Percolation model for a selective response of the resistance of composite semiconducting np-systems towards reducing gases

Stefanie Russ

1Institut für Theoretische Physik, Arnimallee 14, Freie Universität Berlin, 14195 Berlin, Germany

(Dated: July 25, 2014)

It is shown that a two-component percolation model on a simple cubic lattice can explain an experimentally observed behavior \[1\], namely that a network built up by a mixture of sintered nanocrystalline semiconducting n- and p-grains can exhibit selective behavior, i.e. respond with a resistance increase when exposed to a reducing gas A and with a resistance decrease in response to another reducing gas B. To this end, a simple model is developed, where the n- and p-grains are simulated by overlapping spheres, based on realistic assumptions about the gas reactions on the grain surfaces. The resistance is calculated by random walk simulations with nn-, pp- and np-bonds between the grains and the results are found in very good agreement with the experiments. Contrary to former assumptions, the np-bonds are crucial to obtain this accordance.

PACS numbers: 64.60.ah, 68.35.bg, 73.63.Bd

I. INTRODUCTION

The percolation model is well-known for its ability to describe a phase transition between an insulating and a conducting phase and has already been used to describe insulator-conductor transitions in electrolytes, two-component conductors, binary glasses and more (for an overview see e.g. \[2\]). In \[3\], it was proposed that a disordered system of sintered nanocrystalline semiconducting n-grains should act as a gas sensor \[4\], i.e. switch from the insulating to the conducting phase in response to a reducing gas. The mechanism based on the percolation effect is the following: In normal air, according to a standard model \[3, 8\], oxygen adsorbs at the grain surface and traps mobile electrons (see Fig. 1(a)), so that smaller grains are insulating. When the oxygen coverage is reduced by a reaction of the oxygen with a reducing gas, more and more grains become conducting until the concentrations of conducting grains and bonds both exceed the so-called critical concentrations \[9\]. Then, the resistance \( R \) of the system jumps to a much smaller order of magnitude allowing for the detection of the gas. (For an overview of percolation effects in gas sensors see \[10\]).

However, this transition alone delivers no information on the type of the reducing gas. The ability of a sensor to answer differently to different gases is named “selectivity” and is – even if highly desirable – difficult to achieve \[11, 12\]. One approach is to compose a sensor of two types of grains, one of them decreasing and the other one increasing \( R \) with increasing gas concentration, as e.g. semiconducting n- and p-grains \[1, 13\]. Such a composite system should be able to respond with a resistance increase as well as with a decrease to the gas exposure and even a mutual neutralisation of both effects is conceivable. The challenge is to find one specific system that can show both, increase and decrease of \( R \), depending on the gas. Experimentally, such a behavior has been reported on systems of sintered TiO\(_2\) grains in the two representations anatase and rutile \[1\] that have been reported as n- and p-semiconductors, respectively. A sample with a volume ratio 1:3 of n-anatase to p-rutile was found to show (nearly) no response to CH\(_4\) but react with a resistance decrease to CO. Percolation effects have been assumed responsible for this interesting behavior.

In this paper, I develop a simple model, based on the percolation model, that captures the essential properties of composite gas sensors and show by computer simulations that different coexisting percolating pathways can indeed cause a selective behavior towards different reducing gases. Similar to the observations of \[1\] I show that certain composite systems can show no reaction or even an increase of \( R \) to a gas A and a decrease of \( R \) to another gas B. However, contrary to the assumptions of \[1\], I show that bonds between n- and p-grains play a major role for a selective behavior as they couple the two types of paths. Both types of grains are modelled in reasonable approximations under the influence of adsorbed...
oxygen, thereby applying basic microscopical concepts \[3, 14, 16\]. Different gases are distinguished by their reaction rates with the adsorbed oxygen, expressed by appropriate “reaction factors” \( \alpha_n \) and \( \alpha_p \) that describe the ratio of oxygen that reacts with the considered gas on n- and on p-surfaces, respectively. All grains are now conducting (in contrast to the works of \[3, 9\]), i.e. the n-grains are not too small.

The paper is organized as follows: In section II, the microscopical picture of the single grains is explained, while section III describes how the grains are organized in networks and how the resistances are computed. Section IV presents the results and in the final section V, the specifics and simplifications of this model are discussed, as well as possible extensions.

