

Comparing numerical results with experimental data

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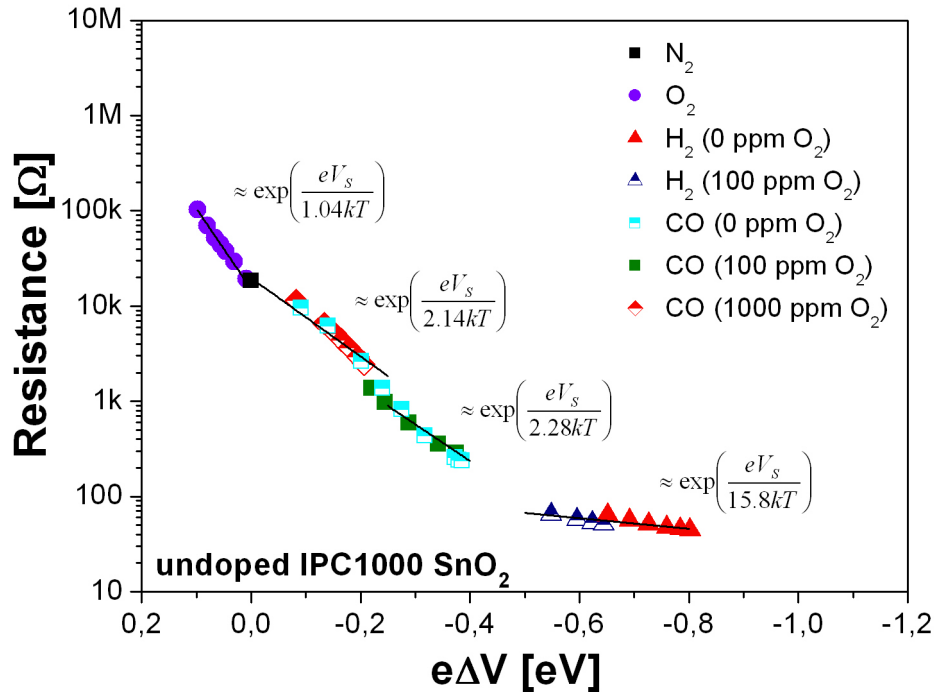
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1 Abstract

Experimental data from simultaneous work function and resistance measurements will be compared with the results from the numerical calculations. Results from an SnO_2 gas sensor measured at 300°C will be used to demonstrate, how numerical data can be used to gain more insights about the measured material. The dataset of the graphical representation below originates from the Phd. thesis of Julia Rebholz: [Reb16].

The data was generated by exposing the sensor to various gas compositions of H_2 , CO , O_2 and N_2 . The surface potential changes ΔV resulting from the different gas atmosphere have been obtained with the Kelvin probe technique. Simultaneously the corresponding resistance was measured. The data point point at $0e\Delta V$ corresponds to the situation in nitrogen.

These experimental data points will be compared with the results obtained from the numerical simulation.



This figure shows the dependency of the resistance on the band bending changes for the undoped SnO_2 nanopowder based gas sensor. $e\Delta = 0$ is denoted as the situation in N_2

2 Fitting experimental data to numerical results

2.1 Importing experimental and numerical data

The experimental data is saved in an excel file, which will be loaded by using the tools provided by pandas.

```
[1]: #Setting up the env.
from part2 import *
import pandas as pd
%pylab inline

#importing the data
calc_dF = pd.read_hdf('numerical_sol.h5','raw')
dF_1000 = pd.read_excel('Kelvin_Data.xlsx', sheet_name='ipc1000').
    ↳sort_values(by='dV')

#instead of unsing the row number
#each row has the value of dV as index
dF_1000.index = dF_1000['dV']
```

