                                                                          | {S-4}                        |
| $j$                        | counter variable for immobile charge carriers                                                                        | {S-4}                        |
| $k$                        | counter variable for calculation steps                                                                               | {S-15}                       |
| $\ell_{i,SCL}^{\parallel}$ | length of the SCL in parallel alignment concerning charge carrier $i$                                                | {S-59}                       |
| $\ell_{i,SCL}^{\perp}$     | length of the SCL in perpendicular alignment concerning charge carrier $i$                                           | {S-61}                       |
| $\ell_{SCL}$               | combined length of the SCL                                                                                           | {S-62}                       |
| $L_1, L_2, L_3$            | sample dimensions                                                                                                    | {S-35}                       |
| $N_{IM}$                   | number of immobile charge carriers                                                                                   | {S-4}                        |
| $N_M$                      | number of mobile charge carriers                                                                                     | {S-4}                        |
| $N_{SCL}^{\parallel}$      | number of parallel aligned SCL in one grain (or layer)                                                               | {S-43}                       |
| $N_{SCL}^{\perp}$          | number of perpendicular aligned SCL in one grain (or layer)                                                          | {S-45}                       |
| $N_{Steps}$                | number of calculation steps                                                                                          | {S-24}                       |
| $r$                        | criterion to define the SCL length (percentage of charge $\Sigma_i$ (or $\Omega_i$ ) inside a SCL of certain length) | {S-59}                       |
| $R_m$                      | DC resistance of a sample (including bulk and boundary contributions)                                                | {S-35}                       |
| $s_i^{\parallel}$          | relative conductivity of charge carrier $i$ in a sample containing only parallel boundaries                          | {S-39}                       |
| $s_i^{\perp}$              | relative conductivity of charge carrier $i$ in a sample containing only perpendicular boundaries                     | {S-40}                       |
| $s_{i,m}$                  | relative conductivity of charge carrier $i$ (including parallel and perpendicular boundary contributions)            | {S-41}                       |
| $T$                        | temperature                                                                                                          | {S-5}                        |
| $u_i$                      | mobility of charge carrier $i$                                                                                       | {S-36}                       |
| $x, x_k$                   | distance from boundary (at calculation step $k$ )                                                                    | {S-1}                        |
| $x_B$                      | coordinate where $E$ becomes zero (for overlapping SCLs)                                                             | {S-67}                       |

