Mott-Schottky analysis from *C-V* simulations, and Admittance Analysis from *C-f* simulations in SCAPS

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2. SCAPS version and files used in this document

The SCAPS application discussed in this document uses:

- SCAPS version 3.3.06 of September 2017, or more recent.

- The following files:
  - Definition files and all-SCAPS files that must be present in the folder [your SCAPS]\def:
    - ✓ `M-S graded NA and epsilon.def`
    - ✓ `M-S graded NA and epsilon with contact barrier.def`
    - ✓ `M-S 6 layers with uniform epsilon.def`
    - ✓ `simple pn for AS defect.def`
  - Script files that must be present in the folder [your SCAPS]\script:
    - ✓ `width of SCL.script`

3. Mott-Schottky analysis for 'graded cells'

3.1 Mott-Schottky analysis of the most ideal solar cell

Consider an ideal, one-sided Shockley p^+n solar cell, with the junction at $x = 0$. 'One-sided' means that the acceptor doping N_A of the p^+ side is much larger than the donor doping N_D of the n side: $N_A \gg N_D$. Further suppose that all cell properties are 'non-graded' (SCAPS terminology; this means that E_g, χ, N_A, N_D, … do not depend on position x in the cell). And that all assumptions for an 'ideal Shockley diode' are fulfilled (see all text books), in particular here the assumption of 'abrupt depletion': the depletion layer will reside completely in the n-side, extend from $x = 0$ to $x = W$ and it will be 'abrupt': full depletion ($n = 0$) with constant charge density $\rho = +qN_D$ for $0 < x < W$, and neutral bulk ($n = N_D$, $\rho = 0$) for $x > W$. All text books and most semiconductor physics courses calculate the depletion capacitance C_j in this simple case as a function of applied voltage V:

$$C_j(V) = \sqrt{\frac{q\varepsilon_s\varepsilon_0 N_D}{2(V_{bi} - V)}} \tag{1}$$

(V_{bi} is the *built-in voltage* or *diffusion voltage*, the other symbols have their usual meaning). When one measures $C_j(V)$ for reverse (and moderate forward) voltage V, and then makes a graph of $1/C_j^2$ *versus* V (this is called a Mott-Schottky plot), one expects a straight line; the intercept with the V axis is V_{bi}, and from the slope one can deduce the doping density N_D:

$$\frac{1}{C_j^2} = \frac{2}{q\varepsilon_s\varepsilon_0 N_D}(V_{bi} - V) \tag{2}$$

Thus, if the slope of the Mott-Schottky plot is

$$\text{slope} = \frac{\partial}{\partial V}\left(\frac{1}{C_j^2}\right) \tag{3}$$

then the value of N_D follows from

$$N_D = \frac{2}{q\varepsilon_s\varepsilon_0} \cdot \frac{-1}{\text{slope}} \tag{4}$$

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Also, the depletion width W can be deduced from the inverse of the depletion capacitance:

$$C_j(V) = \frac{\varepsilon_s \varepsilon_0}{W(V)} \quad \text{thus} \quad W(V) = \frac{\varepsilon_s \varepsilon_0}{C_j(V)} \tag{5}$$

where the depletion width W (within the same idealisations) is given by

$$W = \sqrt{\frac{2\varepsilon_s \varepsilon_0 (V_{bi} - V)}{qN_A}} \tag{6}$$

The extraction of the depletion width $W(V)$ and of the doping density N_D from a measured $C(V)$ curve is called the 'Mott-Schottky analysis'.

In the rest of the document we will note the position of the depletion layer edge as x_W, and the position of the junction as x_j. In this example, the junction was at x_j=0, and thus $x_W = W$. More generally

$$x_W = x_j + W \quad , \quad \text{the SCL extends towards the right side of the junction}$$
$$x_W = x_j - W \quad , \quad \text{the SCL extends towards the left side of the junction} \tag{7}$$

3.2 Mott-Schottky analysis when the doping density $N_D(x)$ is non-uniform

When we relax the requirement of uniform N_D, and allow for an x-dependent doping density $N_D(x)$, but when all other assumptions of the most ideal case above still hold, in particular that the dielectric constant ε_s is non-graded (does not depend on position x), then the results above should only altered slightly:

- o the depletion width $W(V)$ is still given by the inverse of the capacitance, Eq. (5).
- o the Mott-Schottky plot is no longer a straight line
- o … and thus one cannot speak of <u>the</u> slope, but of the <u>local</u> slope: apply Eq. (3) to all points of the Mott-Schottky plot
- o Eq. (4) still holds locally, thus the local slope of the Mott-Schottky plot yields the local doping density:

$$N_D(W) = \frac{-2}{q\varepsilon_s \varepsilon_0} \cdot \frac{1}{\text{slope}\left[V(W)\right]} \tag{8}$$

where the voltage V and the depletion width W are related by Eq. (5).

The doping density calculated with Eq. (8) is the value at the edge of the depletion layer, thus at $x = x_W$. Though many text books mention the results above, most text books leave it to the user to do the derivations… The C-V analysis or Mott-Schottky (M-S) analysis implemented in SCAPS up to version 3.3.05 of December 2016 is based on Eqs. (5) and (8).

3.3 M-S analysis with non-uniform doping $N_D(x)$ <u>and</u> dielectric constant $\varepsilon_s(x)$

When also the dielectric constant becomes graded, that is when $\varepsilon_s(x)$ depends on position x, things becomes more complicated. I have not found text books that treat this case, but I have not searched thoroughly. Fortunately, the mathematical manipulations needed to derive Eqs.

(5) and (8) in the constant ε case can be generalised without too hard difficulties to cover also the $\varepsilon(x)$ case. The result is:

- Eq. (8) for doping density $N_D(x_W)$ at the depletion edge $x = x_W$ still holds, when the constant ε_s is replaced with its value $\varepsilon_s(x_W)$ at the depletion edge:

$$N_D\left(x_W\right) = \frac{-1}{\text{slope}\left[V\left(W\right)\right]} \cdot \frac{2}{q\varepsilon_0\varepsilon_s\left(x_W\right)} \tag{9}$$

- The relation between capacitance and depletion width, thus Eq. (5), should be replaced with:

$$C_j = \frac{\varepsilon_0}{\int_{x_j}^{x_W} \dfrac{dx}{\varepsilon_s\left(x\right)}} \quad \text{SCL at the right side of junction}$$

$$C_j = \frac{\varepsilon_0}{\int_{x_W}^{x_j} \dfrac{dx}{\varepsilon_s\left(x\right)}} \quad \text{SCL at the left side of junction} \tag{10}$$

We can write this Eq. (10) is a more 'eloquent form'

$$C_j = \frac{\varepsilon_0\,\varepsilon_{s,\text{eff}}\left(x_W\right)}{W} \quad \text{or} \quad W = \frac{\varepsilon_0\,\varepsilon_{s,\text{eff}}\left(x_W\right)}{C_j} \tag{11}$$

when we introduce the 'effective dielectric constant' $\varepsilon_{s,\text{eff}}(x_W)$ given by

$$\varepsilon_{s,\text{eff}}\left(x_W\right) = \frac{1}{\left|\dfrac{1}{W}\int_{x_j}^{x_W} \dfrac{dx}{\varepsilon_s\left(x\right)}\right|} \quad \text{or} \quad \frac{1}{\varepsilon_{s,\text{eff}}\left(x_W\right)} = \left|\frac{1}{W}\int_{x_j}^{x_W} \frac{dx}{\varepsilon_s\left(x\right)}\right| \tag{12}$$

We check that $\varepsilon_{s,\text{eff}}(x_W) = \varepsilon_s$ for the uniform ε case; and we note that Eq. (12) strongly reminds us the well known equation for the series connection of capacitors (summing of $1/C$, or of $1/\varepsilon$): this should give confidence in Eqs. (11) and (12).

From SCAPS 3.3.06 (September 2017) onward, the Mott-Schottky analysis in the program can be based on Eqs. (9) and (12), and not only on Eqs. (5) and (8) as it was before. Therefore, the Mott-Schottky analysis panel (available from the *C-V* result panel) has been changed and extended.