Populating the interactive namespace from numpy and matplotlib

2.2 Representing the raw data

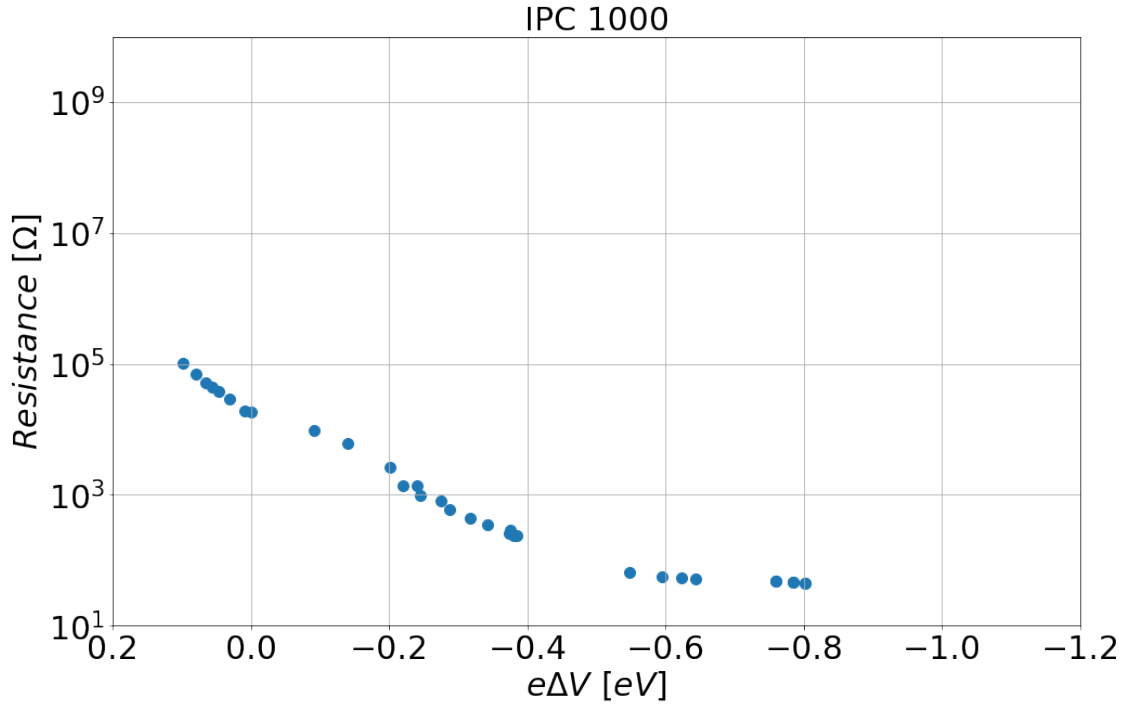
```
[2]: def format_axe(axe, ylabel = None, set_ylim=False):
    labelsz = 30
    if set_ylim:
        axe.set_ylim((1e-4,1e3))
    axe.set_yscale('log')
    axe.set_xlim((0.2,-1.2))
    if ylabel:
        axe.set_ylabel(ylabel, fontsize = labelsz)
    else:
        axe.set_ylabel(r'$\frac{R_{V_S}}{R_{(V_S=0)}}$', fontsize = labelsz)
    axe.set_xlabel('$e\Delta V$ [eV]', fontsize = labelsz)
    axe.tick_params(axis='both', which='both', labelsz=labelsz)
    axe.grid()

fig, axe = subplots(figsize=(16,10))

sens, dF = 'IPC 1000',dF_1000

v_exp = dF['dV']

res_exp = dF['res']
axe.set_title(sens, fontsize = 30)
axe.scatter(v_exp,res_exp, s=100)
format_axe(axe,ylabel='$Resistance$ [$\Omega$]')
axe.set_ylim(res_exp.min()/2,res_exp.max()*2);
axe.set_ylim(10,10e9);
```



This figure represents the experimental data as show before, but plotted using the Python environment. The dependency of the resistance on the band bending changes is shown for the undoped SnO_2 nanopowder based gas sensor. $q\Delta V = 0$ is denoted as the situation in N_2 .

2.3 From R_{V_s} to ΔR_{V_s}

In the experimental dataset the value at $0qV_s$ represent the data points measured under nitrogen. Therefore $\Delta R_{V_s} = \frac{R_{V_s}}{R_0}$ is calculated by :