|                                  |                                                                                                                             |              |
|----------------------------------|-----------------------------------------------------------------------------------------------------------------------------|--------------|
| $x_\rho$                         | coordinate of charge balance point                                                                                          | {S-63}       |
| $z_A$                            | charge number of the immobile acceptor dopant                                                                               | Footnote II  |
| $z_D$                            | charge number of the immobile donor dopant                                                                                  | Footnote II  |
| $z_{depl}$                       | charge number of the depleted charge carrier                                                                                | Section S1.1 |
| $z_i$                            | charge number of mobile charge carrier $i$                                                                                  | {S-4}        |
| $z_{IM,i}$                       | charge number of immobile charge carrier $j$                                                                                | {S-4}        |
| $z_{maj}$                        | charge number of the majority charge carrier                                                                                | {S-9}        |
| $z_{max}$                        | maximum value of all $ z_i $                                                                                                | {S-26}       |
| $\alpha$                         | SCL steepness                                                                                                               | {S-64}       |
| $\Delta\rho$                     | (3-dimensional) charge density difference                                                                                   | {S-22}       |
| $\Delta\sigma_{i,m}$             | change in conductivity of charge carrier $i$ due to both parallel and perpendicular boundaries                              | {S-35}       |
| $\Delta\sigma_{i,m}^{\parallel}$ | change in conductivity of charge carrier $i$ due to parallel boundaries                                                     | {S-37}       |
| $\Delta\sigma_{i,m}^{\perp}$     | change in conductivity of charge carrier $i$ due to perpendicular boundaries                                                | {S-38}       |
| $\Delta s_i^{\parallel}$         | change in relative conductivity of charge carrier $i$ due to parallel boundaries                                            | {S-39}       |
| $\Delta s_i^{\perp}$             | change in relative conductivity of charge carrier $i$ due to perpendicular boundaries                                       | {S-40}       |
| $\Delta s_{i,m}$                 | change in relative conductivity of charge carrier $i$ due to both parallel and perpendicular boundaries                     | {S-41}       |
| $\Delta\Sigma_{Step}$            | part of the SCL charge that is processed in one calculation step (at the first half of the calculation)                     | {S-24}       |
| $\Delta X_k$                     | length interval (at calculation step $k$ )                                                                                  | {S-20}       |
| $\epsilon_r$                     | relative permittivity                                                                                                       | {S-1}        |
| $\lambda$                        | Debye length                                                                                                                | {S-65}       |
| $\lambda^*$                      | screening length in the MS case                                                                                             | {S-11}       |
| $\mathcal{G}_i$                  | “influence parameter” of the SCL for charge carrier $i$                                                                     | {S-65}       |
| $\sigma_{i,\infty}$              | bulk conductivity of charge carrier $i$                                                                                     | {S-35}       |
| $\sigma_{i,m}$                   | total effectively measured conductivity of charge carrier $i$ (including parallel and perpendicular boundary contributions) | {S-35}       |
| $\sigma_{i,m}^{\perp}$           | total effectively measured conductivity of charge carrier $i$ in a sample containing only perpendicular boundaries          | {S-38}       |
| $\sigma_{i,m}^{\parallel}$       | total effectively measured conductivity of charge carrier $i$ in a sample containing only parallel boundaries               | {S-37}       |
| $\rho, \rho_x$                   | (3-dimensional) charge density (at coordinate $x$ )                                                                         | {S-1}        |
| $\rho_{IM}$                      | charge density contribution of immobile charge carriers                                                                     | {S-6}        |
| $\Sigma_i$                       | charge contribution due to the enrichment (or depletion) of mobile charge carrier $i$                                       | {S-32}       |
| $\Sigma_{SCL}$                   | charge of the SCL                                                                                                           | {S-19}       |
| $\Phi, \Phi_x$                   | electric potential (at coordinate $x$ )                                                                                     | {S-2}        |
| $\Phi_{end}$                     | electric potential at the last calculation step (at $x_{N_{Steps}}$ )                                                       | {S-26}       |
| $\Phi_d$                         | SCL potential at the second boundary in case of an asymmetrically overlapping SCL                                           | Footnote XXI |
| $\Omega_i$                       | reduced resistance change of the SCL in perpendicular direction concerning the transport of mobile charge carrier $i$       | {S-34}       |

### S2.1 Selection of the $\Delta x$ intervals

Special care has to be taken for the selection of the interval  $\Delta x$ , since the accuracy of the numerical calculation strongly depends on this choice. Notably, the simple option of using a constant value of  $\Delta x$  throughout the whole SCL leads to a rather large inaccuracy, since the often extremely steep slopes of the SCL concentration (and charge density) profiles close to the boundary rather require the use of smaller intervals in this region.

This can be achieved by using  $x$ -dependent values of  $\Delta x$ , which vary as a function of the accumulated charge. Using eq. {S-18} and {S-19} the accumulated charge of the whole SCL  $\Sigma_{SCL}$  is calculated and divided in  $N_{Steps}$  equally large quantities  $\Delta \Sigma_{Step}$ . The corresponding  $\Delta x$  intervals can then be easily determined using the local charge density:

$$\Delta \Sigma_{Step} = \frac{\Sigma_{SCL}}{N_{Steps}} \quad \text{{S-24}}$$

$$\Delta x_k = \left| \frac{\Delta \Sigma_{Step}}{\rho_{x_{k-1}}} \right|. \quad \text{{S-25}}$$

This was found to be very effective for a precise determination of the profile close to the boundary. However, a drawback of this approach is given by the fact that for large  $x$  the charge density decreases very fast leading to rather large intervals and thus to an inaccurately calculated SCL extent. Therefore,  $\Delta x$  is calculated in two different manners. For this purpose, a potential  $\Phi_{end}$  is defined. It is the value of  $\Phi$ , for which the concentration of the mobile charge carrier ( $c_{end}$ ) having the largest value of  $|z_i|$  ( $z_{max}$ ) differs only marginally from its bulk value (here arbitrarily chosen as the factor  $10^{-7}$ ):

$$\Phi_{end} = \text{sign}(\Phi_0) \cdot \left| \frac{k_B T}{z_{max} e} \ln \left( \frac{c_{end}}{c_\infty} \right) \right|, \quad \text{with} \quad \frac{c_{end} - c_\infty}{c_\infty} \leq 10^{-7}. \quad \text{{S-26}}$$