4. Mott-Schottky analysis in SCAPS ≥ 3.3.06

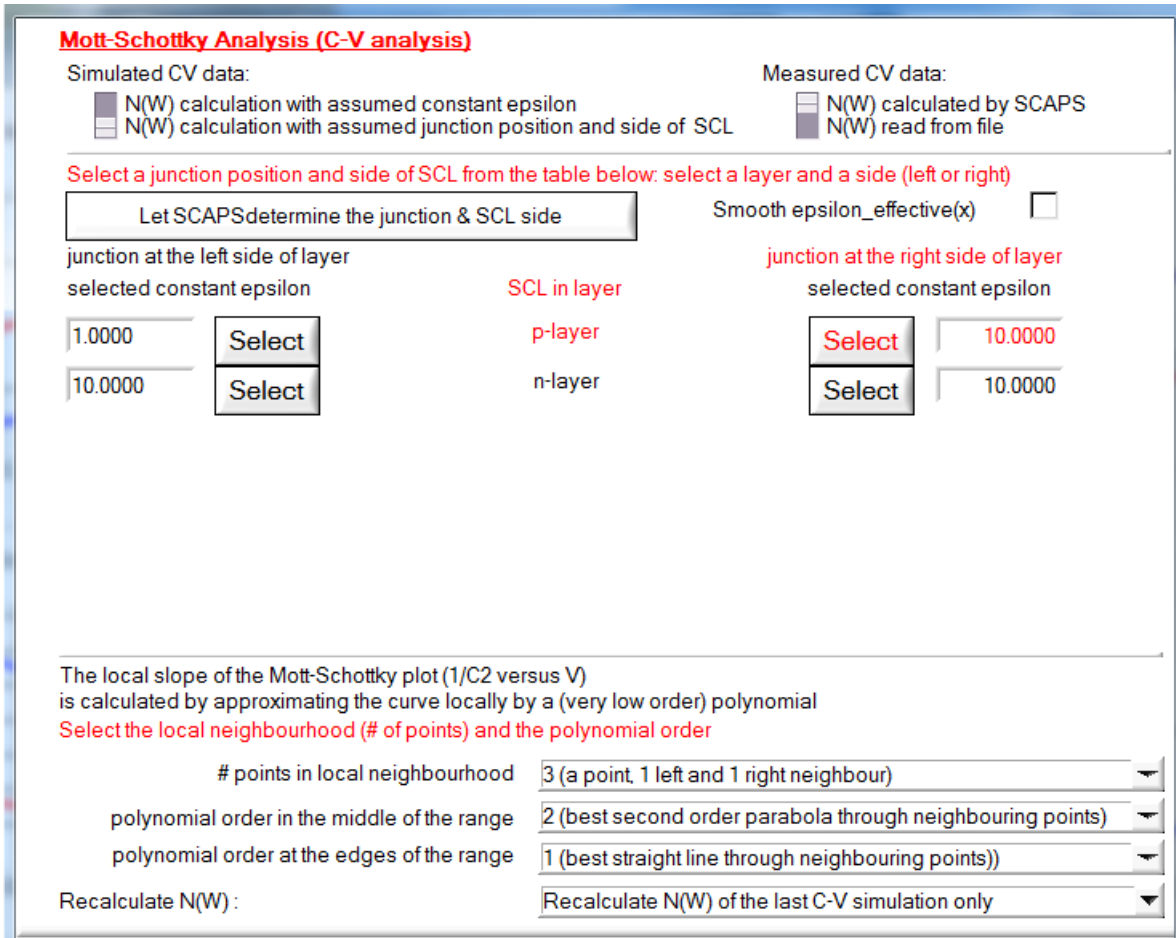The new Mott-Schottky analysis panel is shown in Fig. 1.

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Fig. 1   The Mott-Schottky analysis panel of SCAPS 3.3.06.

One can still choose to work with a constant ε_s value: either to compare with a Mott-Schottky analysis by a previous SCAPS version or by another programme, or because one is analysing a *C-V* measurement and one does not know the graded $\varepsilon_s(x)$. Then the Mott-Schottky analysis panel looks as in Fig. 2.
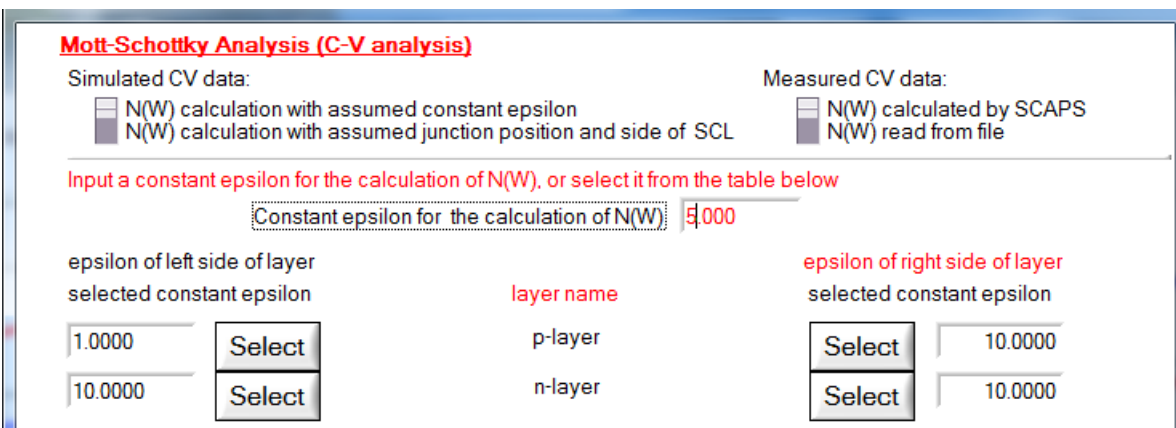
Fig. 2   Mott-Schottky analysis panel when 'work with a constant ε_s' is selected.

One can set any ε_s value, or one can select one of the ε_s values at the layer edges, and use this value as a uniform value over the whole cell; then Eqs. (5) and (8) are used (this is how it was in SCAPS ≤ 3.3.05).

When one selects 'N(W) calculation with assumed junction position and side of SCL' in Fig. 1, one should select a layer where one assumes the space charge layer (SCL), and the side of the layer where one assumes the junction. In Fig. 1 e.g. one assumes that the junction is between layer 1 ('p-layer) and layer 2 ('n-layer'), and that the space charge layer extends towards the left in layer 1 ('p-layer'). SCAPS will calculate $N_D(W)$ based on the position-dependent $\varepsilon_s(x)$ and Eqs. (9) and (12); the position x where this doping density applies is at a distance W to the left from the junction (the interface between layer 1 and 2), in this example. New: one can position the junction and the SCL from own judgement, or one can ask SCAPS to determine these (a new button). SCAPS uses a very coarse algorithm:

- o it determines the doping type (*n* or *p*) of the first layer, only based on the shallow doping density; charge in defects are not accounted for.
- o it determines the doping type of the next layer
- o if this is the same as that of the previous layer, continue.
- o if this differs from that of the previous layer, bingo:
  - ✓ the junction lies between this layer and the previous one
  - ✓ if the net doping density $|N_D\text{-}N_A|_{\text{this layer}} > |N_D\text{-}N_A|_{\text{previous layer}}$, then the SCL resides in the previous layer; otherwise, in this layer.

The meaning of the button 'smooth ε' will be explained later.

Up to now, the settings in the Mott-Schottky analysis panel only become active from the next *C-V* simulation on, there was no automatic recalculation. In SCAPS ≥ 3.3.06, automatic recalculation of $N_D(W)$ with the new parameters is possible (Fig. 3).
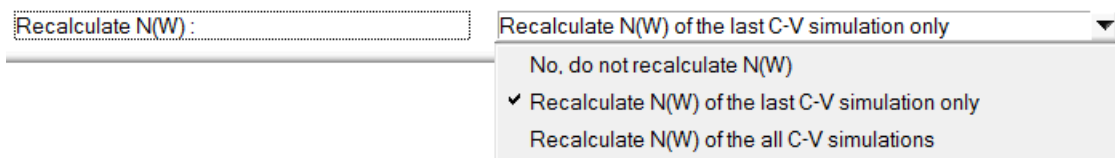

Fig. 3   New options to recalculate or not $N_D(W)$ automatically with the new settings. The default setting is shown.

5. Examples and illustrations of the new Mott-Schottky facilities

5.1 Example: M-S analysis with graded doping density __and__ dielectric constant

The definition file `M-S graded NA and epsilon.def` defines a pn^+ solar cell, where two properties of the lower doped *p*-side are graded: the doping density $N_A(x)$ evolves exponentially (thus: 'linearly in a logarithmic plot') from 10^{15} cm^{-3} at the left contact ($x = 0$) to 10^{14} cm^{-3} at the junction ($x_j = 10$ μm), and the (relative) dielectric constant $\varepsilon_s(x)$ in the same way from 1 at the contact to 10 at the junction; so, at all positions, $\varepsilon_s(x) \times N_A(x) = 10^{15}$ cm^{-3} = constant. See Fig. 4.
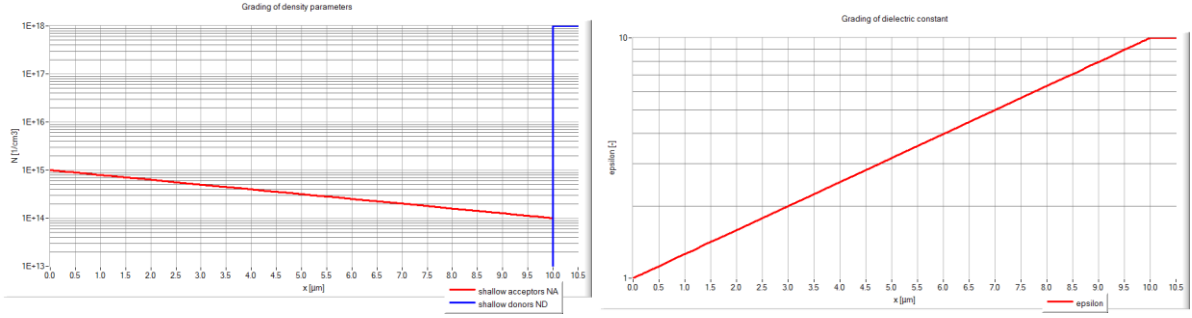
Fig. 4 Graded properties of `M-S graded NA and epsilon.def`. Left: doping density; in red, the acceptor density $N_A(x)$ in the p layer, in blue, the donor density N_D in the n^+ layer. Right: the dielectric constant $\varepsilon_s(x)$.