II. MICROSCOPICAL PICTURE

Surface effects on n-grains

The standard Schottky model of an n-grain under the influence of oxygen \[3, 7, 11, 17, 18\] at not too high temperatures (where surface- are dominant over bulk reactions) is depicted in Fig. 1(a): in normal air, oxygen is adsorbed on the grain surface and traps electrons from the conduction band, so that the grains are covered by oxygen ions. This way, a negative surface charge arises at the grain surface and traps electrons from the conduction band, so that the grains are covered by oxygen ions. In Schottky approximation, one assumes that each gas molecule reacts with one oxygen atom. As fully ionized, adsorbed oxygen by the condition of “charge neutrality” \( eV \) and \( N \) are already been used in \[3, 5, 9, 19, 20\]. From solving the 1D-Poisson equation, where the work function

\[
eV = \exp \left( \frac{eV_s}{k_B T} \right) - \frac{eV_s}{k_B T} - 1 \right)^{1/2} + 1.
\]

The reaction factor \( \alpha_n \) is related to the equilibrium rate of the reaction between oxygen and reducing gas and describes the fraction of gas that reacts with the adsorbed oxygen. A simpler version of Eq. \( \lambda \) has already been used in \[3, 9\] with \( \alpha_n = 1 \), i.e. under the assumption that each gas molecule reacts with one oxygen atom. As surface reactions on different types of grains are compared here, I apply the more realistic assumption that \( \alpha_n \leq 1 \). Clearly, \( \alpha_n \) differs from the respective reaction factor on p-grains.

Surface effects on p-grains

Also the p-grains can be described by a positively charged shell and a neutral core \[10\] (see Fig. 1(b)), where the volume density of positive holes in the core equals the acceptor density \( N_A \). When oxygen adsorbs at the surface of p-grains, it traps electrons from the valence band thereby creating additional holes. Therefore, also on the surface of p-grains a positively charged shell arises but instead of a depletion layer (as on n-grains) it represents an accumulation layer. This means that the density of mobile holes \( N_A^+ \) inside the p-shell is even increased as compared to the hole density of the core, i.e. \( N_A^+ > N_A \). \( N_A^+ \) depends on the potential \( V_s \) and the temperature \( T \) via the Boltzmann distribution. Contrary to the value of \( N_D^-(\text{n-grains}) \) that is simply set to zero, the mean density \( N_A^+ \) of mobile holes in the accumulation layer must also be determined. This has been done in \[16\] based on prior considerations from \[15\] under the assumption that the grain diameter \( D \) is much larger than the thickness of the accumulation layer, yielding

\[
N_A^+ = N_A \left( \frac{\exp \left( \frac{eV_s}{k_B T} \right) - \frac{eV_s}{k_B T} - 1 \right)^{1/2} + 1 \right)^{1/2}.
\]

(In the following, I account for the condition \( D \gg \lambda_p \) by choosing \( D \approx 100 \text{ nm} \).) Also other parameters for p-grains can be taken from \[16\]: The thickness \( \lambda_p(0) \) of the accumulation layer in normal air is normally attributed to the Debye length \( L_D = (\varepsilon_0 \varepsilon_r k_B T / N_A e^2)^{1/2} \) with the Boltzmann constant \( k_B \) as \( \lambda_p(0) \approx \sqrt{2} L_D \), while \( eV_\text{s} \) has been specified as between 0.3 and 0.6 eV and \( N_A \) between 1.4 \( \times 10^{-4} \text{ nm}^3 \) and \( 10^{-1} \text{ nm}^3 \). With \( T \approx 500 \text{ K} \), this leads to \( \lambda_p(0) \) between 0.7 nm and 16.5 nm and a ratio \( N_A^+ / N_A \) between 30 and 1000. The surface density of initially adsorbed oxygen is again obtained via the charge neutrality as \( N_{\text{ox, p}} = \lambda_p(0) \cdot (N_A^+ - N_A) \), leading to values of \( N_{\text{ox, p}}^0 \) between about \( 8 \times 10^{-2} \text{ nm}^2 \) and \( 70 \text{ nm}^2 \), which means that \( N_{\text{ox, p}}^0 \approx N_{\text{ox, n}}^0 \), as already pointed out in \[3\]. In order to control the response of the systems by \( \lambda_p \), I rely to those values (inside this range), where \( \lambda_p(0) \) is not too small, i.e. \( N_A \) not too large.