Note that the potential  $\Phi_{end}$  is also the value of  $\Phi$ , at which the calculation of the charge carrier profiles within the SCL is concluded. Starting from  $\Phi_{end}$ , the factor  $b$  is determined

$$b = \left( \frac{\Phi_{end}}{\Phi_0} \right)^{\frac{1}{2^{N_{Steps}}}}. \quad \text{{S-27}}$$

At the beginning of the calculation, the  $\Delta x$  values are computed using eq. {S-24} and {S-25}. For small  $x$  values, the small intervals lead to potential changes smaller than  $b$ .

$$\frac{\Phi_k}{\Phi_{k-1}} < b \quad \text{{S-28}}$$

However, after about the half of the calculation steps the criterion {S-28} is not fulfilled anymore. From this point on, the factor is recalculated (see {S-29}) and for each subsequent step the potential is reduced by the coefficient  $b'$  in the following manner

$$b' = \left( \frac{\Phi_{end}}{\Phi_{x_{k-1}}} \right)^{\frac{1}{N_{Steps}-k}} \quad \{S-29\}$$

$$\Phi_k = b' \cdot \Phi_{k-1}. \quad \{S-30\}$$

The interval values are then computed by rearranging eq. {S-23}:

$$\Delta x_k = \frac{\varepsilon_r \varepsilon_0}{\rho_{x_{k-1}} + \frac{\Delta \rho}{3}} \cdot \left( -E_{x_{k-1}} \pm \sqrt{E_{x_{k-1}}^2 - \frac{2}{\varepsilon_r \varepsilon_0} (\Phi_{x_k} - \Phi_{x_{k-1}}) \left( \rho_{x_{k-1}} + \frac{\Delta \rho}{3} \right)} \right). \quad \{S-31\}^{xiii}$$

The so-obtained profiles are not only precise in the region close to the interface but they also span accurately over the full range of the SCL and stop only after the potential becomes so small that concentration variations  $< 10^{-7}$  from the bulk value occur.

## S2.2 Effect of the SCLs on the total conductivity

In the framework of the brick layer model, both parallel and perpendicular SCLs (relative to the direction of the electric transport) contribute to the change of the overall conductivity with respect to the bulk properties. In order to quantify the impact of the SCL on the conductivity, the SCL concentration profiles, calculated as described above, need to be integrated. For the transport along parallel boundaries, the charge contribution  $\Sigma_i$  of the considered defect on the total SCL charge is of relevance:

$$\Sigma_i = z_i e \cdot \int_0^\infty (c_i - c_{i,\infty}) dx \approx z_i e \cdot \sum_{k=1}^{N_{Steps}-1} (c_{i,x_k} - c_{i,\infty}) \cdot \Delta x_k. \quad \{S-32\}$$

As expected the sum of all individual charge contributions  $\Sigma_i$  gives the total SCL charge  $\Sigma_{SCL}$ :

$$\Sigma_{SCL} = \sum_{i=1}^{N_M} (\Sigma_i) \quad \{S-33\}$$

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<sup>xiii</sup> Eq. {S-31} gives two  $\Delta x$  values. Here the smallest non negative solution is the physically rational value.

For the transport across perpendicular boundaries the reciprocal concentrations need to be integrated. In analogy to  $\Sigma_i$ , the variable  $\Omega_i$  can be defined:

$$\Omega_i = \frac{1}{|z_i|e} \cdot \int_0^\infty (c_i^{-1} - c_{i,\infty}^{-1}) dx \approx \frac{1}{|z_i|e} \cdot \sum_{k=1}^{N_{Steps}-1} (c_i^{-1} - c_{i,\infty}^{-1}) \cdot \Delta x_k \quad \{\text{S-34}\}^{\text{XIV}}$$