- First: derive the resistance R_0 under nitrogen
- Second: divide all resistance values R_{V_s} by R_0

```
[49]: from scipy.optimize import curve_fit
from scipy.interpolate import interp1d

fig, axe = subplots(1, figsize=(16,10))

#get the value of the flatband (if needed)
#by interpolation
interp_res = interp1d(v_exp,res_exp)
res_flatband = interp_res(0)

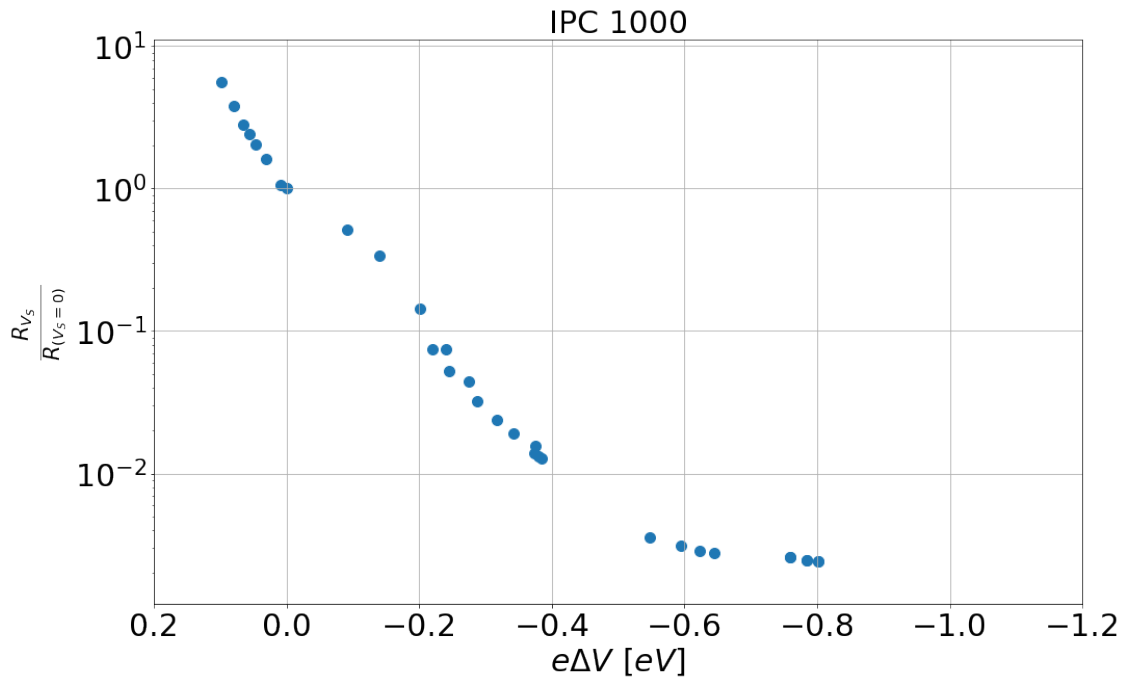
#calcualte the rel. res change
rel_res_exp = dF['res']/res_flatband
```

```

#represent it
format_axe(axe)
axe.scatter(dF['dV'],rel_res_exp, s=100)
axe.set_ylim(rel_res_exp.min()/2,
             rel_res_exp.max()*2);
axe.set_title(sens, fontsize = 30)

```

[49]: Text(0.5, 1.0, 'IPC 1000')



The resistances have been normalized to the resistance at $q\Delta = 0$

2.4 Interpolating the numerical values

In the previous section, the numerical solution for multiple start parameters have been calculated. Nevertheless most probably the calculated dataset will not hold exactly the same values of qV_s as gathered from the experiment. To obtain the numerical value for a specific experimental value of qV_s a interpolation between of the existing numerical values will be used again. For all different numerical grains ΔR_{V_s} will be calculated for all values of qV_s from the experimental data. Once this is done, the different between the numerical model and the exp. data can be calculated and evaluated.

```

[50]: #The dataframe to hold the different
      #of the exp. values to the numerical ones
      #Will be used to find the best fitting num. solution

```

```

num_data_at_exp_pos_dF = pd.DataFrame(index = v_exp)

#group the num. data by its paramters (T, R and ND)
data_by_grain = calc_dF.groupby(['temp', 'R', 'ND'])

for (T, R, ND), calc_dF_grain in data_by_grain:

    num_data_at_exp_pos_dF[(T, R, ND)] = None

    grain = create_grain_from_data(calc_dF_grain)

    flat_band_data = calc_dF_grain[calc_dF_grain['Einit_kT']==0].iloc[0]

    rel_res_num = calc_dF_grain['rel_res_change']

    #express the surace potential in eV
    #to be comparable with the exp. data
    v_num = calc_dF_grain['Einit_kT']*CONST.J_to_eV(grain.material.kT)

    #use interpolation to get the values for the positions
    #of the experiment data points
    interp_rs_num = interp1d(v_num, rel_res_num, bounds_error=False)
    interp_v_num = interp1d(rel_res_num, v_num, bounds_error=False)

    #caculate the numerical value of rel. res at the position
    # of V from the experiment
    res_num_at_exp_pos = interp_rs_num(v_exp)

    #save those values in the new DataFrame
    num_data_at_exp_pos_dF.loc[:, (T, R, ND)] = res_num_at_exp_pos

