

Effects of mobile donors on potential distribution in grain contacts of sintered ceramic semiconductors

Tuomo S. Rantala^{a)} and Vilho Lantto

Microelectronics and Material Physics Laboratories, University of Oulu, FIN-90570 Oulu, Finland

Tapio T. Rantala

Department of Physical Sciences, University of Oulu, FIN-90570 Oulu, Finland

(Received 16 January 1996, accepted for publication 19 March 1996)

Sintered ceramic semiconductors can be used to monitor the surrounding gas atmosphere. It is based on the conductivity response of the semiconductor to the surface reactions on the grains of porous material. Some nonstoichiometry defect donors, like oxygen vacancies in *n*-type semiconductors, may be mobile at relatively low temperatures, where semiconductor gas sensors operate. In such case, the donor concentration may considerably decrease in the space charge layer at the semiconductor surface, which may be reflected in the transport properties of electrons through the neck contacts between grains. We model here various neck contacts between spherical grains and compute the electrical potential at the conductive region from the Poisson–Boltzmann equation in cases of mobile single and double donors. The solutions are evaluated numerically with a finite difference method. According to the Schottky-defect model for oxygen vacancies, the surface concentration of donors is kept a fixed parameter in the calculations. The chosen material parameters are those of tin dioxide, which is the key material of semiconductor gas sensors. It is found that mobile donors may strongly modulate the distribution of electrical potential around the neck contacts, and thus, modify the transducing properties of the microstructure of ceramic semiconductor gas sensors. © 1996 American Institute of Physics. [S0021-8979(96)08912-8]

I. INTRODUCTION

Semiconductor gas sensors utilize the chemical sensitivity of semiconductor surfaces for gas sensing applications. A metal-oxide *n*-type semiconductor is the usual sensing material in these devices. The sensor detects a gas component due to a change in electrical resistance of a polycrystalline ceramic semiconductor. For a basic understanding of a chemical sensor one needs to separate the receptor function which recognizes a chemical substance, and the transducer function which transduces the chemical signal into an electric output signal. In a semiconductor gas sensor, the chemical signal on the semiconductor surface is transduced through the microstructure of the sintered semiconductor into a resistance change. Hence, various grain contacts together with the grain size of the ceramic microstructure are the key concepts for the transducer function.¹ In addition, the mobility of donors, like oxygen vacancies in oxidic semiconductors, may have strong effects on the transducing properties of the sensors.^{2–4}

In the sintering process of a ceramic powder, necks of different shapes and dimensions are formed between the powder particles. There are many theoretical treatments^{1,5–8} in the case of frozen donors for the current transport through necks of different shapes and sizes. In the case of a neck-control model of conductance in Ref. 1, the transducer function is closely related to the neck diameter (grain size) and the depth of the space-charge layer at the surface (the Debye length). The given approximate model explained, to some extent, the observed correlations between the grain size and the H₂ and CO sensitivities of fine-particle SnO₂ samples with grain diameters below 30 nm. Both the H₂ and CO

sensitivities were found to increase with decreasing grain size below 30 nm. A very small value of about 3 nm from Ref. 9 was taken for the depth of the space-charge layer at the surface of undoped SnO₂ in the interpretations in Ref. 1. Accordingly, the observed strong increase of resistance of SnO₂ samples with decreasing grain size below a critical grain diameter of about 6 nm at 300 °C was related to the total depletion of grains from conduction electrons. This critical grain size is also about the same as the minimum size limit of 10 nm for the semiclassical approach of the electron dynamics (effective mass approximation) at 300 °C ($\Delta x \geq 131.6 [m_e / (m_e^* T(K))]^{1/2}$ nm) in tin dioxide with the electron effective mass $m_e^* \approx 0.3m_e$. In very small grains with grain size below the de Broglie wavelength of electrons, the behavior of electrons is very different from that in the bulk material due to the quantum size effect.

In the case of a polycrystalline semiconductor, the band bending (Schottky barrier) at the surfaces of large grains is a consequence of electron trapping at the surfaces, while almost a flatband situation with a thorough depletion may appear in small grains. The Schottky relation, based on an abrupt-depletion approximation in a semiconductor with a constant and frozen distribution of donors, is the usual simple starting point in the treatment of the band bending and depth of the space-charge layer at the semiconductor surface.¹⁰ At higher temperatures, however, donors may be mobile. In particular, this is the case for some nonstoichiometry defect donors, like oxygen vacancies in oxidic semiconductors. Now, the distribution of donors follows the distribution of the electrical potential in the space-charge layer. Semiconductor gas sensors operate at elevated temperatures and metal-oxide semiconductors with wide band gap (above

^{a)}Electronic mail: tuomo.rantala@oulu.fi

3 eV) are used as the sensing material. Therefore, we restrict our treatment here to n -type semiconductors with negligible hole concentrations. Our aim is to consider the potential distribution around neck contacts between two semiconducting grains in the case of mobile donors. The effects of a possible grain boundary across the neck contact are omitted in the treatment. A discussion of grain-boundary effects on the resistance behavior of a ceramic semiconductor is given in Refs. 8 and 11 in the case of frozen donors.