Under the influence of a reducing gas, \( \lambda_p(0) \) can be
estimated in complete analogy to (1) as
\[
\lambda_p(N_r) \approx \frac{N_{ox,p}^0 - \alpha_p N_r}{N_A^+ - N_A} = \lambda_p(0) \cdot (1 - \frac{\alpha_p N_r}{N_{ox,p}^0}),
\]
where \(\alpha_p\) describes the reaction rate between the reducing gas and the oxygen on the surface of p-grains. We can see from Eqs. (1) and (3) that the thicknesses of the shells are largest, when the grain surfaces are covered solely by adsorbed oxygen, i.e. when \(N_r = 0\).

III. NUMERICAL SIMULATIONS

The random walk method

The mapping of a complicated composite system onto a percolation problem has been discussed for several decades [21-24]. In a general system of overlapping conducting particles inside a matrix of lower conductance, different types of contacts between particles may occur. A model example is the "checkerboard", i.e. a 2D or 3D system of squares or cubes of different materials that touch each other by nearest-neighbor contacts (via the borders) and by next-nearest neighbor point contacts via the corners (where paths around the edges through neighboring units may be involved [22]). It has been shown since long that percolation thresholds and exponents of these systems differ from the ones of the corresponding properties of percolating networks, where the squares (or cubes) have been replaced by discrete sites connected by bonds and that the corner contacts between next-nearest neighbors may even lead to a second percolation threshold [21, 23]. Different "mixing rules" telling us, in which geometrical shapes and with which connections disordered heterogeneous media should be mapped onto lattices have been established [24] and tested by comparing the numerical solutions of different physical properties, as e.g. conductance or admittance gained on discretized lattices to the exact solutions [23, 25]. However, while checkerboard problems can be solved analytically and numerically by discretizing the systems [22], for the majority of systems, clear mixing rules are not available [24].

In the systems of this work, n- and p-grains with similar conductances are sintered together. We consider well-sintered grains, where the electron hopping across grain-boundaries can be neglected [19, 20], especially when the grain surfaces are rough [27]. Conductance over next-nearest neighbors by a direct (small) overlap or a point contact is in principle possible if both next-nearest neighbors are big enough, but for the system parameters chosen here the contribution to the conductance can be considered as much smaller than conductance over nearest neighbors (see below for the sintering parameter \(\Theta\)).

Here, it is not our aim to reproduce the exact resistance of a given system, but to understand the qualitative behavior, namely if percolation effects are able to influence the reaction of such systems towards different gases in a way that the same system can show increasing, decreasing or constant resistance as a function of the surface gas density. Therefore, we consider the relative resistance \(R(N_r)/R(0)\), i.e. the ratio between the resistances with and without gas, so that all specific material properties that vary only slowly with \(N_r\) cancel out. The model system has been maintained simple: the resistances have been calculated by random walk simulations [2, 11, 28] on a disordered cubic lattice, where the sites represent simplified n- or p-grains, bonds between nearest-neighbor sites have been estimated from the area of the conducting overlap between them and next-nearest neighbor contacts have been neglected. To this end, the nanogranular films are mapped onto a simple cubic network of size \(N \times N \times N\), and lattice constant \(a\), consisting of sites and bonds between the sites. \(N_z\) is the number of monolayers and \(N \gg N_z\). Random walk simulations are a well-explored method to calculate the specific resistance \(\rho\) of discretized disordered systems. I shortly illustrate the random walk method with the help of Fig. 2 where a single random walk of 50 time steps is shown on a square lattice. The 1st 50 steps of this walk are shown in Fig. 2(a) in a schematized picture, while 2(b) shows \(r(t) = \sqrt{r^2(t)}\) of this walk as a function of \(t\). The walker starts at the lattice site labeled with "0" and performs an irregular trajectory \(r(t)\). Finally, in (c) we see the "mean square displacement" \(\langle r^2(t)\rangle\) averaged over 1, 102 and 104 realizations and can see that in average \(\langle r^2(t)\rangle\) gives a straight line, i.e. \(\langle r^2(t)\rangle \sim t\).