We launched a SCAPS single shot simulation of $C(V)$, with V running from 0 V to -3 V, step 0.05 V. The result of the Mott-Schottky analysis is shown in Fig. 5. It is seen that only the full analysis with position dependent $\varepsilon_s(x)$, thus Eqs. (9) and (12), reproduces the input values of $N_A(x)$. The blue and magenta points in Fig. 5 show the result with earlier versions SCAPS ≤ 3.3.05; these obviously do not give a reliable result when ε is graded!
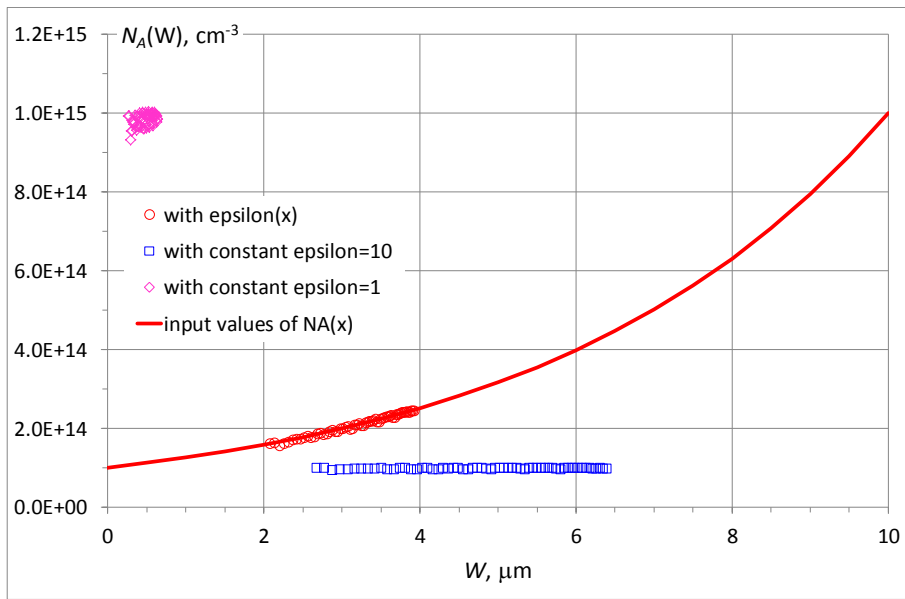

Fig. 5 Mott-Schottky analysis of `M-S graded NA and epsilon.def`. The solid red line is the input value of $N_A(W)$; note that $W = 10$ μm - x, since the SCL was placed (in the Mott-Schottky analysis panel) in the first (p) layer, and the junction at the right side of it, thus at $x = 10$ μm. The symbols are the result of the SCAPS M-S analysis: in red with position dependent $\varepsilon_s(x)$, thus Eqs. (9) and (12); in blue with a constant $\varepsilon_s = 10$ and Eqs. (5) and (8); in magenta with a constant $\varepsilon_s = 1$ and Eqs. (5) and (8).

In Fig. 6, the ε_s values used in the Mott-Schottky analysis are shown.
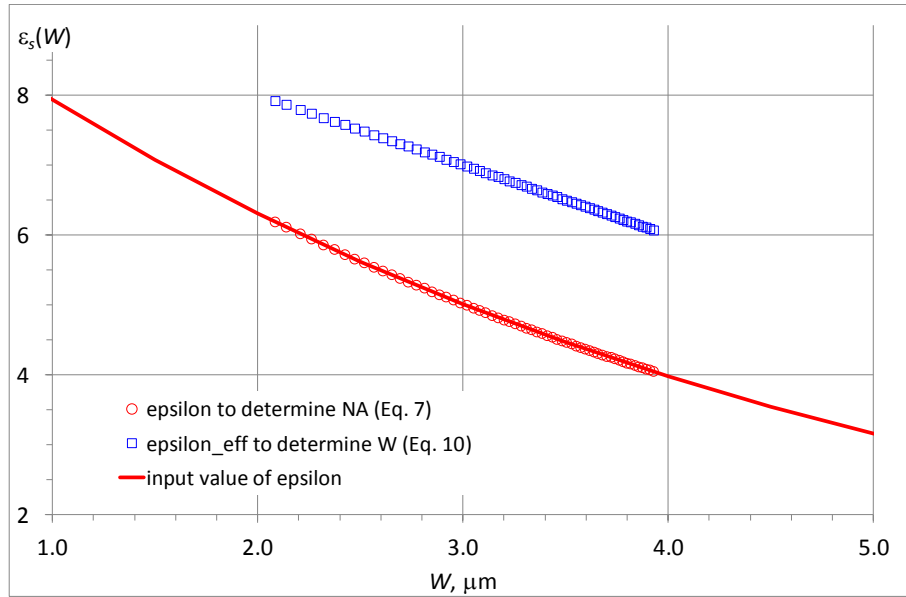
Fig. 6　　　The ε_s values used by SCAPS in the M-S analysis. Solid red line: the input value of $\varepsilon_s(W)$; again note that $W = 10\ \mu m - x_W$. The red circles are the ε_s value used in Eq. (12) to derive N_A from the slope of the Mott-Schottky plot. The blue squares are the ε_s value used in Eq. (9) to derive W from the inverse $1/C_j$ of the capacitance.

5.2　Extending the range of the *C-V* profiling

It is clear from Fig. 5 that the *C-V* profiling (thus the $N_A(W)$ or $N_A(x)$ profile) in this case only scans a small fraction of the *p* layer. To expand Fig. 5 to the left (narrower depletion width, towards higher *x*), one should measure/simulate for more positive voltages. But the forward voltage will be limited to typically $0.3 - 0.5$ V, because the diffusion capacitance overwhelms the depletion capacitance at higher forward voltage. To expand Fig. 5 to the right (thicker depletion width, towards lower *x*), one should measure/simulate for more negative voltages, thus higher reverse voltage. This will be limited by cell breakdown in a measurement, and probably by convergence failure in a SCAPS simulation (the problem above converges until $V = -9.0$ V, where $W = 3.7\ \mu m$ and $x = 6.3\ \mu m$).

When there is a contact barrier present at the left contact, the *C-V* profiling range sometimes can be extended elegantly. The principle was illustrated in e.g.

> M. Burgelman, P. Nollet, S. Degrave, "Electronic behaviour of thin-film CdTe solar cells", *Applied Physics A - Materials Science & Processing*, **69/2** 149-153 (1999).

M-S graded NA and epsilon with contact barrier.def is based on the previous def file M-S graded NA and epsilon.def, but:

o　the thickness of the *p* layer was reduced from 10 μm to 4 μm

o　the grading profiles of $N_A(x)$ and $\varepsilon_s(x)$ were changed from *logarithmic* to *linear*.

o　a hole contact barrier of 0.55 eV (with respect to E_F) or 0.2835 eV (with respect to E_{Vbulk}) was defined at the left contact

o　the simulation was done at 330 K and not 300 K

The *C-V* simulation and the resulting Mott-Schottky plot are shown in Fig. 7. Different parts of the *C-V* curve are determined by different parts of the cell, as explained in the figure caption.
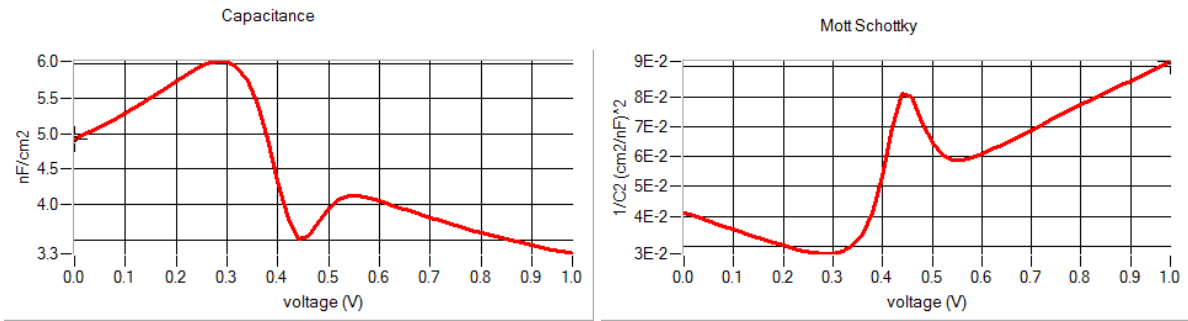

Fig. 7   SCAPS *C-V* simulation of `M-S graded NA and epsilon with contact barrier.def`. The complicated *C-V* behaviour is explained in the reference given in the text. For $x < 0.3$ V, the capacitance is determined by the junction depletion capacitance C_j; this junction is at $x_j = 4$ μm. For $V > 0.55$ V, the capacitance is determined by the contact capacitance C_c, and the 'junction' in the SCAPS analysis should be placed at $x_j = 0$.

We thus do the Mott-Schottky analysis twice:

1. Once with $V = 0.20$ V → -3.0 V, step 0.05 V. The junction is placed at the *p-n⁺* interface ($x_j = 4$ μm), and the SCL is positioned in the *p* layer; thus $x_W = 4$ μm - *W*: red curve in Fig. 8.

2. And then with $V = 0.58$ V → 0.98 V, step 0.02 V (divergence from +1 V on ☹). The junction is placed at the left contact ($x_j = 0$), and the SCL is in the *p* layer; thus $x_W = W$: blue curve in Fig. 8.
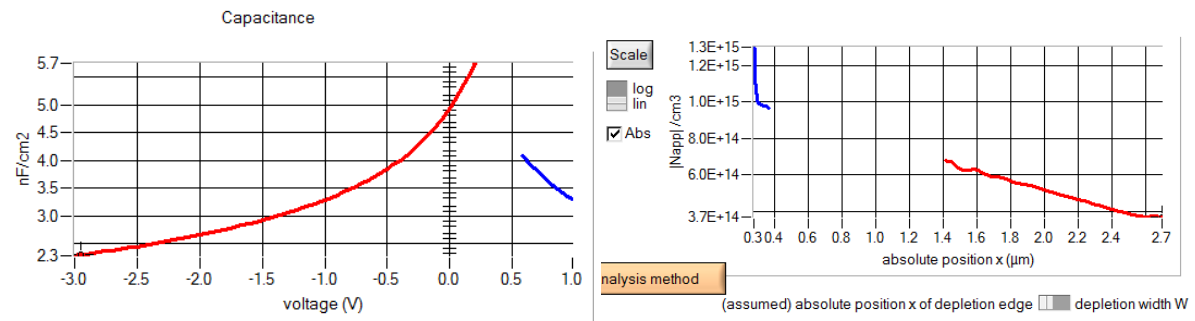
Fig. 8   Mott-Schottky analysis of `M-S graded NA and epsilon with contact barrier.def` in two parts, see text. Note that the contact-originated part (blue) yields $-N_A$ instead of $+N_A$, hence the abs-button (new in SCAPS 3.3.06) should be checked. Also note: because a same *W* value would point to different *x* values (see text), the new option 'absolute position *x*' should be selected.