II. COMPUTATIONAL METHOD

In the space-charge layer at a semiconductor surface there is an electric field which creates a concentration gradient for mobile donors. This, in turn, causes the diffusion of donors in the opposite direction. It is assumed that both the diffusion coefficient and mobility of donors have no spatial or directional dependence and that the Einstein relation holds between them. Then, the electrical potential $\phi(x,y,z)$ in the space-charge layer inside an n -type semiconductor grain is a solution of the Poisson-Boltzmann equation

$$\begin{aligned}\nabla^2 \phi(x,y,z) &= -\frac{\rho(x,y,z)}{\epsilon_s} \\ &= -\frac{emN_{d0}}{\epsilon_s} e^{-m\beta(\phi(x,y,z) - \phi(0,0,0))} \\ &\quad + \frac{en_0}{\epsilon_s} e^{\beta(\phi(x,y,z) - \phi(0,0,0))},\end{aligned}\quad (1)$$

where $m=1$ for single donors and $m=2$ for double donors, e is the elementary charge, $\beta=e/kT$, $\epsilon_s(=\epsilon_r\epsilon_0)$ is the permittivity, and N_{d0} and n_0 are the concentrations of donors and conduction electrons, respectively, at the grain center where the electrical potential is $\phi(0,0,0)$. The connection between the donor concentration at the grain center N_{d0} and at the grain surface N_{ds} is given by $N_{d0}=N_{ds}\exp(m\beta\phi_s)$, where ϕ_s is the potential difference between the surface and center of the grain. Here, we consider mainly spherical grains. The macroscopic Eq. (1) is no longer valid in small spherical grains where the number of donors is small and continuous distributions cannot be assumed. A limiting grain radius of about 6–7 nm was obtained for the validity of Eq. (1) in our earlier study⁴ in the case of $N_{ds}=10^{26}\text{ m}^{-3}$ at 573 K. Because of the wide band gap of metal oxides, the hole concentration is neglected in Eq. (1).

It is known that the equilibrium vacancy distributions are essentially determined by the mechanism of their development. The oxygen vacancy concentration in oxidic semiconductors usually follows the partial pressure of oxygen in the ambient gas phase at the temperatures where the oxygen vacancies are mobile. We adopt here the Schottky-defect model (with exchange of oxygen between the oxide surface and ambient gas phase) and keep the surface concentration of donors (oxygen vacancies) a fixed parameter in our calculations. Oxygen adsorption on tin-dioxide surfaces was used in our earlier study⁴ as an example to demonstrate the maximum size of depleted grains in the case of mobile oxygen-vacancy donors. Surprisingly large values up to about 1 μm were obtained for the limit maximum size of depleted grains.

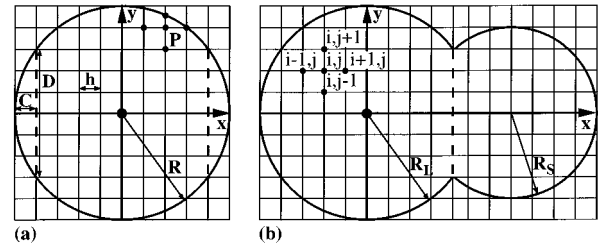


FIG. 1. Schematic illustrations (a) of a spherical grain with radius R in a chain of similar grains and (b) a contact between two grains with different radii R_L and R_S . Dashed lines describe the contact circle with diameter D (cut thickness C) in a neck between two grains. Grids with the mesh size h for numerical solution of Eq. (2) are also shown.

The method of finite differences was used to find numerical solutions of Eq. (1) by taking a constant value of zero for the electrical potential at the grain surfaces. Now, it is possible to derive from Eq. (1) an iterative equation for the electrical potential at a point (i,j,k) (see the Appendix):

$$\begin{aligned}\phi(i,j,k) &= \frac{1}{6} \left[\sum_{i'=1}^6 \phi(i',j',k') + \frac{emh^2}{\epsilon_s} N_{ds} \left(e^{-m\beta\phi(i,j,k)} \right. \right. \\ &\quad \left. \left. - \frac{n_0}{mN_{d0}} e^{\beta(\phi(i,j,k) - (m+1)\phi(0,0,0))} \right) \right],\end{aligned}\quad (2)$$

where $\phi(i',j',k')$'s are the values of the electrical potential at six nearest grid points in a three-dimensional cubic grid, h is the mesh size, and the last two terms relate to the charges at the point (i,j,k) . Figure 1 shows schematic drawings to illustrate two different grain contacts and cubic grids ($R/h=5$, where R is the grain radius) for the solution of the iterative Eq. (2). The sphere in Fig. 1(a) illustrates a grain in a long chain of identical grains. Dashed lines indicate neck contacts (no negative surface charge). The symbols C and D denote the thickness of the contact cut (in the x direction) and the diameter of the corresponding contact circle, respectively. A contact between two spherical grains of different size is illustrated in Fig. 1(b). Our finite difference discretization of derivatives is exact for second-order polynomials, which is true in our procedure also in the case of nonequidistant grid spacing, such as that around the point P (in Fig. 1) next to the surface boundary.

In addition to the boundary condition, the derivatives $d\phi(x,y,z)/dy$ at $y=0$ and $d\phi(x,y,z)/dz$ at $z=0$ vanish due to the symmetry requirements for the structures in Fig. 1. These extra conditions serve as a useful way to reduce the computing time by about 70%. Similarly, it is possible to utilize the symmetry of the structure in the x direction in the case of Fig. 1(a). The calculation of the electrical potential at each point of the network from Eq. (2) is continued until convergence to about 10^{-5} V.

