

Computational approaches to the chemical sensitivity of semiconducting tin dioxide

Tuomo Rantala ^{a,*}, Vilho Lantto ^a, Tapio Rantala ^b

^a *Microelectronics and Materials Physics Laboratories, University of Oulu, Linnanmaa, FIN-90570 Oulu, Finland*

^b *Department of Physical Sciences, University of Oulu, Linnanmaa, FIN-90570 Oulu, Finland*

Received 22 December 1997

Abstract

Some computational approaches to the chemical sensitivity of semiconducting tin dioxide are presented. Chemical sensitivity is often observed using conductance measurement. Therefore, the potential energy barriers in grain contacts between adjacent grains of a polycrystalline semiconductor are the key parameters for transducing the chemical surface sensitivity into the conductance response. The rate equation model describes the electronic exchange between the adsorbed oxygen species and the bulk conduction band of a semiconductor. It predicts the type of the major negative oxygen ion (O_2^- or O^-) at the surface as a function of temperature in agreement with experimental findings. The grain geometry has only a small effect on the potential energy barrier at the surface of finite grains. Even a small neck contact between grains, in the case of mobile donors, decreases strongly the potential energy barrier between grains compared to that in the case of an open grain contact. Results from Monte Carlo simulations with random barrier networks reveal that the current–voltage characteristic of a polycrystalline semiconductor is non-linear at higher voltages and the non-linearity of the network increases with increasing width of the barrier distributions. Electronic-structure calculations with clusters give qualitative information on the role of oxygen vacancies in different atomic planes in SnO_2 and its unrelaxed and unreconstructed (110) surface. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Electronic structure; Grain contact; Mobile donor; Surface energy barrier

1. Introduction

Semiconductor gas sensors utilise the chemical sensitivity of semiconductor surfaces for gas sensing applications. Metal–oxide n-type semiconductors are common sensing materials in these devices. A sensor detects a change in the gas atmosphere due to a change in the electrical resistance of a polycrystalline ceramic semiconductor. Generally speaking, a chemical sensor consists of two functions: the receptor function which recognises a chemical substance at the surfaces of the semiconducting particles, and the transducer function which transduces the chemical signal on the semiconductor surface through the microstructure of the sintered semiconductor into the electric output signal [1]. For basic understanding of a chemical sensor one needs to separate these two functions. Fig. 1(a) illustrates schematically some possible surface and bulk phenom-

ena in an n-type oxidic semiconductor. In tin dioxide, which is a wide band-gap oxide semiconductor, oxygen vacancies behave as singly or doubly ionised donors. Furthermore, these vacancies may be mobile at elevated temperatures. This mobility causes strong changes in the distribution of donors, conduction electrons, electrical potential, electric field and potential energy of electrons below the semiconductor surface compared to those with a constant distribution of donors. Fig. 1(b) describes schematically these distributions in the case of mobile donors. The potential energy barriers between grain contacts play an important role in the electrical conductivity of a polycrystalline semiconductor. The electrical potential in a semiconductor must be solved from the Poisson equation. The mobility of donors (oxygen vacancies) leads to a non-linear Poisson–Boltzmann equation, which is difficult to solve in many cases. Therefore computational methods are natural approaches here. From a practical point of view the $I-U$ characteristic of the sensor is important. However,

* Corresponding author. E-mail: tuomo.rantala@oulu.fi

calculation of this analytically is a very difficult task. One computational approach discussed here is to use Monte Carlo method with a random barrier network. The effects of different defects and dopants in the bulk and at the surface as well as chemical reactions between adsorbates and the surface are not well enough understood at the moment. Powerful computers now give an opportunity to make such electronic-structure calculations for comparison with the existing experimental data. Here we present some results from such calculations with finite clusters modelling unrelaxed SnO_2 (110) 1×1 surface.