```

2.5 Calculating the fit error

num_data_at_exp_pos_dF contains now the values of ΔR_{V_s} at the positions qV_s . From these values the relative error needs to be calculated. The following formula is used to derive the error:

$$\epsilon_{V_s} = \left(\frac{R_{numerical}(qV_s) - R_{experiment}(qV_s)}{R_{experiment}(qV_s)} \right)^2 \quad (1)$$

The sum of all ϵ_{V_s} is the total error of the fit. The numerical model with the lowest value of $\sum \epsilon_{V_s}$ is the model which fits best to the experimental data. The average grain diameter of the material “IPC1000” is known to be in average radius of 55nm (diameter of 110nm) [DRRM⁺99]. The dataset we created in the previous section includes models for grains with radii of 50nm and 100nm. Therefore we can narrow the fit algorithm down, to take only models with a radius of 50nm and 100nm into account

```
[51]: abs_error = num_data_at_exp_pos_dF.subtract(rel_res_exp, axis='index')
rel_error = abs_error.divide(rel_res_exp, axis='index')
rel_error_square = rel_error**2
sum_of_squares = rel_error_square.sum()

valid_index = [i for i in sum_of_squares.index if i[1] in [50e-9,100e-9]]

sum_of_squares_grainsize = sum_of_squares.loc[valid_index].sort_values()

grain_min_error_tuple = sum_of_squares_grainsize.idxmin()
best_fits_error_dF = pd.DataFrame({'error':sum_of_squares_grainsize})

T_temp = [i[0] for i in best_fits_error_dF.index]
R_temp = [i[1] for i in best_fits_error_dF.index]
ND_temp = [i[2] for i in best_fits_error_dF.index]
best_fits_error_dF['T'] = T_temp
best_fits_error_dF['Radius'] = R_temp
best_fits_error_dF['$N_D$'] = ND_temp
best_fits_error_dF.index = range(len(best_fits_error_dF))

display(best_fits_error_dF)

caption = Latex(r'''\begin{center}
Table with the best fit parameters
\end{center}''')
display(caption)
```

	error	T	Radius	N_D
0	6.822288	300.0	5.000000e-08	1.000000e+22
1	7.665906	300.0	1.000000e-07	1.000000e+22
2	14.358742	300.0	1.000000e-07	1.000000e+21
3	18.771491	300.0	5.000000e-08	1.000000e+21
4	175.204658	300.0	5.000000e-08	1.000000e+23
5	1256.744498	300.0	1.000000e-07	1.000000e+23
6	9905.878196	300.0	5.000000e-08	1.000000e+24
7	39709.781227	300.0	1.000000e-07	1.000000e+24