The macroscopic resistance \(R\) of a layer of cross-section \(A\) and length \(L\) is proportional to the specific resistance \(\rho\) by \(R = \rho L/A\), where \(\rho\) is inversely proportional to the diffusion coefficient (and thus to the mobility of the charge carriers), via the Einstein relation [24, 30]. Different definitions of the diffusion coefficient may come into play and the underlying assumption of the random
of non-interacting particles [31, 32]. This means that
tioned, but in the end always found valid for the case
ever, an additional effect might come into play, namely
the dependence of the electron density on the chemical
dition coefficient “chemical diffusion coefficient”
the chemical system. As the Boltzmann statistics is inherent to
eq \frac{1}{2N} \sum_{j \neq i} \left( \frac{1}{2} \delta_{\text{pp}} C_{ij} + \delta_{\text{np}} C_{ij} \right)
while \( D \) is the “thermodynamic factor” that accounts for
between the grains, we find \( \frac{R(N_c)}{R(0)} \) from the
verse ratio of the diffusion constants \( D_s(0)/D_s(N_c) \) that
are computed with an average over \( 10^6 \) systems. For this
first analysis, differences between hole and electron mo-
bility are neglected as well as the different sizes of n- and
in the following. Schematic models of overlapping grains with a geo-
mical neck of diameter \( \Delta_0 \) between them: (a) nn-bond, (b) pp-bond and (c) np-bond.
walk method is therefore the equivalence between the so-
called "transport diffusion coefficient" \( D_t \) and the "self-
or tracer-diffusion coefficient" \( D_s \). \( D_t \) connects the cur-
rent density \( \mathbf{j} \) to the gradient of the particle density \( \nabla c \)
via \( \mathbf{j} = -D_t \nabla c \), while \( D_s \) connects the mean square dis-
placement \( \langle r^2(t) \rangle \) to the diffusion time \( t \) via
\( \langle r^2(t) \rangle = 2dD_st \)
with the Eucledian dimension \( d \) (cf. Fig. 2(c)). The equivalence between \( D_s \) and \( D_t \) has sometimes been ques-
tioned, but in the end always found valid for the case of
non-interacting particles [31, 32]. This means that
\( D_s = D_t \propto 1/\rho \), enabling us to calculate \( \rho \) from the dif-
sion coefficient \( D_s \). In TiO\textsubscript{2} nanoparticle networks, how-
ever, an additional effect might come into play, namely
the dependence of the electron density on the chemical
potential \[30\]. It has become common to introduce the 
"chemical diffusion coefficient" \( D^* \) that differs from \( D_t \)
by the "thermodynamic factor" that accounts for devi-
ations of the electron density from Boltzmann statistics
\[30\]. As the Boltzmann statistics is inherent to Eq. 2 we
rely to \( D_s \) from Eq. 4.

Similar to [3], the lattice points are occupied by spher-
ical grains (with probability \( p \)), or left empty (with prob-
ability \( 1 - p \)), where \( p \geq 0.8 \) in the following. Schematic
pictures of these networks are shown in Fig. 3. The diam-
eters \( D_i \) of the individual grains \( i \) are chosen randomly
from a homogeneous distribution of width \( w = 0.6a \) around a mean diameter \( \langle D \rangle \), so that neighboring spheres
can overlap, thereby forming connections in the shape of
nests with a circular cross-section of (geometrical) diam-
eter \( \Delta_0 \) between them (see Fig. 4). The mean values of
\begin{align}
\langle \Delta_0 \rangle & = \Theta (D) \\
\Theta & = 1/\sqrt{2}
\end{align}
close to experimentally known values [3]. With this value
of \( \Theta \), next-nearest neighbors of a monoisized lattice would
not overlap but just touch each other.

The grains are randomly divided into n-grains with
probability \( p_n \in \{1, 0.75, 0.5, 0.25, 0\} \) and p-grains with
probability \( p_p = 1 - p_n \) which corresponds to the values of
[1], where mass ratios of n-to-p grains of 1 : 0, 3 : 1,
1 : 1, 1 : 3 and 0 : 1 have been considered. Assuming a
constant number of charge carriers and a constant mobility
through the grains, we find \( \frac{R(N_c)}{R(0)} \) from the inverse
ratio of the diffusion constants \( D_s(0)/D_s(N_c) \) that
are computed with an average over \( 10^6 \) systems. For this
first analysis, differences between hole and electron mo-
bility are neglected as well as the different sizes of n- and
p-grains from the experiments of Ref. [1].