2. Computational methods and results

A rate equation model has been constructed in the frame of the Shockley–Hall–Read generation–recombination theory to describe the electronic exchange between adsorbed oxygen species on a planar semi-infinite surface and the bulk conduction band of a semiconductor. Fig. 2(a) describes schematically the model which, with four rate constants, is described in detail elsewhere [3]. In equilibrium we can calculate the potential energy barrier, eV_s , using the expression of the electrical potential solved from the Poisson equation:

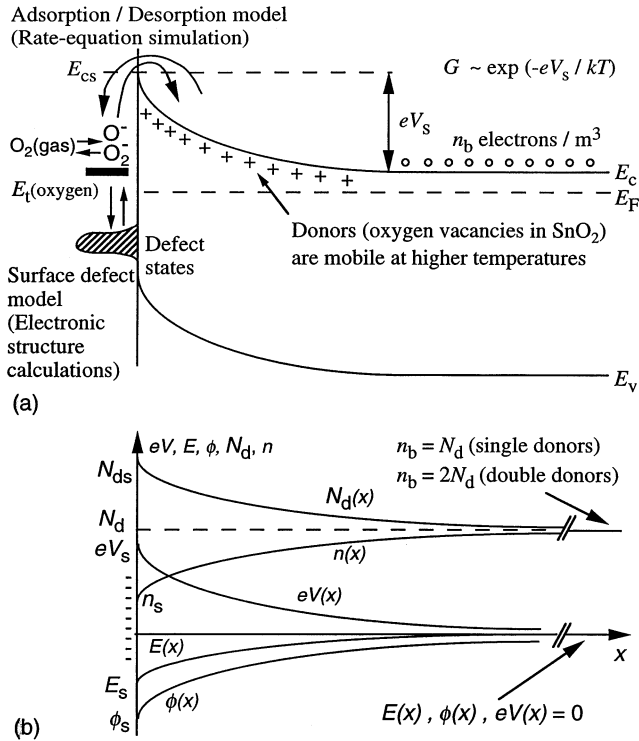


Fig. 1. (a) A schematic drawing describing some possible surface and bulk phenomena in an n-type oxidic semiconductor. (b) A schematic drawing for the illustration of the electrical potential $\phi(x)$, the electric field $E(x)$, the potential energy of electrons $eV(x)$, the distribution of mobile donors $N_d(x)$ and the conduction-electron concentration $n(x)$, together with their values at the surface of a semi-infinite n-type semiconductor [2].

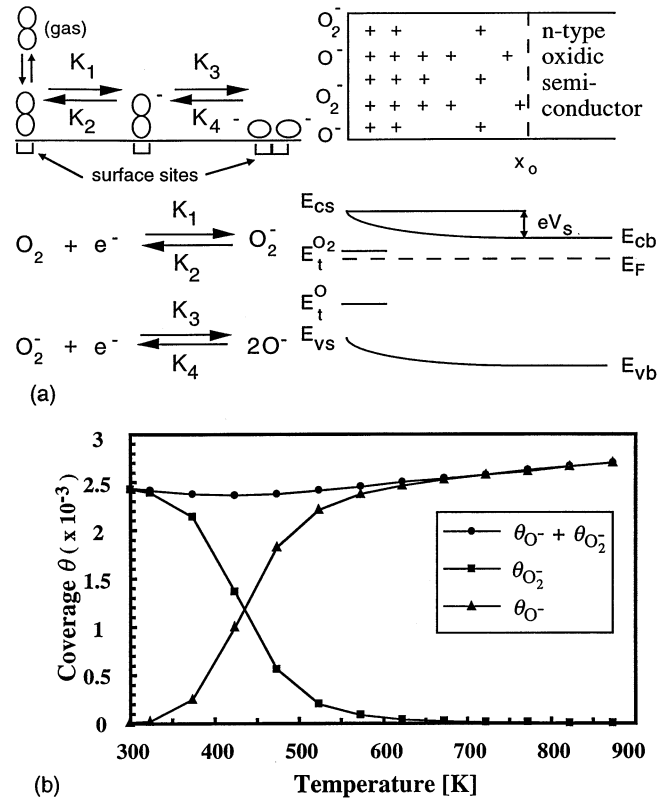


Fig. 2. (a) A schematic illustration with rate equation constants K_i ($i = 1, 2, 3, 4$) of the ionosorption of oxygen on an n-type semiconductor surface with band bending. (b) Simulated coverage (per adsorption site) of O_2^- , O^- and $\text{O}_2^- + \text{O}^-$ as a function of temperature T in dry synthetic air with a constant single donor concentration of $4.5 \times 10^{23} \text{ m}^{-3}$ [3].