The constant electrical potential at the grain surface is a macroscopic approximation. However, if the velocity of the donor diffusion is slow as compared with the lifetime of trapped electrons at the surface, the time average of the surface potential can be taken as the constant boundary potential. The electrons trapped at the surface are in localized states, e.g., in oxygen molecules and atoms, and correspond-

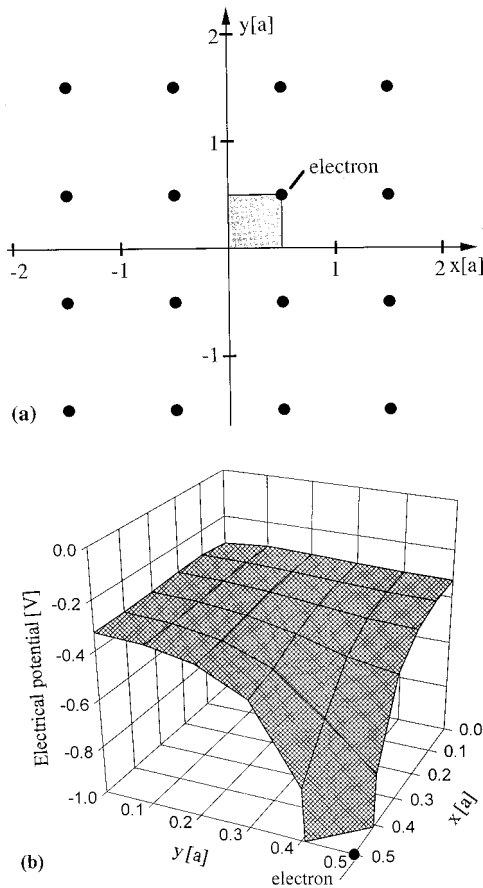


FIG. 2. (a) Sixteen trapped electrons in a square 4×4 lattice with a lattice constant a at the planar surface of a semiconductor. Sixteen single donors are also assumed to locate in a similar lattice at a distance b below electrons. (b) The electrical potential at the shaded surface area in (a), calculated for the case $a=3.5$ nm, $b=5$ nm and ϵ_r (semiconductor)=12.

ingly the instantaneous potential has some variation along the surface. In order to study this variation, the electrical potential was calculated on a planar semiconductor surface for a case of 16 electrons and 16 single donors. The 16 electrons were at lattice points of a square lattice in Fig. 2(a) with a lattice constant a , and the 16 single donors formed a similar lattice at a distance b below the electrons. The method of image charges¹² was used in the calculation of the potential in the interface between two materials with different permittivity (air and semiconductor). Now, the relative permittivity ϵ_r in the familiar expression $q/(4\pi\epsilon_0\epsilon_r r)$ for the electrical potential in the interface plane at a distance r from a point charge q is the arithmetic average of the relative permittivities of air and the semiconductor. The calculated potential in the shaded area in Fig. 2(a) is shown in Fig. 2(b) for the case of $a=3.5$ nm, corresponding to an electron density at 573 K at the surface of a depleted spherical grain with $R=100$ nm and N_{ds} (single donors)= 10^{26} m⁻³, $b=5$ nm, and the relative permittivity of the semiconductor is 12. The potential values refer to a zero potential at infinity from the surface. In the case of only 16 electrons and donors, the potential is rather smooth over the main area in Fig. 2(b).

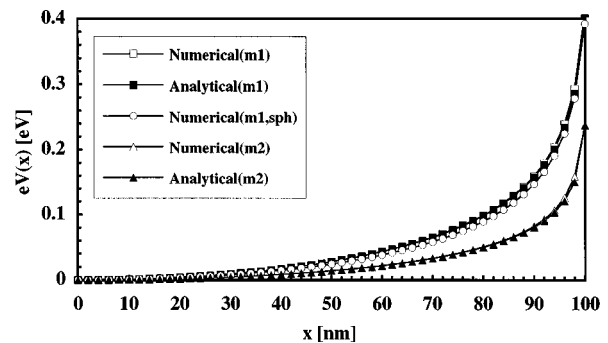


FIG. 3. Numerical and analytical results for the potential energy distribution $eV(x)$ in a cross section of a depleted cylindrical rod-shaped grain with radius $R=100$ nm at 573 K in the case of mobile single (m1) and double (m2) donors with $N_{ds}=10^{26}$ m⁻³. Numerical results are also given for $eV(x)$ in the case of mobile single donors inside a sphere (m1,sph) with the same parameter values.

III. RESULTS AND DISCUSSION

The calculations for neck contacts were carried out for the spherical grain geometries shown in Fig. 1. The ratio between the spherical grain radius and mesh size R/h was found to have a strong effect on the accuracy of the results when the value of the ratio R/h was less than 30. Therefore, a value $R/50$ was used for the mesh size h . For clarity and easy comparison with the results of our earlier study,⁴ the potential energy values $-e\phi$ were shifted to zero at the grain center [of the larger grain in the case of Fig. 1(b)]. Then, $eV(x)=-e\phi(x)$ describes the band bending inside grains and the surface energy barrier $eV_s=-e\phi_s$.