The deviation between the estimated $N_A(x)$ near the contact ($> 10^{15}$ cm⁻³; blue curve in Fig. 8) and the input value (linearly decreasing from 10^{15} cm⁻³ at the contact to 10^{14} cm⁻³ at the

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junction) is because the theory outlined in the referenced paper is only valid far away from the 'artefacts' (the single or (here) double maximum in the *C-V* curve), and we started at 0.58 V, rather close to the second maximum. Fig. 8 is a nice illustration of the novelties in the Mott-Schottky analysis in SCAPS 3.3.06 (but we admit that some playing with the parameters was needed to get the illustration so nice).

5.3   M-S analysis with several layers with uniform, but different ε_s

Now load the definition file `M-S 6 layers with uniform epsilon.def`. It is based on the first file `M-S graded NA and epsilon.def`, but:

- the doping density in the *p* layer is uniform $N_A = 10^{15}$ cm^{-3}.
- the *p* layer is split into 6 sublayers, 4 of 0.25 μm thickness and 2 of 0.1 μm thickness, and different but uniform ε_s within each layer: see Fig. 9.

To do the M-S analysis of the simulated *C-V*, the junction should be placed at x_j = 1.2 μm, between layer 6 and 7. When we want to place the SCL in the *p* layers (because we know that the n^+ layer is much stronger doped than all *p* layers), SCAPS $\leq$ 3.3.05 offered no choice than to place the SCP in the 6$^{\text{th}}$ layer, thus 1.1 μm $< x <$ 1.2 μm, with $\varepsilon_s = 10$. But what if the SCL would be wider than 0.1 μm, and thus would extend into the 5$^{\text{th}}$, the 4$^{\text{th}}$, … layer? Now, in SCAPS 3.3.06, this is handled properly: SCAPS will use the general M-S analysis (Eqs. (9) and (12)), and thus take account of the actual $\varepsilon_s(x)$ value at all positions in each of the layers.
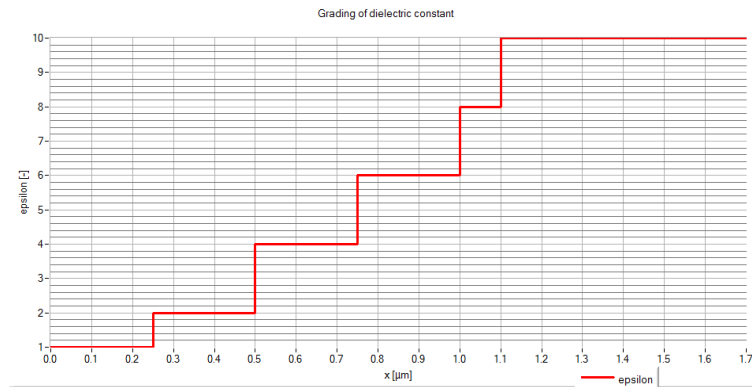

Fig. 9   The evolution of ε_s in the layers of `M-S 6 layers with uniform epsilon.def`. The *pn* junction is at *x*= 1.20 μm, between the 6$^{\text{th}}$ layer (*p* type) and the 7$^{\text{th}}$ layer (n^+ type).

… but will it work properly?

The settings of the Mott-Schottky analysis panel (Fig. 1) are: '$N(W)$ calculation with assumed junction position and side of SCL'; click 'Let SCAPS determine the junction & SCL side', or directly select the right side of layer #6 named 'p eps=10'. And in the $N(W)$ plot in the C-V panel, select as abscissa (horizontal axis) '(assumed) absolute position x of the depletion edge'; 'assumed' means that x is calculated with the assumed position of the junction and side of the SCL, in this case: x_W = 1.2 μm - W. The $N_A(x_W)$ result is shown in Fig. 10. The red curve is when $N_A(W)$ was determined with the true value of $\varepsilon_s(x_W)$; the blue curve will be discussed later.
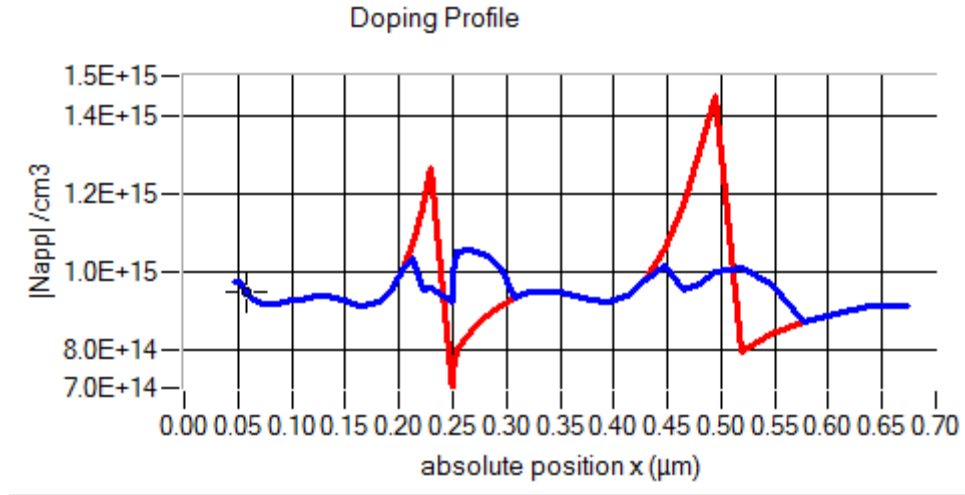
Fig. 10 Mott-Schottky analysis of `M-S 6 layers with uniform epsilon.def` and the settings described in the text. Red: N_A calculated with the true ε_s (W) from Eq. (9). Blue: with $\varepsilon_s(W)$ first smoothed by Eq. (16), and then inserted in Eq. (12) or (15).

Because $\varepsilon_s(x)$ has discontinuities at the layer interfaces $x = 0.25, 0.50, 0.75, 1.00$ and 1.10 μm, also $N_A(x)$ will show these discontinuities (when we assume that the *C-V* curve is smooth, thus without discontinuities in its derivative to the voltage). And indeed, the discontinuities (a jump with a factor of 2) is seen at $x = 0.25$ μm (ε_s jumps from 1 to 2) and at $x = 0.50$ μm (ε_s jumps from 2 to 4); the result is the ugly, spiky red curve of Fig. 10 instead of a nice flat line at the input value $N_A = 10^{15}$ cm^{-3}: this is not satisfying at all.

This is not due to errors or imperfections in Eq. (9); this equations is generally valid (or graded $N_A(x)$ and $\varepsilon_s(x)$, discontinuities allowed), but only <u>within the abrupt depletion approximation</u>. However, SCAPS does not use any such approximations to simulate the *IV*, *C-V*… curves; it solves the full set of semiconductor equations. It turns out that the abrupt depletion is only a very coarse approximation of the reality, see Fig. 11 where the carrier densities *n* and *p* and the total charge density ρ are plotted for `simple pn.def` from the standard SCAPS distribution.
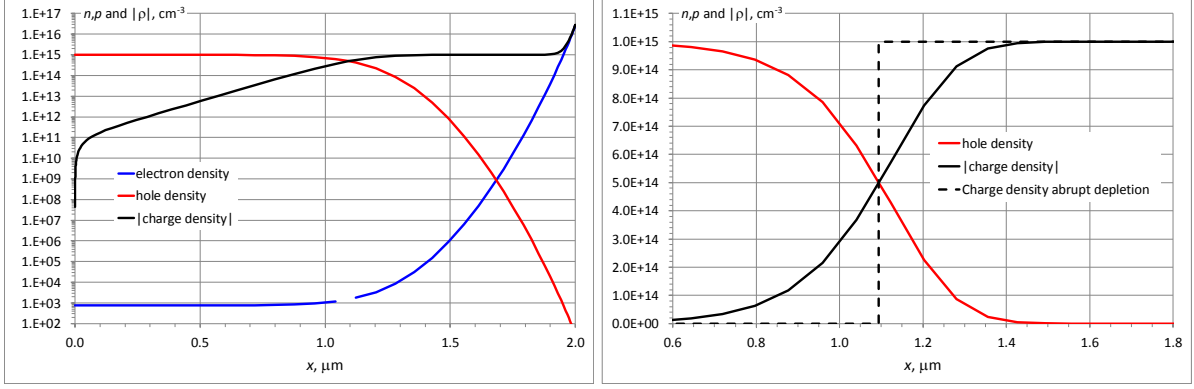
Fig. 11   About the abruptness of the depletion layer. SCAPS simulation of `simple pn.def`: p-layer = (2μm, 10^{15} cm^{-3}) and n-layer = (0.5 μm, 10^{17} cm^{-3}). Left: the densities n, p and $|\rho|$ on a logarithmic scale; only the p-layer is shown. Right: p and $|\rho|$ on a linear scale; the p-layer is shown only until $x = 1.8$ μm to hide the 'inversion layer' near the junction at $x_j = 2$ μm, where $|\rho| \gg N_A = 10^{15}$ cm^{-3}; the abrupt depletion approximation for $\rho(x)$ is shown in a dashed line, with the depletion edge at $x_W = 1.094$ μm ($W = 0.906$ μm).

Two deviations from the ideal 'text book' abrupt depletion behaviour are obvious:

o the 'inversion layer' in the p region near the junction (thus 1.9 μm $< x <$ 2 μm) where electrons from the neighbouring n^+ layer are flooding into the p region: $n \sim |\rho/q| \gg p$. A closer study (more advanced, more difficult text books ☹, or numerical experiments e.g. in SCAPS ☺) learns that this inversion layer has no influence at all, neither on the *IV* characteristics nor at the *C-V* and *C-f* characteristics.

o the depletion edge is not abrupt at all! So, there is some judgement involved to decide what would be the exact position of the depletion edge (since there is no sharp edge). A convenient position is at x_W where $p(x_W) = |\rho(x_W)/q| = N_A/2$, see Fig. 11, right.