In general the effectively measured conductivity of a sample  $\sigma_{i,m}$ , corresponding to a measured DC resistance  $R_m$ , can be separated into the bulk conductivity  $\sigma_{i,\infty}$  and a conductivity change due to the boundary effects (both parallel and perpendicular)  $\Delta\sigma_{i,m}$ :

$$\sigma_{i,m} = \frac{L_1}{L_2 L_3} \cdot \frac{1}{R_m} = \sigma_{i,\infty} + \Delta\sigma_{i,m} \quad \{\text{S-35}\}$$

$$\sigma_{i,\infty} = |z_i| e u_i c_{i,\infty} \quad \{\text{S-36}\}$$

In particular for a hypothetical sample only containing one orientation of SCLs (parallel or perpendicular)<sup>XV</sup> the total conductivity is:

$$\sigma_{i,m}^{\parallel} = \sigma_{i,\infty} + \Delta\sigma_{i,m}^{\parallel} \quad \{\text{S-37}\}$$

$$\sigma_{i,m}^{\perp} = \sigma_{i,\infty} + \Delta\sigma_{i,m}^{\perp} \quad \{\text{S-38}\}$$

Here the conductivity changes due to parallel or perpendicular SCLs are denoted as  $\Delta\sigma_{i,m}^{\parallel}$  and  $\Delta\sigma_{i,m}^{\perp}$ . In order to quantify the effect of SCLs on the total conductivity for many materials with different  $\sigma_{i,\infty}$  it is convenient to consider the relative conductivities  $s_i$  (and relative conductivity changes  $\Delta s_i$ ) which are normalized with respect to  $\sigma_{i,\infty}$ :

$$s_i^{\parallel} = \frac{\sigma_{i,m}^{\parallel}}{\sigma_{i,\infty}} = \Delta s_i^{\parallel} + 1 \quad \{\text{S-39}\}$$

$$s_i^{\perp} = \frac{\sigma_{i,m}^{\perp}}{\sigma_{i,\infty}} = \Delta s_i^{\perp} + 1 \quad \{\text{S-40}\}$$

$$s_{i,m} = \frac{\sigma_{i,m}}{\sigma_{i,\infty}} = \Delta s_{i,m} + 1 \quad \{\text{S-41}\}$$

For the polycrystalline samples treated here, with both parallel and perpendicular SCLs and a grain size much larger than the size of the SCLs (and thus with no SCL overlap), the relative conductivity  $s_{i,m}$  can be expressed as the product of  $s_i^{\parallel}$  and  $s_i^{\perp}$ :

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<sup>XIV</sup> Note that  $\Omega_i$  is defined to be always positive for a depletion and negative for an enrichment of charge carriers, whereas  $\Sigma_i$  is the accumulated charge. Therefore the sign of  $\Sigma_i$  depends not only on whether the charge carrier is enriched or depleted but also on the sign of its charge number  $z_i$ .

<sup>XV</sup> Examples are thin film multilayered structures.

$$s_{i,m} = s_i^{\parallel} \cdot s_i^{\perp} \quad \{S-42\}$$

For the calculation of the  $s_i^{\parallel}$  and  $s_i^{\perp}$  values here a brick layer model is used. Hereby the grains are assumed to be shaped cubically with an edge of length  $d$ . In this model for each single grain (cube with six faces) there are four SCLs parallel to the transport direction and two perpendicular SCLs. Since for each parallel and perpendicular SCL, the conductivity change (i.e.  $\sigma_{i,m}^{\parallel} - \sigma_{i,\infty}$  and  $(\sigma_i^{\perp})^{-1} - \sigma_{i,\infty}^{-1}$ ) is  $u_i \cdot \Sigma_i/d$  and  $u_i^{-1} \cdot \Omega_i/d$ , respectively, eq. {S-43}-{S-46} are valid. Table 2 lists the corresponding relationships for polycrystalline pellets and other sample geometries like thin films.<sup>xvi</sup>

$$\sigma_{i,m}^{\parallel} - \sigma_{i,\infty} = \frac{N_{SCL}^{\parallel} \Sigma_i}{d} \cdot u_i \quad \{S-43\}$$

$$s_i^{\parallel} = \frac{\sigma_{i,m}^{\parallel}}{\sigma_{i,\infty}} = \frac{N_{SCL}^{\parallel}}{d} \cdot \frac{\Sigma_i}{z_i e c_{i,\infty}} + 1 \quad \{S-44\}$$

$$(\sigma_i^{\perp})^{-1} - \sigma_{i,\infty}^{-1} = \frac{N_{SCL}^{\perp} \Omega_i}{d} \cdot u_i^{-1} \quad \{S-45\}$$

$$s_i^{\perp} = \frac{\sigma_i^{\perp}}{\sigma_{i,\infty}} = \frac{d}{N_{SCL}^{\perp} \Omega_i \cdot |z_i| e c_{i,\infty} + d} \quad \{S-46\}$$