The values 10^{26} m⁻³, 573 K, and 100 nm (with $h=2$ nm) were used in calculations for N_{ds} , T , and R , respectively (unless otherwise stated). With these values of N_{ds} and T , tin-dioxide grains were found to be depleted from conduction electrons in atmospheric air in the case of mobile oxygen-vacancy donors up to a diameter of about 1 μ m.⁴ Therefore, the electronic charge term in Eq. (2) was neglected in most calculations (Figs. 3–8). Depleted grains have also been found to control the conductance in a commercial SnO₂-based ceramic sensor.¹³ The value of the energy barrier eV_s , calculated for a totally depleted grain at a certain temperature, corresponds to the maximum band bending in the grain in the case of mobile donors with a fixed surface concentration. In the case of the surface trapping of electrons, however, only a partial depletion of the grains is physically meaningful. In order to study the effect of a partial grain depletion on the band bending in grains, the electronic charge term in Eq. (2) was included in some calculations (Fig. 9). The minimum radius of the smaller grain in Fig. 1(b) was taken to be 10 nm in order that the macroscopic Eq. (1) is valid.⁴ Usually oxygen vacancies behave as double donors in metal-oxide semiconductors. In SnO₂, for instance, two energy levels of the oxygen-vacancy double donors are 30 and 145 meV below the conduction band edge.¹⁴ Therefore, the calculations were made for both single and double donors. The value of permittivity was taken to correspond to the average value of tin dioxide ($\epsilon_r \approx 12$).¹⁵

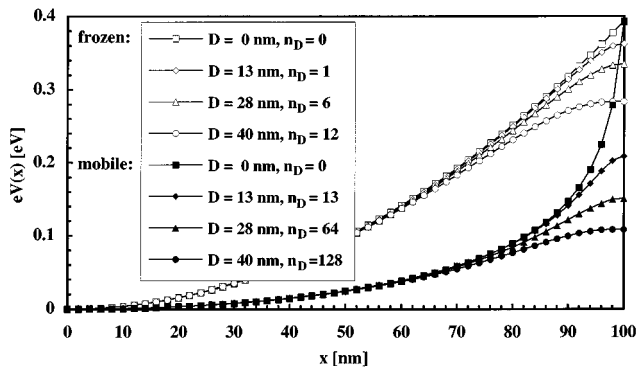


FIG. 4. Potential energy $eV(x)$ at 573 K in a grain ($R=100$ nm) shown in Fig. 1(a) with four different neck diameters D in the case of mobile (full symbols) and frozen (open symbols) single donors with $N_{ds}=10^{26} \text{ m}^{-3}$ and constant $N_d=1.56 \times 10^{23} \text{ m}^{-3}$, respectively. The average number of trapped electrons n_D is also given for different areas of the contact circles in the case of both mobile and frozen donors.

The present numerical calculations are compared with corresponding analytical results⁴ in Fig. 3, where potential energy curves $eV(x)$ are shown in a two-dimensional circle with $R=100$ nm (cylindrical rod-shaped grain) for both single (m1) and double (m2) mobile donors. In addition, the numerical results are also shown for a sphere with the same radius in the case of single donors. The differences between the numerical and analytical results in Fig. 3 are very small, which supports the accuracy of our numerical approach with Eq. (2) and $h=R/50$. The small differences in the numerical results between cylindrical and spherical grains with mobile single donors are also in good agreement with our earlier findings.⁴

A comparison of the potential energy $eV(x)$, in a grain of a chain of identical grains [Fig. 1(a)], between frozen and mobile single donors is shown in Fig. 4 at different diameters D of the contact circle. The constant, frozen concentration of single donors $N_d=1.56 \times 10^{23} \text{ m}^{-3}$ gave the same total surface barrier eV_s as the surface concentration $N_{ds}=10^{26} \text{ m}^{-3}$ in the case of mobile single donors. The average number of electrons n_D on a surface area of equal size with the area of the contact circle, corresponding to the charge density of trapped electrons on the free grain surface in the case of both frozen and mobile single donors, is also given in Fig. 4 for different areas of the contact circles. The surface density of trapped electrons is an order of magnitude smaller for frozen donors. In the case of mobile donors, the decrease of $eV(x)$ is very steep near the surface (the curve $D=0$). At the center of the contact circle, the potential energy also decreases strongly with increasing circle diameter D in the case of mobile donors.

The potential energies $eV(x)$ through the center of the contact circle ($y=z=0$), calculated for a neck contact between two spherical grains with radii R_L and R_S [Fig. 1(b)], are shown in Figs. 5(a) and 5(b) for mobile single and double donors, respectively. The results are given for three different smaller grain radii $R_S=10, 30$, and 50 nm when the radius R_L of the larger grain was 100 nm and the diameter D of the contact circle was 9 nm. The mesh size h was 2 nm in all three cases. Scaling of the $eV(x)$ values for single donors in