One observes that the transition from neutral bulk to full depletion is rather gradual; it turns out that the transition width is of the order of one Debye length L_D left and one L_D right of the depletion edge as defined above. Refer to your courses/text books for the definition of L_D ('extrinsic Debye length in a homogeneous p-layer'):

$$L_D = \sqrt{\frac{\varepsilon_s \varepsilon_0 kT}{q^2 N_A}} \qquad (13)$$

The depletion width *W*, in the abrupt depletion approximation and with the idealisations of section 3.1, thus given by Eq. (6), turns out to be a small multiple of the Debye length:

$$W = L_D \sqrt{\frac{2q(V_{bi} - V)}{kT}} \qquad (14)$$

Take e.g. equilibrium ($V = 0$), room temperature ($kT/q = 25$ mV) and a typical $V_{bi} = 0.8$ V, then $W \sim 8L_D$: the depletion width is thus not that much larger than the transition width $2L_D$.

At forward voltage this is even worse. Only at large reverse voltages the transition width is negligible against the depletion width, and the depletion edge can be considered as 'abrupt'.

Our equation Eq. (9) to extract $N_A(x)$ from a C-V measurement is based on abrupt depletion. But the depletion is gradual over a distance of about two Debye lengths. Thus it makes sense not to use the exact $\varepsilon_s(W)$ in Eq. (9), but an ε_s value that is smoothed out over a range of about x_W - L_D to $x_W + L_D$. So, in the SCAPS Mott-Schottky analysis panel, there is now an option to 'smooth ε_s'. Then Eq. (9) is replaced with

$$N_D\left(x_W\right) = \frac{-1}{\text{slope}\left[V\left(W\right)\right]} \cdot \frac{2}{q\varepsilon_0\varepsilon_{s,\text{smoothed}}\left(x_W\right)} \tag{15}$$

with $\varepsilon_{s,\text{smoothed}}$ given by

$$\varepsilon_{s,\text{smoothed}}\left(x_W\right) = \frac{\displaystyle\int_{x_W-aL_D}^{x_W+aL_D} \varepsilon_s\left(x\right)\exp\left(-b\left(\frac{x-x_W}{L_D}\right)^2\right)dx}{\displaystyle\int_{x_W-aL_D}^{x_W+aL_D} \exp\left(-b\left(\frac{x-x_W}{L_D}\right)^2\right)dx} \tag{16}$$

Thus, we smooth out with a Gaussian weight function, from a position aL_D left of the depletion edge to a position the same distance right of the depletion edge. As of now (15-10-2017), the smoothing parameters used are $a = 1.0$ and $b = 2.0$. These values are not (yet?) accessible by the user; I am still experimenting with it.

In the blue curve of Fig. 10, $\varepsilon_s(x)$ was smoothed by Eq. (16) before use in Eq. (15). This result may still look rather ugly – it is still not at all a flat line at $N_A = 10^{15}$ cm^{-3} – but it is already much better then the red result with unsmoothed ε_s. In fact the relative error is < 15 %... and 15 % accuracy is not so bad for a doping density.

5.4   About the calculation of depletion width W

The reader has noted that so far we used two definitions, or two ways to calculate, the depletion layer width W, or the:

- o   the depletion edge is at position x_W where the depletion space charge density has fallen to half of its value in the 'uniform depletion layer': $p(x_W) = |\rho(x_W)/q| = N_A/2$. It would be more complicated when the doping density $N_A(x)$ were graded: then $p(x_W) = |\rho(x_W)/q| = N_A(x_W)/2$ should be used.
- o   the depletion width is determined by the inverse of the depletion capacitance, thus by $1/C_j$, Eq. (5) or the more general Eq. (11). These equations are derived assuming an abrupt depletion layer, not a gradual one.

… but are these two definitions leading to the same result when there is a gradual transition from neutral bulk to the fully depleted SCL, as is the reality? SCAPS can give the answer, using the powerful facilities of the SCAPS script. So, load the script file `width of SCL.script` and run it. The script is annotated with plenty of comments, but even so, scripting in SCAPS is not so easy and intuitive as the basic, interactive use of the program; this script might serve as an example of SCAPS scripting. The result (the script graphs) are shown

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in Fig. 12. The agreement between the two definitions/algorithms for W is excellent! In the script, an adaption was made to the problem simple pn.def: the n layer was more heavily doped (10^{18} instead of 10^{17} cm^{-3}) to make the junction more extrinsic (pn^+-type); and the p-layer thickness was varied together with its doping density N_A, to accommodate for the depletion width W and for some neutral bulk region (it should be there, but it must not be too thick compared to W, to avoid convergence problems).
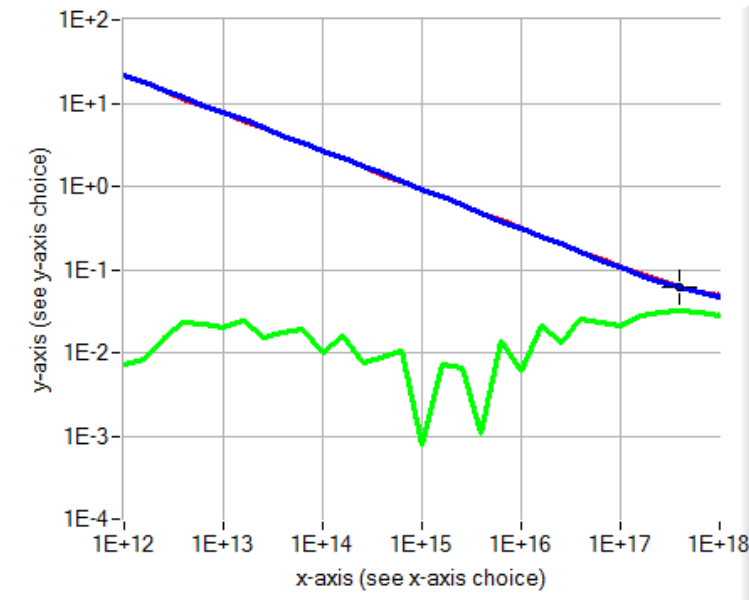

Fig. 12   Result of the SCAPS script `width of SCL.script`: W (in μm) vs. N_A (in cm^{-3}). The problem file is based on `simple pn.def`, see text. The SCL width W is once calculated from $p(x_W) = N_A/2$ (red curve) and once from $\varepsilon_s\varepsilon_0/C_j$ (blue curve): both are practically coinciding. The green curve is the relative difference between the two W's; it is a few % and even below 1 % over most of the doping range.

6. Novelties in the SCAPS ac-panel

After a SCAPS simulation of capacitance (C-V or C-f simulation), the ac-panel is accessible to illustrate the ac behaviour (or small-signal behaviour) of the current densities (electrons, holes, displacement and total) (left side of the ac-panel), and the potential/energy levels (electrostatic potential, electron and hole Fermi level) (right side of the ac-panel). All these properties have complex values, and thus there was an amplitude graph (e.g. |n|) at the top of the ac-panel, and a graph of the argument or phase (e.g. arg(n)) at the bottom of the ac-panel. Sometimes a view of the real and imaginary part is more informative/acquainted by the user than a view of amplitude/phase. And sometimes a graph of the (ac) charrier densities (electrons, holes, all defects together, total) would also be desirable.

All this is now implemented in SCAPS 3.3.06. Both for the left and for the right side of the ac-panel, the user can opt for 6 sets of graphs, see Fig. 13.
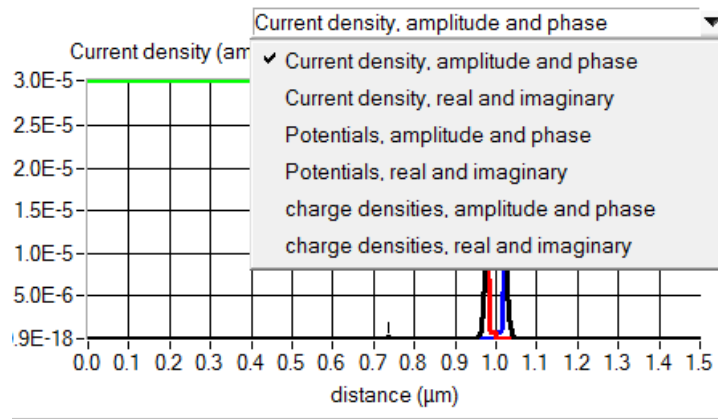
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Fig. 13　　　　　New graph options in the ac-panel of SCAPS 3.3.06

In this way, one can display e.g. the two representations of the potentials (thus $|\Phi|$ and $\arg(\Phi)$ left, and $\text{Re}(\Phi)$ and $\text{Im}(\Phi)$ right) in Fig. 14. Or a view of the currents left and of the carrier densities right as in Fig. 15.