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<sup>xvi</sup> By using the parallel and perpendicular contributions (see eq. {S-42}), the total conductivity change can be determined. Please note that while eq. {S-42} is generally valid for non-overlapping SCLs, in the most cases it is either the parallel part (for an enrichment of charge carriers) or the perpendicular contribution (for a depletion of charge carriers) that dominates. This follows directly from eq. {S-44} and {S-46}. For a depletion of charge carriers,  $|\Sigma_i|$  cannot become larger than  $|z_i| e c_{i,\infty} \cdot \ell_{SCL}$  (see eq. {S-59}) with  $\ell_{SCL}$  being the extent of the SCL. Hence, for  $\ell_{SCL} \ll d$  the absolute value of  $s_i^{\parallel}$  (eq. {S-44}) becomes  $\approx 1$  in this case. For an enrichment of charge carriers the situation is analogous. Here  $|\Omega_i|$  cannot become larger than  $(|z_i| e c_{i,\infty})^{-1} \cdot \ell_{SCL}$  leading again to  $s_i^{\perp} \approx 1$  in eq. {S-46}. However, although the parallel (perpendicular) contribution is less important for a charge carrier depletion (enrichment), still in some cases also the conductivity changes due to such a more subtle effect are important (e.g. for special geometries, such as multilayers, in which the constituting films are very thin).

**Table 2** The brick layer model applied to different sample geometries.

| Geometry                                                                                                                       | $s_i^{\parallel} =$                                                     | $s_i^{\perp} =$                                           |
|--------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------|-----------------------------------------------------------|
| pellet                                                                                                                         | $\frac{4}{d} \cdot \frac{\Sigma_i}{z_i e c_{i,\infty}} + 1$ {S-47}      | $\frac{d}{2\Omega_i  z_i  e c_{i,\infty} + d}$ {S-48}     |
| thin film with polycrystalline, columnar structure, measurement parallel to the substrate                                      | $\frac{2}{d} \cdot \frac{\Sigma_i}{z_i e c_{i,\infty}} + 1$ {S-49}      | $\frac{d}{2\Omega_i  z_i  e c_{i,\infty} + d}$ {S-50}     |
| thin film with polycrystalline, columnar structure, measurement perpendicular to the substrate                                 | $\frac{4}{d} \cdot \frac{\Sigma_i}{z_i e c_{i,\infty}} + 1$ {S-51}      | 1 {S-52}                                                  |
| thin film with epitaxial multilayers, measurement parallel to the substrate                                                    | $\frac{2}{d_L} \cdot \frac{\Sigma_i}{z_i e c_{i,\infty}} + 1$ {S-53}    | 1 {S-54}                                                  |
| thin film with epitaxial multilayers, measurement perpendicular to the substrate                                               | 1 {S-55}                                                                | $\frac{d_L}{2\Omega_i  z_i  e c_{i,\infty} + d_L}$ {S-56} |
| epitaxial thin film with a SCL at the film substrate interface (or at the film surface), measurement parallel to the substrate | $\frac{1}{d_{TF}} \cdot \frac{\Sigma_i}{z_i e c_{i,\infty}} + 1$ {S-57} | 1 {S-58}                                                  |

### S2.3 Other properties of the SCL

In addition to the possibility of investigating the SCL effects without the use of any approximation, one should not overlook the fact that this numerical algorithm allows for the determination of the entire SCL profile accurately. This allows for a further and accurate study of the properties of such profiles. In the following, some parameters are introduced to describe some of the profile's properties.

First let us consider the extent of the SCL. Since the SCL profile itself is continuous there is no “natural” border indicating the end of it. Therefore, various definitions of the SCL size are possible. Here, the impact on the charge accumulation (or depletion) is used to quantify the extent: As shown in eq. {S-32} for the determination of the enriched (or depleted) charge of a certain charge carrier the profile is integrated from 0 to  $+\infty$ . The size of the SCL  $\ell_{i,SCL}^{\parallel}$  can be defined as the upper limit of integration that is required to reach a certain fraction  $r$  of the charge  $\Sigma_i^{XVII}$ :

$$r \cdot \Sigma_i = r \cdot z_i e \cdot \int_0^{\infty} (c_i - c_{i,\infty}) dx = z_i e \cdot \int_0^{\ell_{i,SCL}^{\parallel}} (c_i - c_{i,\infty}) dx \quad \text{{S-59}}$$

$$0 < r < 1 \quad \text{{S-60}}$$

<sup>XVII</sup> In the present study usually  $r = 0.99$  was used.