Table with the best fit parameters

2.6 Representation of the fit

Finally the best fit results can be represented graphically.

```
[70]: fig, axe = subplots(figsize = (16,10))
#for grain_tuple in num_data_at_exp_pos_dF.keys():
for grain_tuple in sum_of_squares.index:
    if grain_tuple == grain_min_error_tuple:
```

```

        linestyle = '*-'
        linewidth = 5
        alpha = 0.5
        label = 'Best Fit'
    elif grain_tuple in sum_of_squares_grainsize.index[0:2]:
        linestyle = '-o'
        linewidth = 5
        alpha = 0.3
        label = 'Second best fit'
    else:
        linestyle = '-.'
        linewidth = 1
        alpha = 0.3
        label = 'Other solution'

    axe.plot(num_data_at_exp_pos_dF.index,
            num_data_at_exp_pos_dF[grain_tuple],
            linestyle, linewidth=linewidth, alpha = alpha,
            label =label)

    last_x = num_data_at_exp_pos_dF.index[0]
    last_y = num_data_at_exp_pos_dF.iloc[0][grain_tuple]

    if grain_tuple in sum_of_squares_grainsize.index[0:1]:
        axe.text(last_x-0.05,last_y,
            f'Radius:{grain_tuple[1]*1e9:.0f}nm\n{n$N_D$:{grain_tuple[2]:.2} 1/m3',
            fontsize=22)
format_axe(axe)

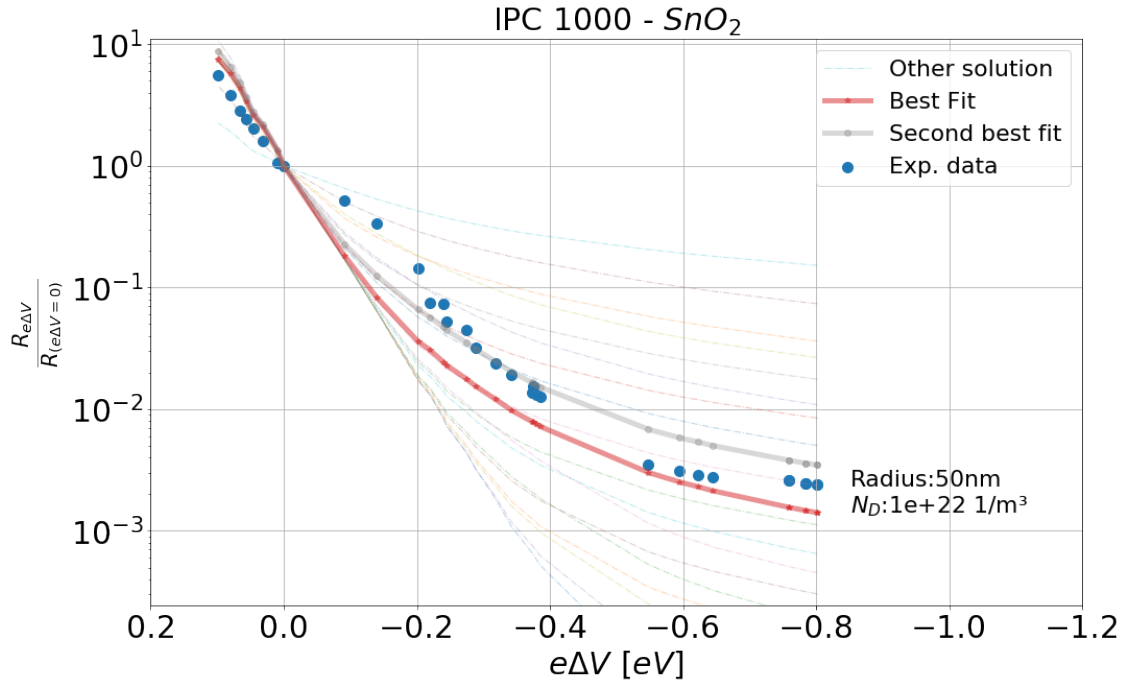
axe.scatter(rel_res_exp.index,
            rel_res_exp,
            s=100,
            label = 'Exp. data'
            )

axe.set_ylim(rel_res_exp.min()/10,
            rel_res_exp.max()*2);

l = {h[1]:h[0] for h in zip(*axe.get_legend_handles_labels())}.keys()
h = {h[1]:h[0] for h in zip(*axe.get_legend_handles_labels())}.values()
axe.legend(h,l,loc=1, fontsize = 22)
axe.set_title(sens, fontsize = 30)

```


[70]: Text(0.5, 1.0, 'IPC 1000 - SnO_2 ')



Comparison of the numerical results with the experimental data points

2.7 Summary

The two best fits do not fit perfectly to the experimental data. One obvious reason is the coarse screening of the grain size and N_D . A additional simulation of grains with a radius of 55 nm and a finer screening of N_D will turn out to be helpful for a better result of the fit. On the other side the fitting shows, that the experimental data fits will to a grain with approximately 50nm radius and a defect concentration of around $N_D = 1 \times 10^{22} \text{ 1/m}^3$ at 300°C.