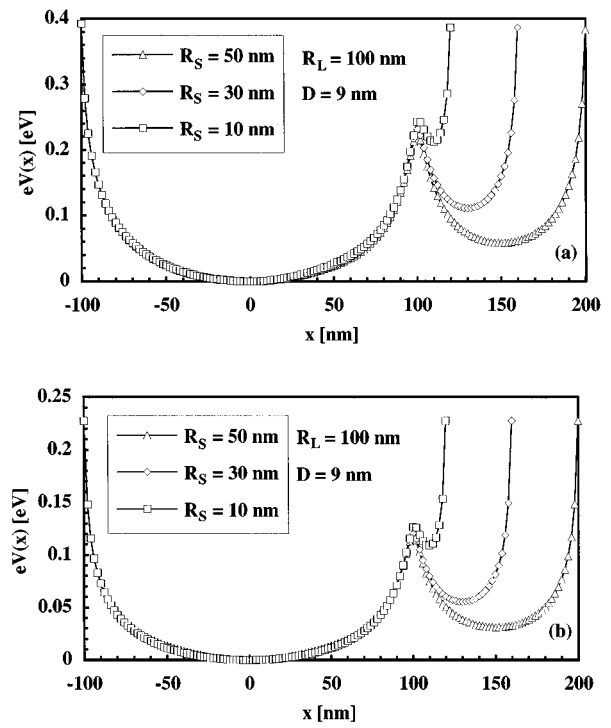


FIG. 5. Potential energy $eV(x)$ at 573 K through the neck contact ($D=9$ nm) between two different sized grains shown in Fig. 1(b) with $R_L=100$ nm and $R_S=10, 30$, and 50 nm in the case of mobile (a) single and (b) double donors with $N_{ds}=10^{26} \text{ m}^{-3}$.

Fig. 5(a) by a factor of about 0.56 gives approximately the $eV(x)$ values for double donors in Fig. 5(b). At the center of the contact circle, the amount of the band bending in the larger grain ($R_L=100$ nm) is only about 60% of the value eV_s at the free surface in both Figs. 5(a) and 5(b). In the smaller grain with $R_S=10$ nm, the energy barriers between the grain center and the center of the contact circle are only 0.025 and 0.015 eV in the cases of single and double donors, respectively. These energy barriers are lower than the thermal energy $kT=0.049$ eV at 573 K. The Fermi energy in thermal equilibrium is constant throughout the structure, which means that the average electron concentration in the smaller grain with $R_S=10$ nm is much lower than that in the

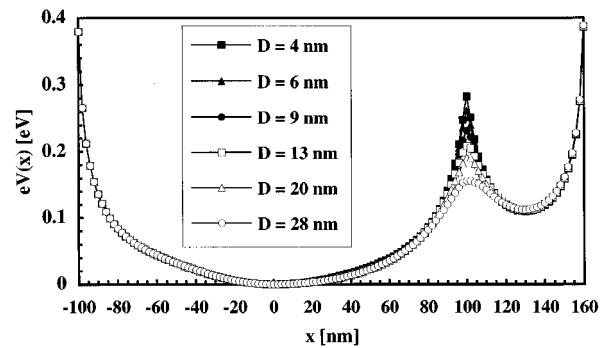


FIG. 6. Potential energy $eV(x)$ at 573 K through various neck contacts ($D=4, 6, 9, 13, 20$, and 28 nm) between two grains shown in Fig. 1(b) with $R_L=100$ nm and $R_S=30$ nm in the case of mobile single donors with $N_{ds}=10^{26} \text{ m}^{-3}$.

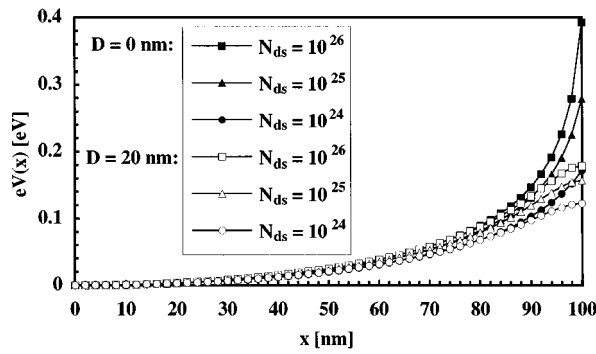


FIG. 7. Potential energy $eV(x)$ at 573 K in a grain ($R=100$ nm) shown in Fig. 1(a) with $D=0$ (full symbols) and 20 nm (open symbols) in the case of mobile single donors with three different values of N_{ds} 10^{24} , 10^{25} , and 10^{26} m^{-3} .

larger one. The situation in the smaller grain with decreasing R_S approaches the flat-band situation.

Figure 6 shows the potential energy $eV(x)$ in the case of mobile single donors through the center of the contact circle in a structure in Fig. 1(b) where the radii R_L and R_S are 100 and 30 nm, respectively, and the diameter of the contact circle has six different values between 4 and 28 nm. In the case of a very small contact circle with $D=4$ nm, the potential energy barrier between the grains decreases by about 0.1 eV from the case where the free surfaces of the grains are in contact (pressed pellet). In the case of the largest contact with $D=28$ nm in Fig. 6, the energy barrier between grains decreases by about 0.25 eV from the value eV_s .