For perpendicularly aligned SCLs it is the integration of  $c_i^{-1}$  that is crucial. Here an analogous variable  $\ell_{i,SCL}^\perp$  can be introduced:

$$r \cdot \Omega_i = \frac{r}{|z_i|e} \cdot \int_0^\infty (c_i^{-1} - c_{i,\infty}^{-1}) dx = \frac{1}{|z_i|e} \cdot \int_0^{\ell_{i,SCL}^\perp} (c_i^{-1} - c_{i,\infty}^{-1}) dx \quad \{S-61\}$$

The values of the so-calculated SCL extent vary with the chosen charge carrier and SCL orientation<sup>XVIII</sup>. The obtained data is much more situation-dependent, and thus versatile, than a uniform SCL size, such as the effective SCL sizes used in the most analytical approximations<sup>XIX</sup>. However, it is still helpful to define an extent variable that characterizes the SCL independent of the considered alignment and charge carrier. A simple way to do so is to take the maximum of all individually calculated  $\ell_{i,SCL}^\parallel$  and  $\ell_{i,SCL}^\perp$  values. In this way the conditions defined in {S-59} and {S-61} are reached upon the integration for all charge carriers.

$$\ell_{SCL} = \max(\ell_{1,SCL}^\parallel, \ell_{1,SCL}^\perp, \ell_{2,SCL}^\parallel, \ell_{2,SCL}^\perp, \dots, \ell_{i,SCL}^\parallel, \ell_{i,SCL}^\perp, \dots, \ell_{N_M,SCL}^\parallel, \ell_{N_M,SCL}^\perp) \quad \{S-62\}$$

Other useful parameters are the charge balance point  $x_\rho$  and the SCL profile steepness  $\alpha$ :

$$x_\rho = \frac{\int_0^{+\infty} x \rho \cdot dx}{\int_0^{+\infty} \rho \cdot dx} \approx \frac{\sum_{k=1}^{N_{Steps}-1} (x_k \cdot \rho_{x_k})}{\Sigma_{SCL}} \quad \{S-63\}$$

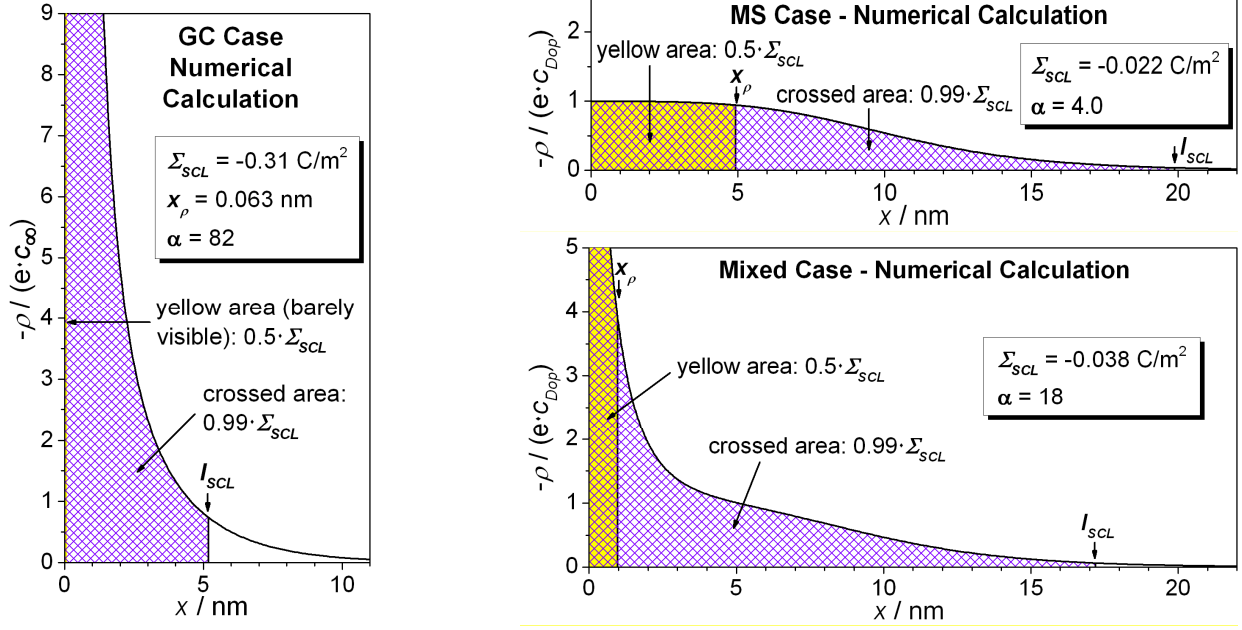
$$\alpha = \ell_{SCL} / x_\rho \quad \{S-64\}$$