3 Second iteration

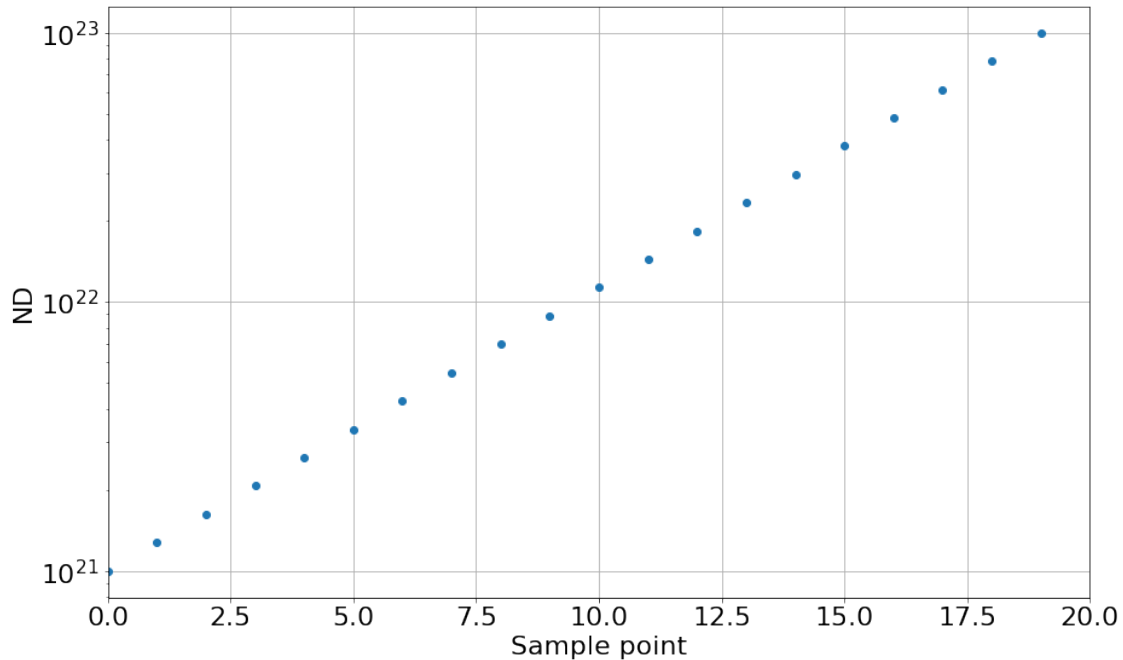
With the approximate values of the correct model, the previous steps of creating a look-up table for multiple model is repeated. This steps is not shown in this work. Basically the screening of the parameters is limited to grains with a radius of 55 nm and a value of N_D between 1×10^{21} and 1×10^{23} . For the second iteration 20 values between these boundaries have been selected. The points are evenly spaced on a logarithmic scale. The numpy function logspace was used for this purpose.

```
[7]: NDs = np.logspace(21,23,20)
fig, axe = subplots(figsize=((1+5**0.5)/2*9,9))
axe.plot(NDs, 'o')
axe.set_yscale('log')
```

```

axe.set_ylabel('ND', fontsize = 22)
axe.set_xlabel('Sample point', fontsize = 22)
axe.set_xlim(0,20)
axe.tick_params(axis='both', which='both', labelsize=22)
axe.grid()

```



The results from the new numerical calculation are saved in a file called “numerical_sol_4_part_4_ipc1000_55nm.h5” and will be loaded in the next cell. For refitting the results the above procedure is repeated with the new numerical dataset. The required steps to fit the data and represent the results are exported in a new function called `fit_exp_with_num_data`. This function needs the exp. dataset, the numerical dataset, a title for the figure and optionally a text for the caption. With these arguments the output of the fit is represented in the notebook.

```

[4]: from IPython.display import display, Math, Latex
      from fit_exp_data import fit_exp_with_num_data

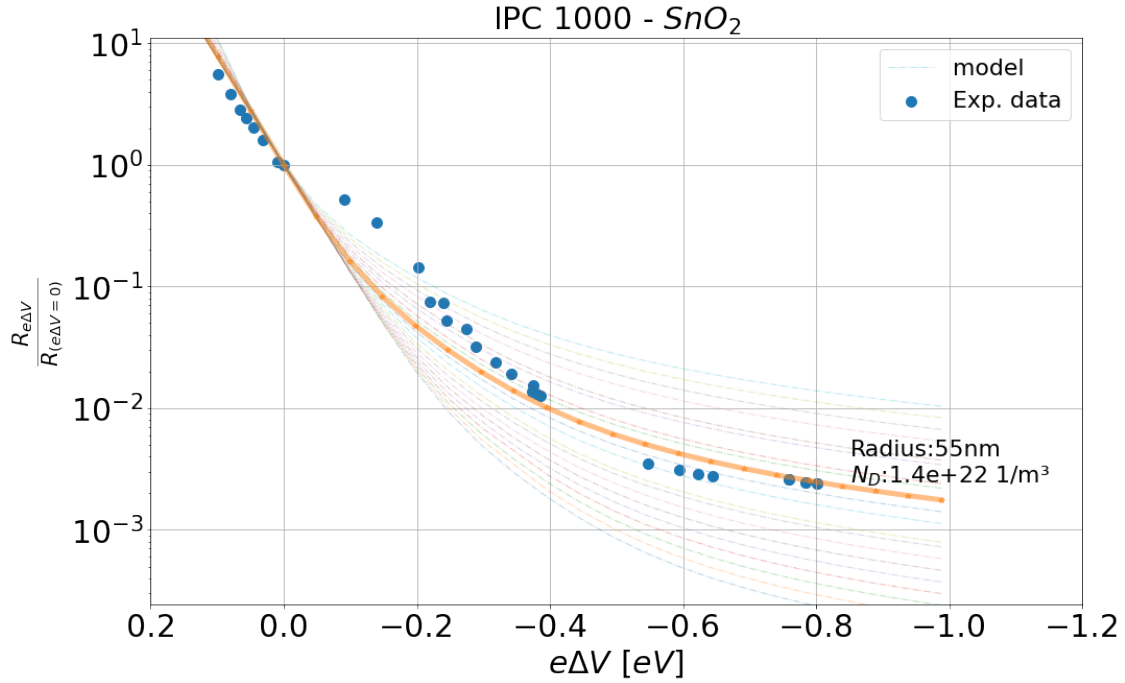
      calc_dF = pd.read_hdf('numerical_sol_4_part_4_ipc1000_55nm.h5', 'raw')

      #calc_dF = pd.read_hdf('numerical_sol.h5', 'raw')
      dF_exp = pd.read_excel('Kelvin_Data.xlsx', sheet_name='ipc1000').
          ↳sort_values(by='dV')

      caption_figure = 'Optimized fit with a finer screening of the parameters'