The concentration of mobile donors at the grain surface has a strong effect on the band bending in a depleted grain. Figure 7 shows the situation for mobile single donors with fixed concentrations of 10^{24} , 10^{25} , and 10^{26} m^{-3} at the surface of a depleted grain with $R=100$ nm. A strong decrease is seen in the values of the energy barrier eV_s with decreasing N_{ds} . In the case of a neck contact in Fig. 7 [$D=20$ nm in the geometry of Fig. 1(a)], however, the energy barrier between two grains through the center of the contact circle is insensitive to N_{ds} . This energy barrier changes by only about 0.05 eV between the values 10^{24} and 10^{26} m^{-3} of N_{ds} . Thus, the decrease in the energy barrier from the value at the neck

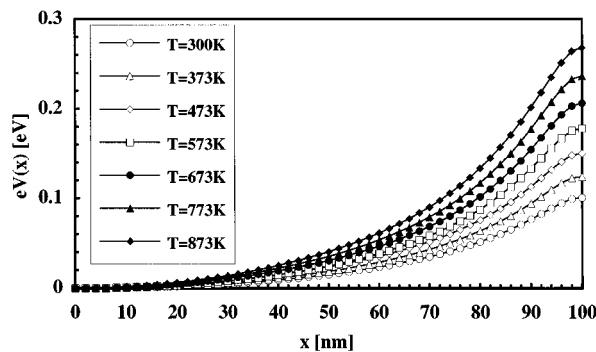


FIG. 8. Potential energy $eV(x)$ at seven different temperatures between 300 and 873 K in a grain ($R=100$ nm) shown in Fig. 1(a) with $D=20$ nm in the case of mobile single donors $N_{ds}=10^{26}$ m^{-3} .

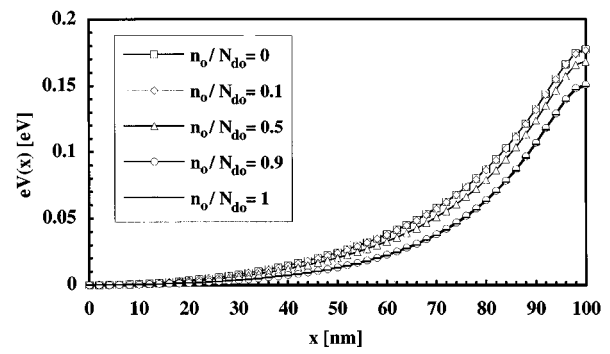


FIG. 9. Potential energy $eV(x)$ at 573 K in a grain ($R=100$ nm) shown in Fig. 1(a) with $D=20$ nm, calculated in the case of mobile single donors ($N_{ds}=10^{26}$ m^{-3}) with five different values 0, 0.1, 0.5, 0.9, and 1 of the ratio n_o/N_{do} .

surface (eV_s) to that at the center of the contact circle is very sensitive to N_{ds} in the depleted grain as shown in Fig. 7.

The potential energy barrier between the grains changes also with changing temperature. Figure 8 shows the variation of the $eV(x)$ with temperature between 300 and 873 K in a grain of Fig. 1(a) where the grain radius is $R_L=100$ nm and the diameter of the contact circle is $D=20$ nm. The potential energy barrier between the grains at the center of the contact circle increases with increasing temperature. At temperatures near room temperature, however, the diffusion may be very slow and the donor distributions are practically frozen. A temperature change of 300 K in Fig. 8 corresponds to the change of about 0.1 eV in the energy barrier between the grains.

The electron charge distribution in Eq. (2) (the second term on the right-hand side) was neglected in the calculations of the results shown in Figs. 3–8. Some calculations were also carried out with the electron charge distribution. The ratio n_o/N_{do} at the grain center [Eq. (2)] was used as a parameter in the calculations. In large grains the ratio approaches 1 in the case of single donors (2 for double donors). The results of a calculation with five different values of n_o/N_{do} between 0 and 1 are shown in Fig. 9, where the grain geometry and the contact circle are the same as in the case of Fig. 8. The results show that the energy barriers between the grains at the center of the contact circle are very insensitive to the electron charge distribution. The maximum effect, with $n_o/N_{do}=1$ (the grain center not being depleted), on the energy barrier between the grains is only about 0.03 eV. In the case of almost total depletion, however, $n_o/N_{do} \ll 1$.

A schematic neck contact between two grains of different sizes is shown in Fig. 10 together with a corresponding band diagram. In the treatment of electron transport through neck contacts (constant distribution of frozen donors) in Ref. 7, it was found that the minimum energy barrier at the center of the neck contact (E_{act} in Fig. 10) corresponds to the activation energy of conductance for the current through the neck. In the case of mobile donors, the potential energy across the neck contact, $eV(y)$ in Fig. 10, becomes steeper from the surface toward the center of the neck contact than in the case of constant distribution of frozen donors [parabolic $eV(y)$]. Thus, the conductance G for current through the