In particular,  $\alpha$  is very informative since it corresponds to the steepness of the SCL profile (in a linear plot). It is worth noting that in a MS case, for which (in an extreme approximation) the mobile charge carriers are depleted so strongly that  $\rho \approx \rho_{IM}$  throughout the SCL,  $\alpha$  approaches its minimum value of 2. In a GC case instead (enrichment of charge carriers),  $\alpha$  can reach very high values depending on how steeply the concentration is increased when approaching the boundary. Fig. S1 illustrates such variations for different charge density profiles.

<sup>XVIII</sup> While testing the algorithm it was found that these differences often can be larger than even one order of magnitude.

<sup>XIX</sup> As an example a SCL in acceptor doped CeO<sub>2</sub> with a depletion of oxygen vacancies at the SCL can be taken. Here in the most cases the relevant SCL size concerning the perpendicular SCLs  $\ell_{V_O^{\bullet},SCL}^\perp$  will be much smaller than the one of the

parallel SCLs  $\ell_{V_O^{\bullet},SCL}^\parallel$ . This is of importance for the lower limit of the grain size (or layer thickness) for which SCLs can still be treated as non overlapping: For instance for thin film multilayer structures measured in a perpendicular geometry the SCLs can be treated as non overlapping also for very small layer thicknesses, whereas the layers need to be larger to apply the same assumption if the measurement geometry is in-plane (parallel).



**Fig. S1** Extent of the space charge length, balance point  $x_\rho$  and steepness  $\alpha$  for three different situations namely Gouy-Chapman, Mott-Schottky and a mixed case. At the charge balance point  $x_\rho$  the area below the charge density profile is divided in two equal parts of  $0.5 \cdot \Sigma_{SCL}$ . On contrast to the MS case in the GC case the majority of the charge is located very close to the interface. This corresponds to a charge balance point extremely close to zero and results in a large value of  $\alpha$ . Parameters used here:  $\epsilon_r = 26$ ,  $\theta = 700^\circ\text{C}$ ,  $z_{maj} = z_{IM} = -z_{depl} = -1$ . For the GC case:  $c_{maj,\infty} = c_{depl,\infty} = 1.25 \cdot 10^{19} \text{ cm}^{-3}$ ,  $c_{IM} = 0$ ; for the MS case:  $c_{depl,\infty} = c_{IM} = 1.25 \cdot 10^{19} \text{ cm}^{-3}$ ; for the mixed case:  $c_{IM} = 1.25 \cdot 10^{19} \text{ cm}^{-3}$ ,  $c_{maj,\infty} = 0.01 \cdot c_{IM}$ ,  $c_{depl,\infty} = 1.01 \cdot c_{IM}$ .

### S3 Accuracy of the Numerical Algorithm

It is helpful to check the accuracy of the profiles computed numerically by comparing it with the outcomes of the exact analytical solutions. While nearly all analytical solutions rely on approximations (such as a very strong enrichment or depletion), there is only one case for which the SCL profile can be given analytically without simplifying assumptions (see section S1.1): The symmetric GC case (two mobile charge carriers with  $z_1 = -z_2$  and  $\rho_{Dop} = 0$ . Here the effect on the conductivity is given by (see e.g. ref [1, 2]):

$$\Sigma_i = 4\lambda \cdot z_i e c_{i,\infty} \frac{g_i}{1 - g_i}, \quad s_i^{\parallel} = \frac{4N_{SCL}^{\parallel} \lambda}{d} \frac{g_i}{1 - g_i} + 1 \quad \{\text{S-65}\}$$

$$\Omega_i = \frac{-4\lambda}{|z_i| e c_{i,\infty}} \frac{g_i}{1 + g_i}, \quad s_i^{\perp} = \frac{d}{-4N_{SCL}^{\perp} \lambda \frac{g_i}{1 + g_i} + d} \quad \{\text{S-66}\}$$