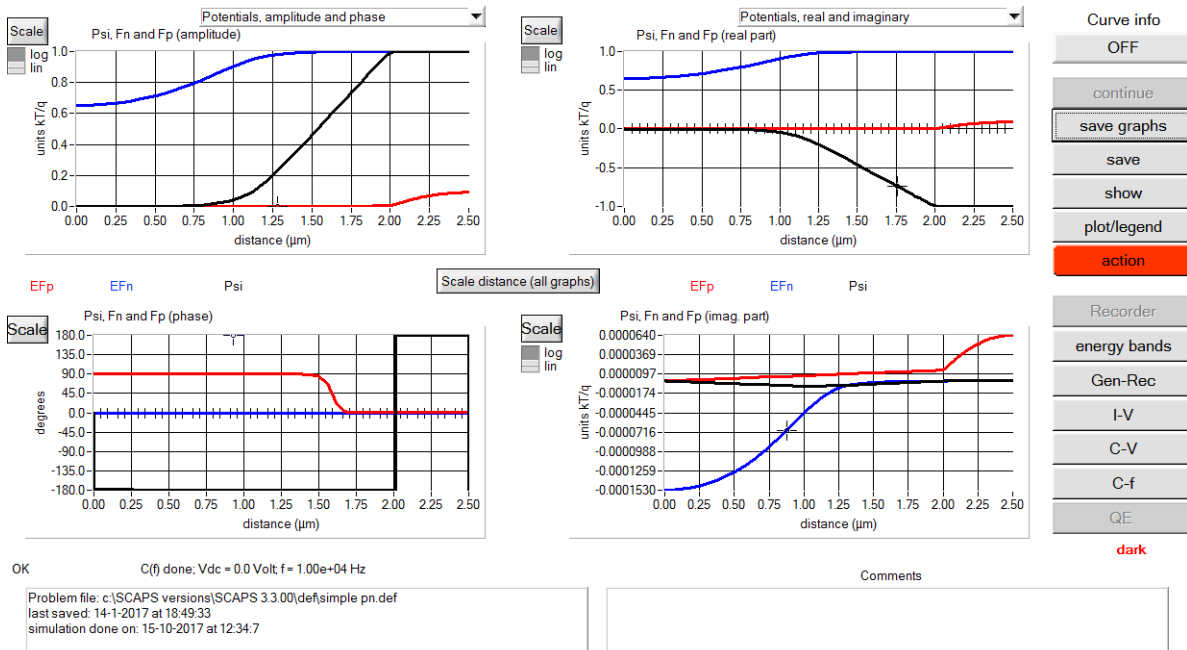Fig. 14　　　　　Example of an ac-panel view: the (ac-component or small signal component of) the electric potential Φ, and the Fermi levels E_{Fn} and E_{Fp}. Top left the amplitudes $|\Phi|$…; bottom left the arguments $\arg(\Phi)$…; top right the real parts $\text{Re}(\Phi)$…; and bottom right the imaginary parts $\text{Im}(\Phi)$. The problem is simple pn.def, and the calculation is at $V = 0$ and $f = 10$ kHz.
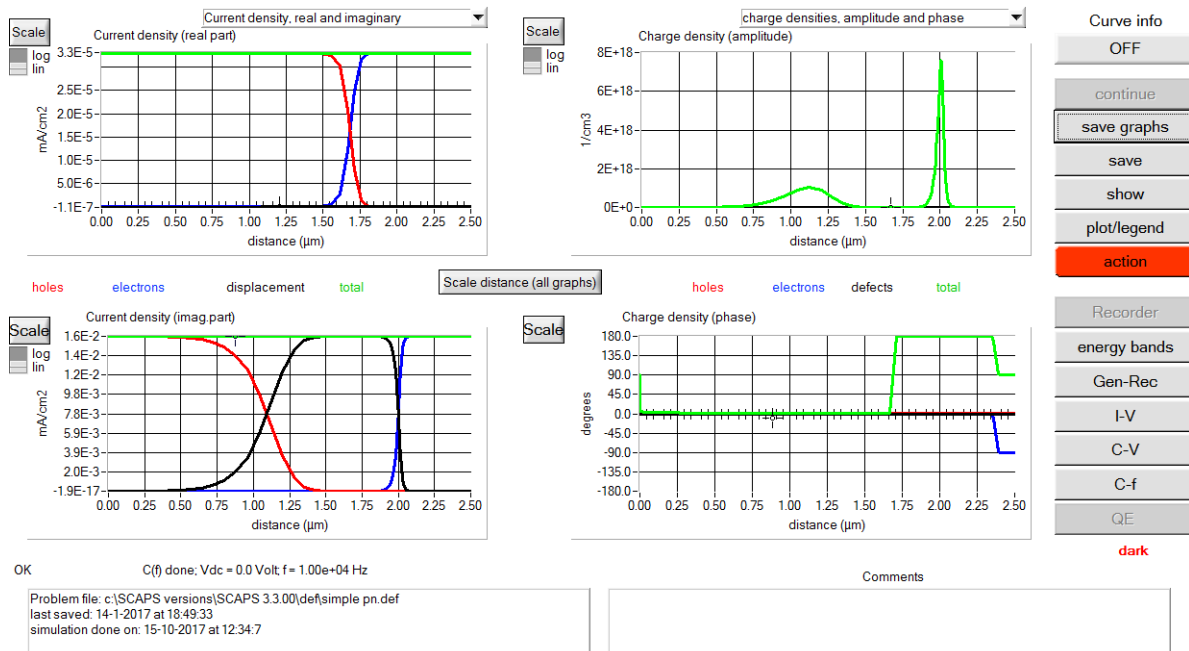
Fig. 15   Example of an ac-panel view. Left: the (ac-component or small signal component of) the current densities J_n, J_p, J_{displ} and J_{tot}; the amplitudes in the top left graph, the phases in the bottom left graph. Right: the carrier densities n, p and ρ_{tot}/q; the real part top right, the imaginary part bottom right. The problem is simple pn.def, and the calculation is at $V = 0$ and $f = 10$ kHz.

Note that the amplitude of the (ac-part of the) carrier densities is plotted linearly (logarithmically would be more customarily). The total charge density in green is obscuring the electron and hole density where they practically coincide (yes, I should still work a bit on the aesthetics of the graphs…). The small hump around $x = 1.1$ μm comes from the ac hole density $|\tilde{p}|$, and the higher, narrower peak at $x = 2$ μm from the ac electron density $|\tilde{n}|$. These two humps/peaks illustrate the 'capacitance action' (the adaption of ac carrier densities to the ac signal). Playing somewhat with the SCAPS parameters (the voltage of the work point) confirms what our physical intuition already knows: the adaption of electrons is always (= with varying V) at the same place $x = x_j = 2$ μm; and the position of ac hole adaption varies with bias voltage: further away from the junction for higher reverse bias. Plots like Fig. 15 can be used to point out where precisely the 'capacitance action' is taking place: at a contact? at some interface? in which layer?... but be warned, in complicated cases it can be very … complicated to interpret…

7. SCAPS Admittance Analysis (AS) of *C-f* simulations or measurements

The purpose of Admittance Analysis (AS) is to determine the defect density as a function of trap energy $N_t(E_t)$ from a set of $C(f, T)$ simulations or measurements; and to do so for each defect assumedly present in the cell. This topic is very advanced, and the user definitely should consult and closely follow the dedicated literature. As a start point, the article referenced below can be used, with other work referenced therein.

K. Decock, S. Khelifi, S. Buecheler, F. Pianezzi, A.N. Tiwari, M. Burgelman, "Defect distributions in thin film solar cells deduced from admittance measurements under different bias voltages", *Journal of Applied Physics*, **110/6**, 063722 (2011).

The notation and terminology of this article are closely followed in the SCAPS Admittance Analysis Panel. To set-up the parameters and assumptions used to display the AS results, the same panel is used as for setting up the Mott-Schottky analysis: the "Admittance (Capacitance) Analysis Panel". The top part of that panel is relevant to the M-S analysis and was already discussed and shown in Fig. 1. The bottom part of that panel is shown in Fig. 16.
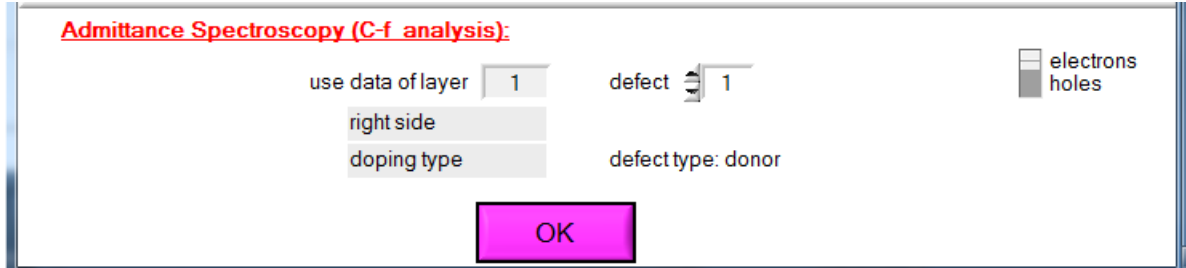

Fig. 16   The AS-part of the Admittance (Capacitance) Analysis Set-up Panel.

Here the defect for which the $N_t(E_t)$ will be determined should be identified:

- ✓ The layer containing the defect should be selected in the M-S part of the set-up panel, see Fig. 1. Information on the side of the selected layer where the junction was assumed, and of the (shallow!) doping type (*n* or *p*) of the selected layer is displayed.
- ✓ The defect number in the selected layer. As information the charge type is displayed (donor, acceptor, double donor or acceptor, amphoteric, user defined multivalent). A warning is given when the selected defect is a "neutral defect", that cannot contribute to capacitance.
- ✓ The level of the defect, if a multilevel defect was selected.
- ✓ The carrier type (*e* or *h*) that assumedly has the dominant contribution to the capacitance.

7.1   Terminology and method to determine $N_t(E_t)$: overview

To interpret the AS result panel, we briefly summarise the terminology and method used.