Calculation of the jump probabilities

Before performing random walk simulations, we have to
define the jump probabilities \( p_{ij} \) proportional to the conduc-
tances along the bonds, i.e. for nn-, pp- and np-
connections between the grains (which we address as \( p_{nn}^{ij} \),
\( p_{pp}^{ij} \) and \( p_{np}^{ij} \), respectively). Fig. 4 shows how the
bonds between the grains are modelled microscopically by
follow-
IV. RESULTS

We now discuss the results gained for not too high gas concentrations \( N_r \), i.e. the simulations are stopped when the thickness \( \lambda_n(N_r) \) of the depletion layer of the n-grains becomes 0. For still higher gas concentrations, \( \lambda_n \) would no longer play a role for controlling the sensor response and \( R \) would simply increase with \( N_r \), thereby only reflecting the response of the p-grains to the gas.

In all figures, the symbols and colors symbolize the different values of \( p_n \), i.e. they stand for systems (from bottom to top) of only n-grains, 1:3 ratio of p:n, 1:1 ratio of p:n, 3:1 ratio of p:n, only p-grains. For the n-grains, I refer to the parameters of \( 3 \) that have also been used in \( 3 \) and for the p-grains, I test three parameter sets, close to the ones reported in Ref. \( 16 \) (see above) covering the situations \( \lambda_p(0) > \lambda_n(0) \), \( \lambda_p(0) \approx \lambda_n(0) \) and \( \lambda_p(0) < \lambda_n(0) \). For clarity, \( \lambda_n(N_r) \) and \( \lambda_p(N_r) \) are shown in the corresponding inset of each figure. In the simulations, I tested many values for \( \langle D \rangle \in [50 \text{\,nm}, 200 \text{\,nm}] \), \( p \in [0.6, 1] \) as well as variations of \( N_z \), \( N_D \) and \( N_4 \).

I found that \( R(0) \) depends on the specific parameter choice, but the normalized curves \( R(N_r)/R(0) \) are qualitatively very similar for all parameters (except for smaller values of \( p \), where infinite percolation clusters do not exist in every system). The results shown here should therefore be understood as typical examples.

Unity reaction factors

Figures 5 and 6 show \( R(N_r)/R(0) \) as a function of \( N_r \) for systems of mean grain diameters \( \langle D \rangle = 100 \text{\,nm} \) and \( \langle D \rangle = 200 \text{\,nm} \), respectively. For this first test, the reaction factors are set to \( \alpha_n = \alpha_p = 1 \), i.e. each gas molecule at the (n- or p-) grain surfaces is considered to react with one oxygen ion. The three columns show the different parameter sets for the p-grains, whereas the n-grains are always the same. For the simulations shown in the top rows (a,c,e), also the np-bonds have been considered conducting, while they have been considered as cut in (b,d,f) (bottom rows). In the 1st case, in agreement with the experimental data from \( 3 \), all curves are separated well from each other. In the second case, the two lowest curves, \( p_n \geq 0.75 \), (black circles and red squares) of each figure as well as the two top curves, \( p_n \leq 0.25 \), (blue triangles up and cyan triangles down) fall together. With a critical percolation threshold of \( p_c \approx 0.3 \) it is clear that only the n-paths percolate for \( p_n \geq 0.75 \), while only the p-paths percolate for \( p_n \leq 0.25 \). Without np-bonds, both paths decouple and \( R(N_r)/R(0) \) reflects only the change of the dominant grain type with the gas, while the behavior of the non-percolating grain type plays no role. Otherwise speaking, \( p_n \) is unimportant and the curves of each type fall together. A third class of curves (green diamonds) is formed by the systems with \( p_n = 0.5 \), where both paths percolate simultaneously and \( R(N_r)/R(0) \) shows an intermediate behavior. However, the range of \( p_n \)-values with percolating n- and p-paths is quite small, giving a total occupation probability of 0.8. In summary, without including the np-bonds into the simulations, the experimental results that show individual characteristic curves for each system cannot
Reactions to different gases