For the definition of  $\lambda$  and  $\vartheta_i$  see eq. {S-12} and {S-13}. The so-obtained  $\Sigma_i$  and  $\Omega_i$  values were compared with the results of the numerical algorithm for several different input parameters. The differences were found to be very small: For small and moderate potentials the observed relative differences were only in the range between  $10^{-10}$  % and  $10^{-3}$  %; whereas even for difficultly calculable, very steep profiles with unrealistically high potentials (such as 5 V) they were smaller as 0.1 %.<sup>xx</sup>

Note that while the error of the numerical calculation of the profiles was found to be very small, this outcome does not include the systematical deviation made by the assumption of the brick layer model, which depends on the microstructure of the actual sample: For well-defined systems, such as thin film multilayers, this approximation is very good, whereas for other samples, such as pellets with non-uniformly shaped grains, it might lack accuracy.

#### 4 One Dimensional Overlapping SCL Profiles

Using the algorithm described above with only a few changes it is also possible to calculate one-dimensional SCL profiles that overlap. This is for instance of relevance for SCLs in thin film multilayer structures with very small layer thicknesses  $d_L$  (i.e.  $d_L \leq \ell_{SCL}$ ). For the symmetrically overlapping SCLs ( $\Phi_0 = \Phi_{d_L}$ ) the position where the electric field vanishes  $x_B$  is in the middle of the layer ( $x_B = d_L/2$ ). However, the potential  $\Phi_{x_B}$  is still different from zero. The integration of eq. {S-14} between an arbitrary position  $x_k$  and  $x_B$  results:

$$E_{x_B}^2 - E_{x_k}^2 = \frac{-2}{\epsilon_r \epsilon_0} \int_{\Phi_{x_k}}^{\Phi_{x_B}} \rho \cdot d\Phi, \quad \text{{S-67}}$$

where

$$E_{x_B} = 0 \quad \text{{S-68}}$$

and

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<sup>xx</sup> This data was calculated for a number of calculation steps of  $N_{Steps} = 10^6$ . Here the calculation time for one profile is about one second using a nowadays personal computer. For smaller values (e.g.  $N_{Steps} = 10^3$ ) the relative differences are between  $10^{-4}$  % to 0.01 % for small and moderate potentials and also less than 0.1 % for very large potentials.

$$E_{x_k} = \text{sgn}(\Phi_{x_k}) \cdot \sqrt{\frac{2k_B T}{\varepsilon_r \varepsilon_0} \left( \sum_{i=1}^{N_M} (c_{i,x_k} - c_{i,x_B}) + \frac{\rho_D}{k_B T} (\Phi_{x_B} - \Phi_{x_k}) \right)}. \quad \{\text{S-69}\}$$

Eq. {S-69} contains  $\Phi_{x_B}$  as an additional parameter. One should note, however, that at the beginning of the calculation  $\Phi_{x_B}$  is usually unknown while the length  $d_L/2$  is the input parameter. Numerically, this is solved by firstly calculating the profile using an arbitrary value of  $\Phi_{x_B}$  ranging between 0 and  $\Phi_0$ . In such a situation, the coordinate  $x_B$ , at which the electric field vanishes, differs from  $d_L/2$ . The profile is thus iteratively computed and at each step the value of  $\Phi_{x_B}$  is refined until the discrepancy between both positions ( $x_B$  and  $d_L/2$ ) becomes insignificantly small.<sup>XXI</sup>

## References

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<sup>XXI</sup> Also for the less common case of asymmetrically overlapping SCLs (with different potentials on both sides of the layer  $\Phi_0 \neq \Phi_d$ ) the calculation is possible if  $\Phi_0$ ,  $\Phi_d$  and  $d$  are known. Since  $x_B$  is unknown in this case ( $x_B \neq d_L/2$ ) a slightly more complex solution is necessary. Here two profiles (one with  $\Phi_0$  and another one with  $\Phi_0' = \Phi_d$ ) are calculated. The potential  $\Phi_{x_B}$  (which is a common value for both profiles) is then refined until the difference of  $x_B + x_B'$  and  $d_L$  becomes negligible.