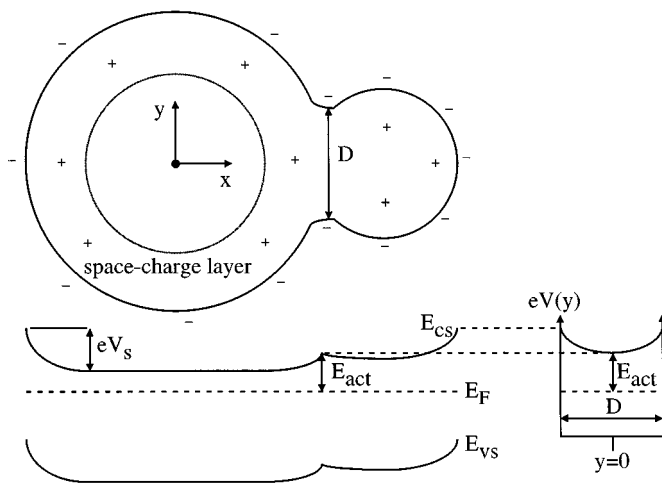


FIG. 10. Schematic illustration of a grain contact between large grain with a neutral region around the grain center and a totally depleted small grain together with a corresponding band diagram along x axis in the case of mobile donors. Potential energy distribution of electrons through the cross section of the neck in y direction $eV(y)$ is also shown (drawing at the right-hand side).

neck in Fig. 10 is proportional to the Arrhenius factor:

$$G \propto \exp(-E_{\text{act}}/kT) \quad (3)$$

and is strongly dependent on the diameter D of the neck contact.

Now, the calculated results above show that the mobility of donors may have strong effects on the electron transport properties through the neck contacts in ceramic semiconductors. In addition, the mobility of donors may strongly modify the transducing properties of the ceramic microstructure in the case of gas sensing with semiconductor sensors. The comparison of the results in Fig. 4 between frozen and mobile donors shows that the decrease of the potential energy at the surface is very steep in the case of mobile donors. The potential energy decreases to a value of about half of eV_s at the distance of about 5 nm from the surface in the case of both single and double mobile donors (Figs. 3 and 5). This steep decrease of the potential energy is the reason for the strong potential modulation inside neck contacts in the case of mobile donors (Figs. 4 and 5). The potential energy barrier between the grains is also very sensitive to the size of the neck contact between the grains (Fig. 6). Thus, neck contacts in a ceramic semiconductor with mobile donors may determine, to a large extent, the activation energy of conductance and strongly modulate the conductivity properties of the material.

In the case of oxidic semiconductor gas sensors, the role of the adsorption/desorption mechanism and that of the surface defect mechanism in the creation of the transducing conductance signal is, to some extent, in a controversial state.¹¹ In the case of the adsorption/desorption model, a Fermi-energy shift at the surface controls the surface density of conduction electrons and balances, by an electron capture rate, the injection rate of electrons from the surface traps into the conduction band. In small grains in the flat-band case, the Fermi-energy shift corresponds to the activation energy of

conductance. In larger grains with band bending the activation energy of conductance decreases due to the decrease of the potential energy inside neck contacts. The decrease is especially strong in the case of mobile donors (Figs. 4 and 6). The eV_s modulation by gas exposure in the adsorption/desorption model is mixed in the conductance response of sensors with a neck modulation through mobile donors. In the case of a slow donor diffusion the redistribution of donors is slow, which means long response and recovery times for the sensors. In the surface defect model, on the other hand, reaction of the lattice oxygen with an adsorbed gas component increases the concentration of the oxygen-vacancy donors at the surface. As shown in Fig. 7, the increase in donor concentration at the surface may strongly modulate the conductance, especially in the case of thin neck contacts (small D). The diffusion speed of donors is also now related to the response and recovery times of the sensors.

Possible effects of a grain boundary across the neck contact were omitted in the treatment. However, it may be a very rare situation that two powder particles with the same crystal face in contact, sinter to an ideal single crystal, although, the (110) face is the most stable, and thus, the dominant crystal-lite face in SnO_2 .¹⁶ Stoneham¹⁷ describes the basic types of grain boundaries in oxides. Open pipe structures appear, for instance, in tilt grain boundaries for easy access to gas molecules. Possibly slow (and random) diffusion of ions through neck contacts along the grain boundaries may disturb the potential distribution inside the neck contacts and cause, for instance, instability to the behavior of semiconductor gas sensors. The possibility that oxygen ions do not come only from the gas phase, but emerge also from the lattice sites¹⁸ into grain boundaries, may also be a reason for disturbances in the potential behavior inside the neck contacts.

IV. CONCLUSIONS

A theoretical treatment based on a numerical solution of the Poisson–Boltzmann equation is given for the electrical potential inside spherical grains and different neck contacts in n -type ceramic semiconductors in the case of mobile single and double donors. Tin dioxide is used as an example material in the calculations. At the operating temperature of semiconductor gas sensors, around 500 °C, the potential decrease is very steep at the grain surfaces in the case of mobile donors. Therefore, thin neck contacts between large grains modulate strongly the potential energy barrier between the grains in the case of mobile donors. The modulation also has strong effects on the conductivity properties of ceramic semiconductors. In the case of gas sensing the mobility of donors may also strongly modify the transducing properties of the microstructure of a ceramic semiconductor sensor, if there is substantial band bending within the grains. In small grains with band bending less than kT , the neck contacts lose their importance for conductivity and gas response modulation. The Fermi-energy shift in depleted grains is now a characteristic parameter for the conductivity and gas-response behavior of the material.

ACKNOWLEDGMENTS

This work was supported by the Academy of Finland. We also thank the Center for Scientific Computing (CSC, Espoo, Finland) for computational resources. T.S.R. wants to thank the Imatran Voima Foundation, the Jenny and Antti Wihuri Foundation, and the Foundation for the Advancement of Technology in Finland for financial support.