Before discussing the numerical results for different reaction factors, we first take a look on some of the experimental data from Ref. [1] that are redrawn in Fig. 7. Figure (a) shows five samples with different mass relations of n-anatase to p-rutile under the influence of one specific reducing gas (CH$_4$). One can see that – depending on the n-to-p ratio of the sample – the relative resistance $R/R_0$ may increase or decrease in complete analogy to the numerical data of Figs. 5 and 6. (The succession of the different subfigures (a)-(f), different pairs of reaction factors, we first take a look on some of the experimental data from Ref. [1] that are redrawn in Fig. 7. Fig. 8: [Color online] $R(N_r)/R(0)$ is plotted versus $N_r$ for different reaction factors $(a) \alpha_n = 0.75, \alpha_p = 1, (b) \alpha_n = 0.5, \alpha_p = 1, (c) \alpha_n = 0.3, \alpha_p = 1, (d) \alpha_n = 1, \alpha_p = 0.75, (e) \alpha_n = 1, \alpha_p = 0.5, (f) \alpha_n = 1, \alpha_p = 0.3$. All other parameters are the same as in Fig. 5(a), as well as the meaning of the different colors, symbols and of the insets (g-l), i.e. the data represent the material of Fig. 5(a) under the influence of different gases.

be found and only three groups of curves appear instead.

FIG. 7: Some data of Fig. 5 of Ref. [1] are redrawn: (a) $R/R_0$ under the influence of CH$_4$ for five films of anatase-rutile (n-p) composites with different mass ratios n-anatase:p-rutile: 1:0 (circles), 5:1 (boxes), 1:1 (diamonds), 1:3 (triangles up) and 0:1 (triangles down). (b) $R/R_0$ for the sample with 1:3 ratio of n-anatase:p-rutile under the influence of CH$_4$ (open triangles up, see also a.) and CO (filled triangles up). One can see that $R/R_0$ stays (nearly) constant under CH$_4$, while it decreases considerably under CO.
FIG. 9: [Color online] $R(N_r)/R(0)$ is plotted versus $N_r$ for different reaction factors $\alpha_n = 0.75$, $\alpha_p = 1$, (b) $\alpha_n = 0.5$, $\alpha_p = 1$, (c) $\alpha_n = 0.3$, $\alpha_p = 1$, (d) $\alpha_n = 1$, $\alpha_p = 0.75$, (e) $\alpha_n = 1$, $\alpha_p = 0.5$, (f) $\alpha_n = 1$, $\alpha_p = 0.3$. All other parameters are the same as in Fig. 8(c), as well as the meaning of the different colors, symbols and of the insets (g-l).

FIG. 10: [Color online] $R(N_r)/R(0)$ is plotted versus $N_r$ for the occupation probability $p = 1$. All other parameters and the reaction factors are the same as in Fig. 9.

FIG. 11: [Color online] Some numerical data from Fig. 9 are shown for comparison with the experimental data from Fig. 7. The same system (same value of $p_n$) may show increase, decrease or (nearly) constant behavior of $R$ with $N_r$. From top to bottom: (a) Curves for $p_n = 0.25$ from Fig. 9(c) - open triangles up, (a - small triangles up) and (f - big filled triangle up). (b) Curves for $p_n = 0.5$ from Fig. 9(c) and (f).

roughly 2, the values of $R(N_r)/R(0)$ are practically identical, indicating that also the geometrical structure of the system is not important for the considered question.

To conclude the basic finding of this paper, I present the results in Fig. 11 in a similar way as in Fig. 7, i.e. I show one specific system in reaction to different gases (reaction factors). Fig. 11(a) shows the system of Fig. 9 with $p_n = 0.25$ (blue triangles up) and $(\alpha_n, \alpha_p)$ equal to $(0.3, 1)$, $(0.75, 1)$ and $(1, 0.3)$ and we see that the curve may increase or decrease, depending on the gas. Fig. 11(b) shows the system of Fig. 9 with $p_n = 0.5$ (green diamonds) for the two values of $(\alpha_n, \alpha_p)$ equal to $(0.3, 1)$ and $(1, 0.3)$. One can see that this figure is very similar to Fig. 7(b), i.e. to the experimental curves.