- ○ From the *C-f* measurement, the "derivative" is calculated (the angular frequency ω = 2π*f* where *f* is the frequency):

$$"derivative" = \omega \cdot \frac{dC}{d\omega} = f \cdot \frac{dC}{df} = \frac{dC}{d\log\omega} = \frac{dC}{d\log f} \qquad (17)$$

- ○ The trap density is calculated from the 'derivative'. The equation used depends on assumptions on band bending in the space charge layer SCL. In the most simple case of 'constant-linear' band bending, one gets (see referenced article)

$$N_t = \frac{1}{q^2 W} \cdot \frac{V_{bi} - V}{kT/q} \cdot \left(-\omega \frac{dC}{d\omega} \right) \qquad (18)$$

- More complicated assumptions for the band bending yield (slightly) more complicated equations, see article.
- This trap density applies at an energy level E_ω that has a different meaning and is calculated differently, depending on the assumed carrier type for the capacitance contribution of the defect under study:

$$E_\omega = E_t - E_V = kT \ln\left(\frac{2\omega_{esc,p}}{\omega}\right) \qquad \text{hole dominated}$$

$$E_\omega = E_C - E_t = kT \ln\left(\frac{2\omega_{esc,n}}{\omega}\right) \qquad \text{electron dominated}$$

(19)

- To establish this relation Eq. (19) between (assumed) energy E_ω and measurement frequency f or angular frequency $\omega = 2\pi f$, two escape frequencies were defined:

$$\omega_{esc,p} = \sigma_p v_{th,p} N_V \quad \text{and} \quad \omega_{esc,n} = \sigma_n v_{th,n} N_C \qquad (20)$$

- The ω_{esc} of the dominant carrier (for the capacitance) is often called 'the escape frequency' ν_0. Since in Eq. (20) v_{th} is proportional to $T^{1/2}$, and N_V and N_V to $T^{3/2}$, the escape frequency ν_0 is proportional to T^2, assuming that the capture cross sections σ do not depend on temperature. So, the temperature dependence of $\nu_0(T)$ is conveniently written as:

$$\nu_0(T) = \frac{\xi_0 T^2}{2} \quad \text{escape frequency} \qquad (21)$$

- here ξ is the (lower case) greek letter 'ksi'. Hence ξ_0 is named 'ksi_0' in the input field of the SCAPS AS results panel.

7.2 Determination of $N_t(E_t)$ from one C-f measurement only? Rather from an extended set of $C(f,T)$ measurements!

The method outlined above allows to determine the trap distribution $N_t(E_t)$:

- calculate the escape frequency either as $\omega_{esc,p}$ or $\omega_{esc,n}$ with Eq. (20), depending on the setting e or h in the AS set-up panel, or directly from Eq. (21) with the value of ξ_0 in the AS result panel.
- Convert the (angular) frequency range ω of the measurements into an energy range E_ω with Eq. (19)
- Convert the (derivative of) the measured capacitance to a trap density (e.g. in $cm^{-3}eV^{-1}$) with Eq. (18) or a more elaborate equation according to the settings in the AS result panel (setting 'band type').
- SCAPS does all this for you in the AS result panel

… and there is the trap distribution $N_t(E_t)$!

But look what happens when one is doing so for all C-f curves of a set of $C(f, T)$ measurements. We take the definition file `simple pn for AS defect.def`, that is derived from the good old `simple pn.def`, with changes: defect 1 (the only defect) of the p-layer is of donor type, single level at $E_V + 0.40$ eV and with $\sigma_n = \sigma_p = 10^{-14}$ cm^2. The $N_t(E_t)$

distribution derived by the SCAPS AS facility from a set of $C(f, T)$ measurements is shown in Fig. 17.

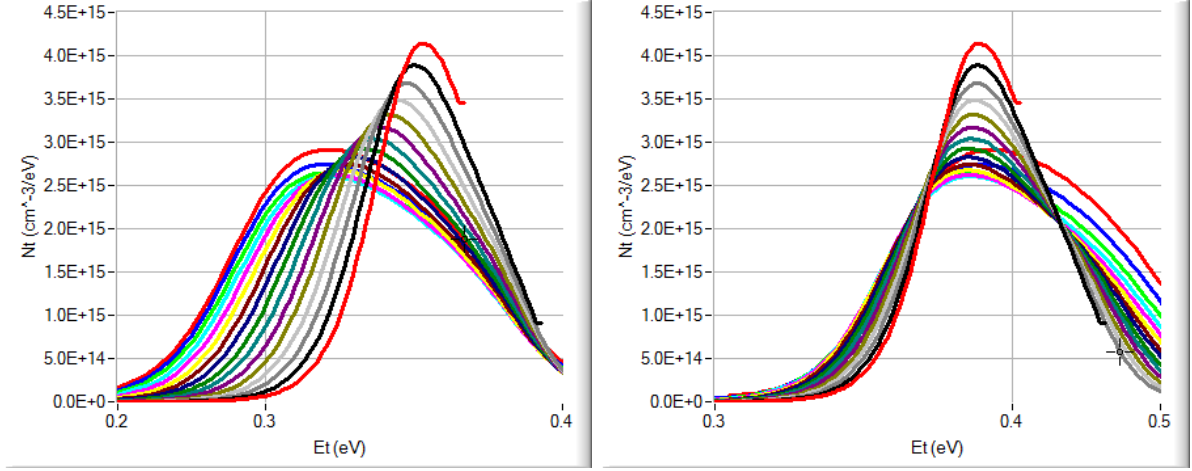Fig. 17 AS analysis: trap density $N_t(E_t)$ of problem `simple pn` for AS `defect.def`. The *C-f* simulations were run from 10^{-2} Hz to 10^7 Hz with 20 points/decade. The temperature was varied from 300 K to 150 K, step 10 K. Left: with the escape frequency calculated from the definition file (click the button in the AS result panel, this yields $\nu_0 = 2.5\times10^{11}$ Hz). Right: with ν_0 set (empirically) to 4.05×10^{12} Hz.

Be not surprised that one sees a Gaussian-like distribution instead of a Dirac pulse distribution, that corresponds to a single level: theory in the cited article predicts a full-width-at-half-maximum with of the obtained 'apparent' $N_t(E_t)$ distribution of FWHM = kT ln[(1+√2)/(1-√2)] ~ 1.76 kT; this is about 45 eV at 300 K and 23 eV at 150 K.

However, it is rather unacceptable that the $N_t(E_t)$ distribution seems to shift with temperature: the peak energy in Fig. 17 Left, interpreted as the trap energy E_t, shifts from $E_V + 0.320$ eV at 150 K to $E_V + 0.353$ eV at 300 K… while we know that the trap energy position in the definition file is fixed at $E_V + 0.40$ eV. We get a better result when we vary the escape frequency ν_0 or the parameter ξ_0 in the AS result panel empirically. With $\nu_0 = 4\times10^{12}$ Hz, we get Fig. 17 Right: the apparent trap energy E_t now is rather constant when T is varied between 150 K and 300 K, and yields $E_t = E_V + 0.39$ eV, almost the input value (10 meV error only). Though this result is satisfying, the method we used to obtain it (trial and error variation of ν_0) is not very satisfying (though in practice often faster than the 'decent' method described below ☺).

7.3 Determination of the trap energy E_t by an 'Arrhenius plot of ω_0'

From a simulated or measured *C-f* curve, one characteristic frequency f_0 or angular frequency $\omega_0 = 2\pi f_0$ per defect can in principle be determined. This is based on the fact that several phenomena, if present alone, give rise to the same frequency dependence of the capacitance

$$C(\omega) = C_\infty + (C_0 - C_\infty)\frac{\omega_0^2}{\omega^2 + \omega_0^2} \quad \text{or} \quad C(f) = C_\infty + (C_0 - C_\infty)\frac{f_0^2}{f^2 + f_0^2} \tag{22}$$

Sometimes, this f_0 (or ω_0) is called the (angular) frequency of the inflection point, or short, the 'inflection frequency'. When one would deduce ω_0 from an inflection point (not advised!), some remarks:

- It is always difficult to position an inflection point on a curve, the result is often inaccurate.
- If more than one defect is present, and thus several contributions as in Eq. (22) are summed, it will be almost impossible (and always inaccurate) to resolve and position all inflection points.
- The C-f curve given by Eq. (22) indeed has an inflection point… not at frequency f_0 but at frequency $f_0\sqrt{3}$! This is sometimes mentioned (and used as definition for f_0 or ω_0 in older articles). But a linear-linear C-f plot is very impractical when the frequency range extends over several decades, as usually is the case.
- So, one better works with a linear-logarithmic plot, thus C vs. $\log f$ or $\log\omega$. This plot has (in the case of Eq. (22)) an inflection point… at exactly f_0 or ω_0!
- More recent articles thus call ω_0 the '(angular) inflection frequency', often without specifying that it is seen and determined in a C-$\log\omega$ plot.

It is better to deduce f_0 or ω_0 from the 'derivative of the capacitance plot'. Also here, the authors mean the derivative in the C-$\log f$ or C-$\log\omega$ plot, and <u>not</u> the derivative in the C-f or C-ω plot, even when they do not state so explicitly. Thus:

$$\text{derivative} = \frac{dC}{d\log(\omega)} = \omega\frac{dC}{d\omega} = f\frac{dC}{df}, \quad |\text{derivative}| = \text{maximum at } \omega = \omega_0 \text{ or } f = f_0 \quad (23)$$

This 'derivative' has a maximum (of the absolute value) at exactly f_0 or ω_0; and often it is a sharp maximum, thus easy and precise to determine; in a lin-log plot, the maximum is usually sharper and thus better to determine than in a log-log plot. The statements above are illustrated for `simple pn for AS defect.def` in Fig. 18 and Fig. 19.
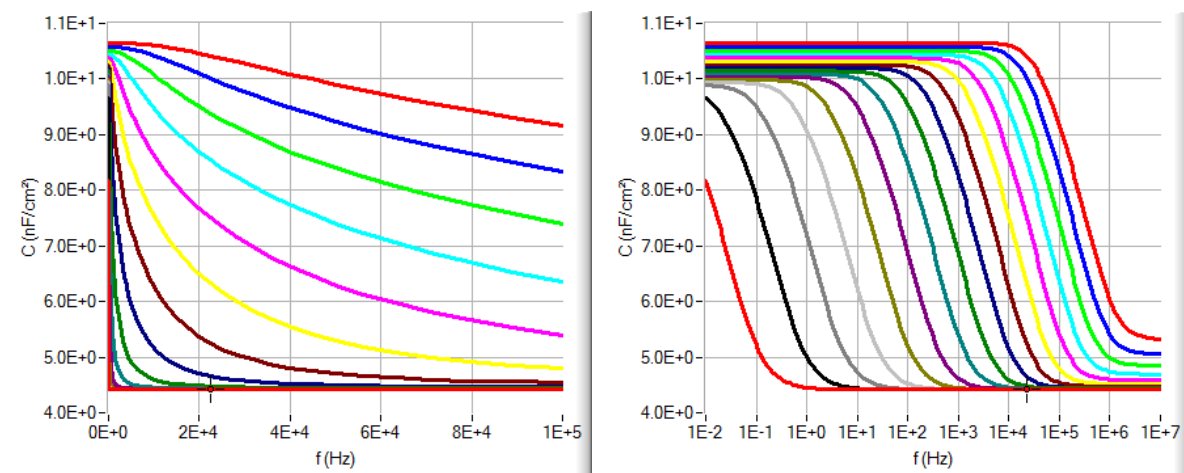