APPENDIX: DISCRETIZATION OF THE POISSON–BOLTZMANN EQ. (1)

It is possible to rewrite the Poisson–Boltzmann Eq. (1) in the following form:

$$\begin{aligned}\nabla^2 \phi(x, y, z) &= -\frac{\rho(x, y, z)}{\epsilon_s} \\ &= -\frac{emN_{d0}}{\epsilon_s} e^{-m\beta(\phi(x, y, z) - \phi(0,0,0))} \\ &\quad + \frac{en_0}{\epsilon_s} e^{\beta(\phi(x, y, z) - \phi(0,0,0))}.\end{aligned}\quad (\text{A1})$$

A discretized form of the left-hand side of Eq. (A1) according to Fig. 1 is

$$\frac{1}{h^2} \left[\left(\sum_1^6 \phi(i', j', k') \right) - 6\phi(i, j, k) \right]. \quad (\text{A2})$$

By taking the value of zero for the electrical potential ϕ at grain surfaces, it is possible to express the connection between the donor concentrations at the grain center and surface by $N_{d0} = N_{ds} e^{-m\beta\phi(0,0,0)}$.

The discretization of the right-hand side of Eq. (A1) gives

$$\begin{aligned}& -\frac{em}{\epsilon_s} N_{ds} e^{-m\beta\phi(i, j, k)} + \frac{em}{\epsilon_s} \frac{n_0}{mN_{d0}} N_{d0} e^{\beta(\phi(i, j, k) - \phi(0,0,0))} \\ &= -\frac{em}{\epsilon_s} \left[N_{ds} e^{-m\beta\phi(i, j, k)} \right. \\ &\quad \left. - \frac{n_0}{mN_{d0}} N_{ds} e^{-m\beta\phi(0,0,0)} e^{\beta(\phi(i, j, k) - \phi(0,0,0))} \right] \\ &= -\frac{em}{\epsilon_s} N_{ds} \left[e^{-m\beta\phi(i, j, k)} \right. \\ &\quad \left. - \frac{n_0}{mN_{d0}} e^{\beta(\phi(i, j, k) - (m+1)\phi(0,0,0))} \right].\end{aligned}\quad (\text{A3})$$

Finally, by solving $\phi(i, j, k)$ from the equality of expressions (A2) and (A3) we get

$$\begin{aligned}\phi(i, j, k) &= \frac{1}{6} \left[\sum_1^6 \phi(i', j', k') + \frac{emh^2}{\epsilon_s} N_{ds} \left(e^{-m\beta\phi(i, j, k)} \right. \right. \\ &\quad \left. \left. - \frac{n_0}{mN_{d0}} e^{\beta(\phi(i, j, k) - (m+1)\phi(0,0,0))} \right) \right]\end{aligned}\quad (\text{A4})$$

which is the form of Eq. (2).

¹N. Yamazoe, *Sensors Actuators B* **5**, 7 (1991).

²D. Kohl, in *Gas Sensors*, edited by G. Sberveglieri (Kluwer, Dordrecht, 1992), pp. 43–88.

³V. Lantto and T. S. Rantala, *Sensors Actuators B* **18–19**, 711 (1994).

⁴T. S. Rantala and V. Lantto, 15th European Conference on Surface Science, Lille, France, 4–8 September 1995 [*Surf. Sci.* (in press)].

⁵J. F. McAleer, P. T. Moseley, J. O. W. Norris, and D. E. Williams, *J. Chem. Soc. Faraday Trans. I* **83**, 1326 (1987).

⁶D. E. Williams, in *Solid State Gas Sensors*, edited by P. T. Moseley and B. C. Tofteld (Adam Hilger, Bristol, 1987), pp. 71–123.

⁷P. Romppainen and V. Lantto, *J. Appl. Phys.* **63**, 5159 (1988).

⁸X. Wang, S. S. Yee, and W. P. Carey, *Sensors Actuators B* **24–25**, 454 (1995).

⁹H. Ogawa, M. Nishikawa, and A. Abe, *J. Appl. Phys.* **53**, 4448 (1982).

¹⁰S. Roy Morrison, *The Chemical Physics of Surfaces* (Plenum, New York, 1977), p. 29.

¹¹V. Lantto, in Ref. 2, pp. 117–167.

¹²L. D. Landau, E. M. Lifshitz, and L. P. Pitaevskii, *Electrodynamics of Continuous Media*, 2nd ed. (Pergamon, Oxford, 1984), p. 37.

¹³K. D. Schierbaum, U. Weimar, W. Göpel, and R. Kowalkowski, *Sensors Actuators B* **3**, 205 (1991).

¹⁴S. Samson and C. G. Fonstad, *J. Appl. Phys.* **44**, 4618 (1973).

¹⁵Z. M. Jarzebski and J. P. Marton, *J. Electrochem. Soc.* **123**, 333C (1976).

¹⁶Z. M. Jarzebski and J. P. Marton, *J. Electrochem. Soc.* **123**, 199C (1976).

¹⁷A. M. Stoneham, in Ref. 6, pp. 151–168.

¹⁸G. Heiland and D. Kohl, in *Chemical Sensor Technology*, edited by T. Seiyama (Elsevier, Amsterdam, 1988), Vol. I, pp. 15–38.