V. Summary, Conclusions and Outlook

In summary, I have developed a simple model to describe the resistance change of nanocrystalline composite systems of sintered n- and p-grains in response to different reducing gases. The systems are mapped onto discrete lattices, where the different grains are simulated by overlapping spheres and the bonds between them are estimated from the conducting overlap (channel).

This work concentrates on the question, whether percolation effects are able to explain the experimentally observed selective behavior towards different gases. It turned out that despite several simplifications, the overall agreement with former experimental results is very good and the percolation model can explain in which way a system can distinguish between different gases, namely by the development of percolating pathways of n- and p-grains that react in different ways to the gas. The observed selective behavior of the systems can be attributed to the different responses of the space charge layers (shells) of the n- and the p-grains that react in different ways to the gas.

Clearly, several simplifications have been applied in order to keep the numerical effort feasible: First, the gas concentration $N_r$ used in this work is a surface concentration, while in the experimental curve of [1], volume gas densities have been applied. The surface gas density normally depends on the volume density in a non-linear way, which influences the shape of the curves. Second, the systems have been discretized on a lattice, a procedure that is under discussion since long and it is not clear which kind of “mixing rules” are best suited for the present problem. The discretization, therefore, is a further simplification with the main aim to keep the pa-
rameters simple and clear. For the same reason, also the systems have been standardized: instead of the different experimental shapes and sizes for the n- and the p-grains, all grains have been assumed as spherical with the same medium size of n- and p-grains. Conductances over next-nearest neighbors have been neglected, while in reality a multitude of paths between adjacent grains (including paths over edges and corners) may come into play. The conductances over the bonds have been estimated in a simplified way, without including e.g. different mobilities of electrons and holes.

Therefore, I have estimated the influence of these various factors on the global qualitative behavior by testing a lot of different values for particle sizes, occupation probabilities, width of the disorder and others. As shown in the figures, these differences are only important for the value of $R(0)$, but play nearly no role for the change of $R$ with $N_r$. Therefore, the basic challenge to find out by which mechanisms percolation effects can lead to a selective behavior of a gas sensor composed of n- and p-grains has been answered by introducing the appropriate reaction factors $\alpha_n$ and $\alpha_p$ that describe the number of gas molecules that react with the adsorbed oxygen. This mechanism is quite simple, the results are extremely stable against all kind of parameter changes other than either the strengths of the np-bonds or $\alpha_n$ and $\alpha_p$ themselves. Future work on more realistic continuous systems is of course highly desirable in order to optimize the performance of the sensors.

ACKNOWLEDGEMENTS

I gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft (project RU 854/2-1) and valuable discussions with Claus-Dieter Kohl, Jörg Hennemann and Tilman Sauerwald. Claus-Dieter Kohl has given many insightful advices on the physics of surfaces and of gas sensing.