$$\frac{d^2\phi}{dx^2} = -\frac{\rho(x)}{\epsilon_s} \quad (1)$$

For constant distribution of single donors, N_d , $\rho(x) = eN_d$, and a simple solution is $eV_s = -e\phi_s = e^2N_t^2 / (2\epsilon_s N_d)$ where N_t is the density of trapped electrons on the surface ($N_t = [\text{O}_2^-] + [\text{O}^-]$) and ϵ_s is permittivity. Fig. 2(b) shows the coverages of negative oxygen species from a simulation as a function of T . Results are in agreement with some experimental findings [4]. In the case of mobile single donors, we must solve the Poisson–Boltzmann equation (semi-infinite surface):

$$\frac{d^2\phi}{dx^2} = -\frac{eN_d}{\epsilon_s} [\exp(-\beta\phi) - \exp(\beta\phi)] \quad (2)$$

where $\beta = e/kT$. The solution is now $eV_s = -kT \ln[1 - (e^2N_t^2 / (2\epsilon_s N_{ds} kT))]$ [2,3], where N_{ds} is the surface donor concentration of mobile donors (Fig. 1(b)). The rate equation simulation with mobile donors gave much smaller and also more realistic values for eV_s compared to those calculated with constant distribution of donors [5].

The semi-infinite planar surface approximation used above is reasonable even for spherical but big grains. However, with smaller grains, finite-size effects may be

important. The electrical potential inside grains with different grain geometries shown in Fig. 3(a) is a solution of the one-dimensional Poisson–Boltzmann equation for a slab, two-dimensional for a cylinder and three-dimensional for a sphere, respectively. A detailed mathematical analysis is presented elsewhere [2,6]. Fig. 3(b) shows eV_s at different grain radii for different grain geometries. The grain geometry has a marked relative effect on the eV_s values only in grains with $L < 10$ nm. For a larger L , the differences in eV_s between different geometries seem to be a small constant value [6].

In the sintering process of an oxide powder, contacts between adjacent grains can be assumed to vary from open grain contacts to necks of different shapes and dimensions. The assumption of mobile donors calls for numerical approach if one wants to solve electrical potential inside grain contacts. Fig. 4(a) illustrates a contact between two grains with radii R_L and R_S and a ‘cubic’ grid with mesh size h for the solution of the electrical potential with a finite-difference method. A detailed mathematical analysis is presented in Ref. [7]. The symbol D is the diameter of the contact circle in the neck between the grains. Fig. 4(b) shows the potential energies through the neck contact with different values of D . Even with the smallest value of $D = 4$ nm, the potential energy barrier was decreased by about 0.1 eV compared to that with $D = 0$. Such strong influence

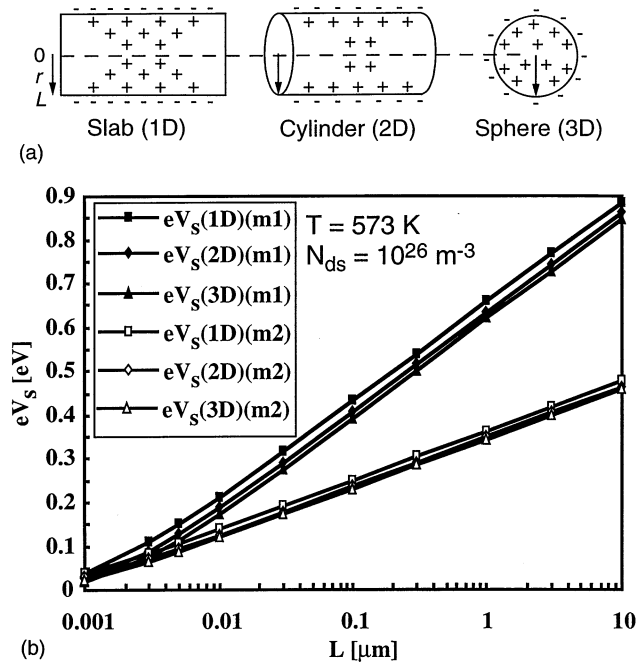


Fig. 3. (a) Schematic illustration for three different grain geometries used in the solutions of the Poisson–Boltzmann equation. (b) Surface energy barriers eV_s at different grain radii L calculated at 573 K for slab, cylindrical and spherical grain geometries for totally depleted grains with surface donor concentration $N_{ds} = 10^{26} \text{ m}^{-3}$ in the case of mobile single (m1) and double (m2) donors [6].