```

```
sens = 'IPC 1000 - $SnO_2$'
bf = fit_exp_with_num_data(dF_exp, calc_dF, sens=sens, caption_figure='Best fit_
→results with finer screening of parameters.')
```



Best fit results with finer screening of parameters.

	error	T [°C]	Radius [nm]	N_D [1/m]
0	4.427580	300.0	55.0	1.438450e+22
1	4.782059	300.0	55.0	1.128838e+22
2	5.665853	300.0	55.0	1.832981e+22
3	5.986754	300.0	55.0	8.858668e+21
4	6.967131	300.0	55.0	2.335721e+22
5	8.322148	300.0	55.0	6.951928e+21
6	9.304737	300.0	55.0	5.455595e+21
7	10.971085	300.0	55.0	4.281332e+21
8	12.569745	300.0	55.0	3.359818e+21
9	13.993224	300.0	55.0	2.636651e+21

Table with the best fit parameters

IPC 1000 - SnO_2	
$E_C - E_F$	0.29 eV
N_D	1.44e+22 1/m ³
n_b	2.87e+22 1/m ³
L_D	30.60 nm

Table with material properties of the best fitting material.

4 Results for a commercial available SnO_2

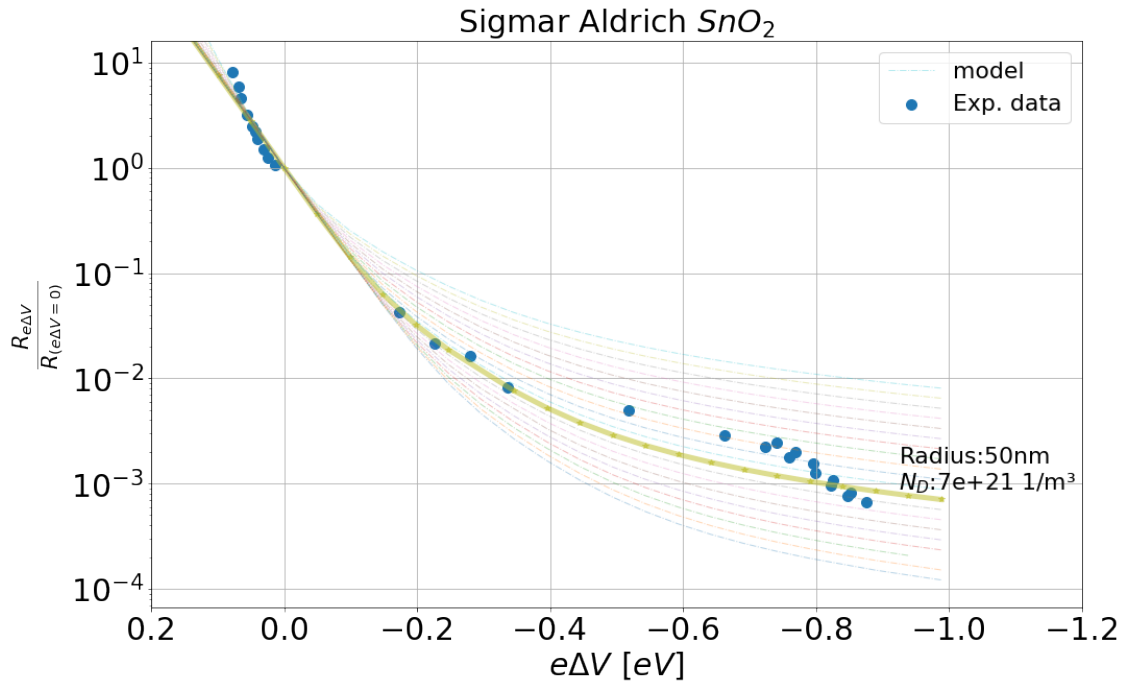
In the thesis of Julia Rebholz [Reb16] the commercially available " SnO_2 " from Sigmar Aldrich was also tested. In the next part experimental results from simultaneous work function and resistance measurements are being fitted with numerical results. The average grain radius of this material is around 50nm

```
[67]: from IPython.display import display, Math, Latex
      from fit_exp_data import *

      calc_dF = pd.read_hdf('numerical_sol_4_part_4_SA_50nm.h5','full')

      dF_exp = pd.read_excel('Kelvin_Data.xlsx', sheet_name='SA_Benni').
      →sort_values(by='dV')

      caption_figure = 'Optimized fit with a finer screening of the parameters'
      sens = 'IPC 1001'
      bf = fit_exp_with_num_data(dF_exp, calc_dF, sens='Sigmar Aldrich $SnO_2$',
      →caption_figure='Best fit results with finer screening of parameters.')
```