[1] N. O. Savage, B. Chwieroth, A. Ginwalla, B. R. Patton, S. A. Akbar and P. K. Dutta; Sens. Actuators B 79 (2001) 17 and N. O. Savage, S. A. Akbar and P. K. Dutta; Sens. Actuators B 72 (2001) 239.
[2] Fractals and Disordered Systems, 2nd ed., edited by A. Bunde and S. Havlin (Springer, Berlin, 1996); D. Stauffer and A. Aharony Introduction to percolation theory, 2nd ed., (Taylor and Francis, London, 1994).
[3] M. Ulrich, C.-D. Kohl and A. Bunde, Thin Solid Films 391 (2001) 299 and M. Ulrich, A. Bunde and C.-D. Kohl, Appl. Phys. Lett. 85 (2004) 242.
[4] G. Heiland, Sens. Actuators 2 (1982) 343.
[5] C.-D. Kohl, J. Phys. D 34 (2001) R125.
[6] S. R. Morrison; Sens. Actuators B 12 (1987) 425.
[7] M. Tiemann; Chem. Eur. J. 13, (2007) 8376.
[8] C. O. Park and S. Akbar; J. Mat. Sci 38, (2003) 4611.
[9] J. Dräger, S. Russ, T. Sauerwald, C.-D. Kohl and A. Bunde; J. Appl. Phys. 113, (2013) 223701.
[10] T. Sauerwald and S. Russ in Gas Sensing Fundamentals, ed. by C.-D. Kohl and T. Wagner, Springer Series on Chemical Sensors and Biosensors (Springer Verlag Berlin Heidelberg 2013), Doi 10.1007/5346_2013_53.
[11] G. G. Mandayo, E. Castano, F. J. Gracia, A. Cirera, A. Cornet and J. R. Morante; Sens. Actuators B 95 (2003) 90.
[12] A. Heilig, N. Barsan, U. Weimar, M. Schweizer-Berberich, J. W. Gardner and W. Göpel; Sens. Actuators B 43 (1997) 45 and A. Heilig, N. Barsan, U. Weimar and W. Göpel; Sens. Actuators B 58 (1999) 302.
[13] D. H. Yoon, J. H. Yu and G. M. Choi; Sens. Actuators B 46 (1998) 15, S.-T Jun and G. M. Choi; J. Am. Ceram. Soc. 81 (1998) 695 and W. J. Moon, J. H. Yu and G. M. Choi; Sens. Actuators B 80 (2001) 21.
[14] J.-W. Yoon, J.-K. Choi and J.-H. Lee; Sens. and Act. B 161, (2012) 570.
[15] S. R. Morrison, The Chemical Physics of Surfaces (Plenum Press, New York, 1977), section 2.2.
[16] N. Barsan, C. Simion, T. Heine, S. Pokhreui and U. Weimar; J. Electroceram 25, (2010) 11.
[17] C.-D. Kohl, Sens. Actuators 18 (1989) 71.
[18] V. V. Sysoev, T. Schneider, I. Kiselev, W. Habicht, H. Hahn, E. Strelcov and A. Kolmakov; Sens. and Act. B 139, 699 (2009) and J. Bisquert; Journal of Chem. Physics 128, 064703 (2008)
[19] X. Wang, S. S. Yee and W. P. Carey, Sens. Actuators 24-25, (1995) 454.
[20] C. Xu, J. Tamaki, N. Miura and N. Yamazoe, Sens. and Act. B 3, (1991) 147.
[21] L. Berlyand and K. Golden; Phys. Rev. B 50,2114 (1994).
[22] S. Feng, B. I. Halperin and P. N. Sen; Phys. Rev. B 35 (1987) 197 and P. Sheng and R. V. Kohn; Phys. Rev. B 26 (1982) 1331.
[23] Y. Chen and C. A. Schuh; Phys. Rev. E 80 040103(R) (2009).
[24] A. Sihvola; Photonics and nanostructures – Fund. and Appl. 11 364 (2013) and L. Jylhä and A. Sihvola; Dielectrics and electrical insulation, IEEE Trans. on 13, 760 (2006).
[25] J. Helsing; J. Comp. Phys. 230, (2011) 1171 and J. Helsing; J. Comp. Phys. 230, (2011) 7533.
[26] F. Willot, L. Gillibert and D. Jeulin; Int. J. of Solids and Structures 50, (2013) 1699.
[27] B Sapoval, S Russ and J-N Chazalviel, J. Phys.: Condens. Matter 8, (1996) 6235.
[28] Y. Gefen and I. Goldhirsh; Phys. Rev. B 35 (1987) 8639.
[29] D. ben-Avraham and S. Havlin; Diffusion and Reactions in Fractals and Disordered Systems, Cambridge University Press, (Cambridge, UK, 2004).
[30] J. Bisquert; Phys. Chem. Chem. Phys. 10 (2008) 3175 and J. van de Lagemaat, N. Kopidakis, N. R. Neale and A. J. Frank; Phys. Rev. B 71, 035304 (2005) and R. Gomer; Rep. Prog. Phys. 53, 917 (1990).
[31] S. Russ, S. Zschiege, A. Bunde and J. Käger; Phys. Rev. E 72, (2005) 030101(R) and S. Zschiege, S. Russ, R. Valiullin, M.-O. Coppens, A.-J. Dammers, A. Bunde and J. Käger; Eur. Phys. J. 161, 109 (2008).
[32] P. Comets, S. Popov, G. M. Schütz and M. Vachkovskaia; J. Stat. Phys. 140, (2010) 948.
[33] C.-D. Kohl; (private communication).