Fig. 18 C-f simulation of `simple pn for AS defect.def` with varying T (see caption of Fig. 17). Left: a lin-lin plot, thus $C(f)$. Right: a lin-log plot, thus $C(\log f)$.
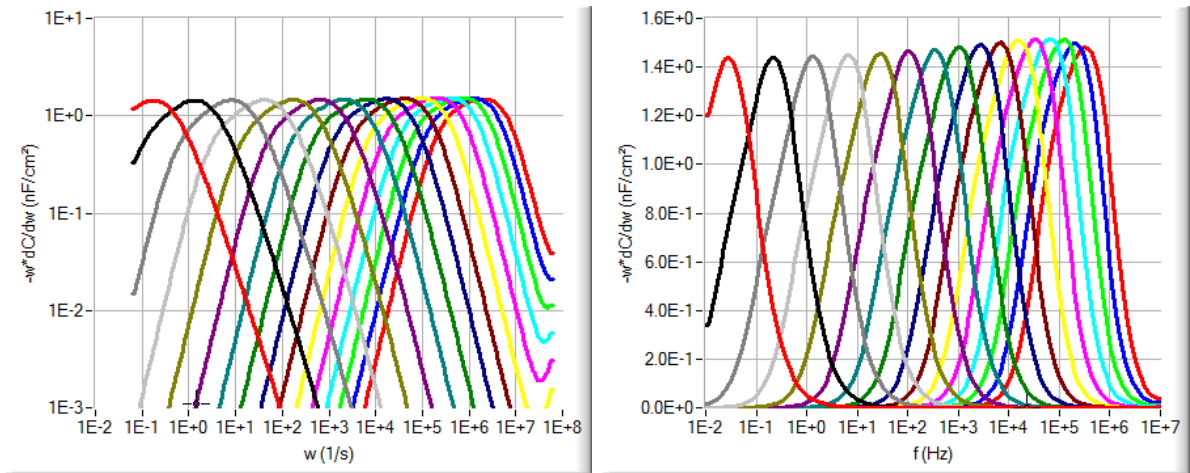
Fig. 19   Simulation of `simple pn for AS defect.def` with varying T (see caption of Fig. 17): The 'derivative' $|\omega dC/d\omega|$ in the AS panel, Left in a log-log plot, Right in a lin-log plot.

One thus should determine $\omega_0(T)$, preferably from simulations or measurements processed and presented as in Fig. 19 Right. A direct 'Arrhenius plot' would be to plot $\ln(\omega_0)$ vs. $1/T$. From theory (see cited article) we know that a straight line would be obtained when we plot ω_0/T^2 instead of just ω_0. A 'suitable Arrhenius plot' is then to make a plot:

- ✓ ordinate or y-axis: ω_0/T^2 on a logarithmic scale
- ✓ abscissa or x-axis: 1000 Kelvin$/T$; this has the advantage that it is dimensionless, and leads to 'comfortable numbers': e.g. room temperature is at 3.333
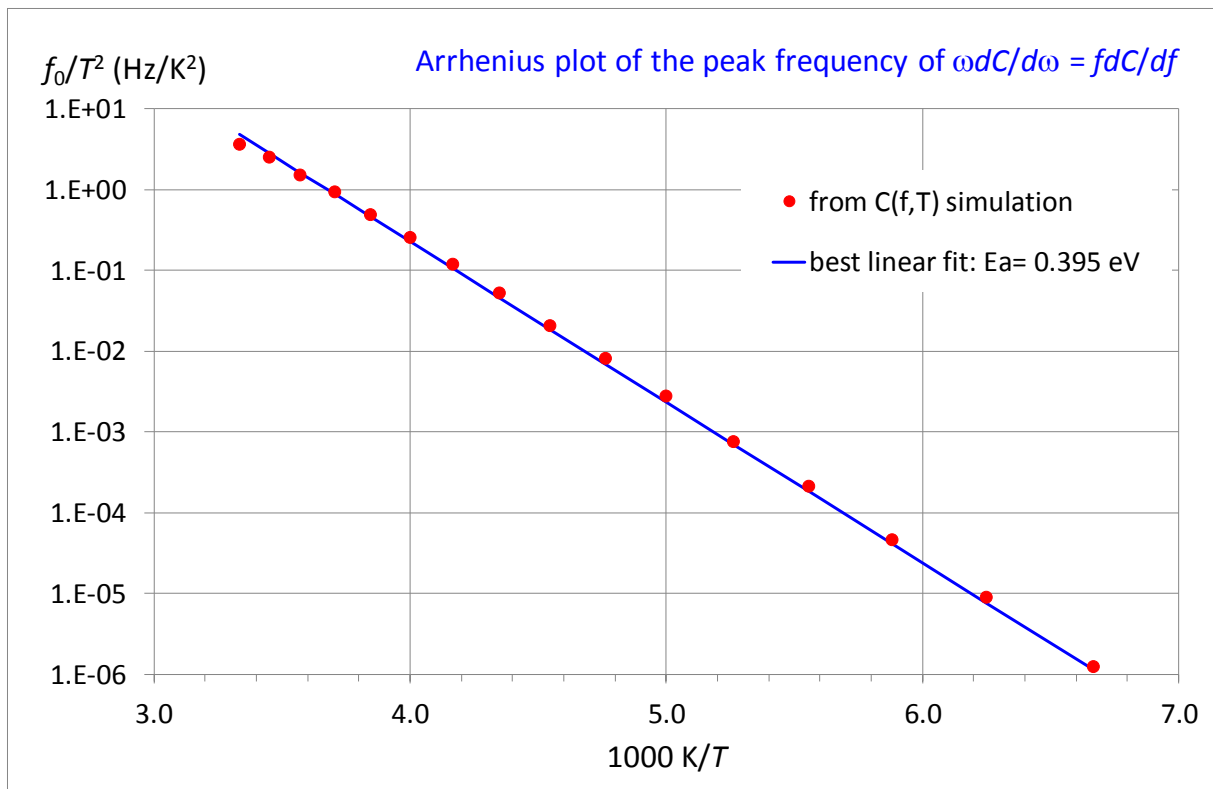
This is shown in Fig. 20.

Fig. 20   'Suitable' Arrhenius plot of f_0, the 'inflection frequency' or 'peak frequency' of the 'derivative' (see text for this terminology). From the slope, an activation energy of 0.395 eV is deduced, meaning that the trap level is at E_V + 0.395 eV (holes assumed) or E_C − 0.395 eV (electrons assumed). From the intercept with the vertical axis, $\xi_0 = 2 \times 10^7$ Hz/K^2 is deduced.

The activation energy deduced from this Arrhenius plot is E_a = 0.395 eV. It is an excellent estimation of the trap energy input value of 0.40 eV. The ξ_0 value derived from the intercept with the vertical axis deviates from the value we found by trial and error in the previous section; one should realise there is much more inaccuracy in determining an intercept by extrapolation, than a slope.

7.4   AS analysis of real measurements

AS analysis of real $C(f, T)$ measurements is a lot more complicated than could be thought after seeing the nicely 'constructed example' of the previous sections. A few thoughts:

- Since numerical derivation is involved, the *C-f* measurements or simulations should contain enough frequency points; 10 points per decade seems a minimum
- Numerical derivation of measurement data is always inaccurate: the measurement could contain stochastic measurements errors, causing oscillations in the derivative. Often, a set of $C(f, T)$ measurement can take advantage of a smart smoothing of the data before processing (involving taking the derivative).
- In a real cell that is measured, one cannot know in advantage how many different defects are involved/play a role. An indication can be the number of maxima seen in the |derivative| of a single *C-f* curve. But some defects could only be visible (as a maximum) at the lower temperatures of the measurement *T*-range, others at the higher temperatures. And in general, it could be quite problematic to follow a

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specific maximum, attributed to a specific defect number) over the different $C(f, T)$ measurements. In any case, it is advantageous to measure with small ΔT intervals.

- o For each maximum seen, one can, if all goes well, draw the suitable Arrhenius plot, and thus derive the (E_a, ξ_0) values of this defect. But the method, and thus the SCAPS AS panel, cannot tell you in which layer the defects are located, and if the charge/discharge process of the defects are by electrons or holes: that is interpretation (guess?) work for the user. All extra information about defects will be welcome!
- o The text above should be considered as a tutorial for beginners entering the field of defect research in solar cells, nothing more. Consult and study the vast (and not always easy) literature!

8. New script commands in SCAPS 3.3.06

The SCAPS script has been extended to handle the new functionalities in the Mott-Schottky analysis panel, see Table 1.

Table 1 SCAPS script commands associated to the Mott-Schottky analysis panel. Some were already existing, others are new in SCAPS 3.3.06.

	Value
set numerical.CV-analysis.NW-mode.constant_epsilon	
set numerical.CV-analysis.NW-mode.actual_epsilon	
set numerical.CV-analysis.constant_epsilon	ε_s value
set numerical.CV-analysis.layer	layer number
set numerical.CV-analysis.side	+ = right, - = left
set numerical.CV-analysis.points	for numerical
set numerical.CV-analysis.order_middle	derivation
set numerical.CV-analysis.order_edge	$d(1/C^2)/dV$
set numerical.Cf-analysis.layer	same as … CV-analysis…
set numerical.Cf-analysis.defect	defect number
set numerical.Cf-analysis.level	level number
set numerical.Cf-analysis.eh-type.electrons	
set numerical.Cf-analysis.eh-type.holes	