	error	T [°C]	Radius [nm]	N_D [1/m]
0	2.379963	300.0	50.0	6.951928e+21
1	2.546552	300.0	50.0	8.858668e+21
2	3.129596	300.0	50.0	5.455595e+21
3	4.300544	300.0	50.0	4.281332e+21
4	4.370771	300.0	50.0	1.128838e+22
5	5.592128	300.0	50.0	3.359818e+21
6	6.953802	300.0	50.0	2.636651e+21
7	8.195738	300.0	50.0	2.069138e+21
8	9.110344	300.0	50.0	1.438450e+22
9	9.314258	300.0	50.0	1.623777e+21

Table with the best fit parameters

	Sigmar Aldrich SnO_2
$E_C - E_F$	0.33 eV
N_D	6.95e+21 1/m ³
n_b	1.39e+22 1/m ³
L_D	44.01 nm

Table with material properties of the best fitting material.

5 Conclusion

In this last section the calculations from the numerical model have been fine tuned for different SnO_2 materials. The model's parameter of the grain radius and temperature have been fixed corresponding to the values from the experimental results. Additionally the parameter of the defect concentration N_D was screen in fine grained steps around the estimated value. The resulting numerical datapoints were fitted against the experimental results. With the best fitting numerical model otherwise hidden intrinsic properties of the semiconducting material have been computed.

It could be shown, that the numerical method to describe the relation between surface potential change ΔV_S and resistance change ΔR with respect to the grain radius R , operation temperature T and defect concentration N_D is suitable to fit experimental results and gain additional information about the sensor as:

1. Distance between the conduction band (E_C) and the Fermi level (E_F)
2. Concentration of defects in the bulk N_D
3. Concentration of free charge carriers in the conduction band in the bulk n_b
4. Debye length L_D of the semiconductor

6 Bibliography section

References

[DRRM⁺99] DIÉGUEZ, A. ; ROMANO-RODRÍGUEZ, A. ; MORANTE, J. R. ; KAPPLER, J. ; BÂRSAN, N. ; GÖPEL, W.: Nanoparticle engineering for gas sensor optimization: Improved

sol-gel fabricated nanocrystalline SnO₂ thick film gas sensor for NO₂ detection by calcination, catalytic metal introduction and grinding treatments. In: *Sensors and Actuators, B: Chemical* 60 (1999), nov, Nr. 2, S. 125–137. [http://dx.doi.org/10.1016/S0925-4005\(99\)00258-0](http://dx.doi.org/10.1016/S0925-4005(99)00258-0). – DOI 10.1016/S0925-4005(99)00258-0. – ISSN 09254005

- [Reb16] REBHOLZ, Julia M.: *Influence of Conduction Mechanism Changes and Related Effects on the Sensing Performance of Metal Oxide Based Gas Sensors*. Shaker Verlag, 2016. – 127 S. – ISBN 978-3-8440-4832-2