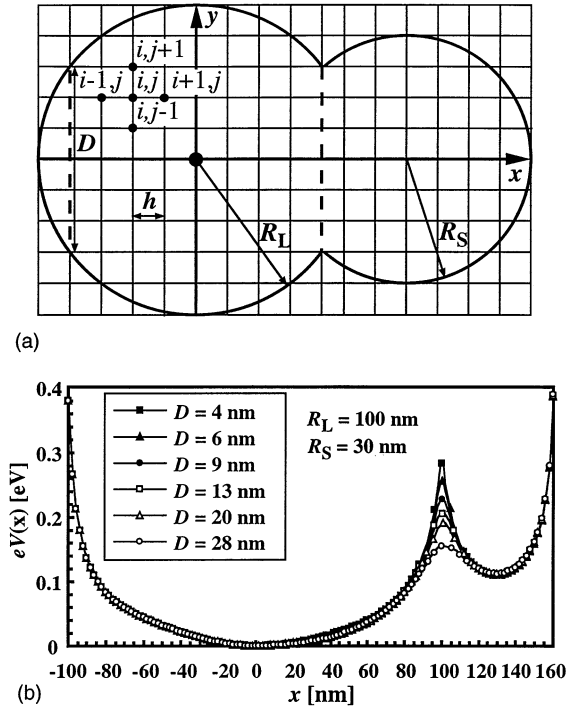


Fig. 4. (a) Schematic illustrations of a contact between two grains with different radii R_L and R_S . D is the diameter of the contact circle in a neck and h is the mesh size used in the numerical solution. (b) Potential energies $eV(x)$ through various neck contacts between two spherical grains with $R_L = 100$ nm and $R_S = 30$ nm calculated at 573 K in the case of mobile single donors with $N_{ds} = 10^{26} \text{ m}^{-3}$ [7].

of D on the energy barrier between the grains also strongly affects the electrical conductance between the grains.

The heights of potential energy barriers may vary due to grain size, or size and shape of the necks between grains. This, in turn, affects electrical conductance of a whole polycrystalline oxide semiconductor. Analytical calculation of the electrical conductance is again a very difficult task due to the non-linear $I-U$ characteristic of a single grain contact. Here, the Monte Carlo method is a possible method. Fig. 5(a) illustrates a small cubic-like network modelling a polycrystalline semiconductor. The resistive components obey a non-linear $I-U$ characteristic, which is realistic in grain contacts at higher voltages [8]. The potential energy barriers, being variables in the $I-U$ characteristic of each component, are taken randomly from a uniform distribution. The results in Fig. 5(b) (in arbitrary units) are from a simulation with different widths of the barrier distributions with a network containing 420 resistive components. The non-linearity of the network increases with increasing width of the barrier distributions. Moreover, the non-linearity of the network decreases with increasing temperature and increasing average coordination number (number of contacts with adjacent grains) of the network [9]. A detailed description of the method and more results are given in Ref. [9].

In tin dioxide, oxygen vacancies play an important role. As surface defects they may affect chemical reactions with adsorbates, for example. On the other hand, they behave as donors in the bulk. Hence, an understanding of the role of oxygen vacancies is essential if one wishes to understand the basis of the chemical sensitivity of the oxide surface.

Fig. 6(a) illustrates the cluster $\text{Sn}_{32}\text{O}_{71}$ modelling the unrelaxed SnO_2 (110) 1×1 surface. Our computations are based on the linear combination of atomic orbitals (LCAO) method and a local-density approximation (LDA). LCAO allows us to project the electronic levels of the cluster onto the atomic orbitals, which are used as basis functions. The calculated one-electron levels in three cases (see figure caption) are shown in Fig. 6(b)–(d). The symbols above the energy levels indicate the strongest atomic-orbital component in that molecular orbital with an atom number as a subscript. Creation of oxygen vacancies introduce new levels in the ‘band gap’. Moreover, the vacancies at bridge sites (98) cause an overall shift of

the levels upwards which is related to the change of the electron affinity of a semiconductor [10].

At the moment, the bulk and surface electronic-structure calculations would be much more feasible to carry out, for example, with the commercially available *ab initio* code DSolid. It allows calculation of electronic structures using, for example, periodic slab structures. In our preliminary calculation, a supercell structure containing six atomic layers and six vacuum layers was found to be relatively good for a quantitative description of the relaxation of two surface layers (layers below these two were rigid). A similar procedure was successfully applied to the calculation of the relaxation of a CdS (10 $\bar{1}$ 0) surface [11]. Our preliminary tests in the case of an SnO_2 (110) surface with DSolid have shown that unit cells containing even 30 atoms with surface relaxation allowed for 11 atoms (four layers) can be calculated in moderate times. However, the description of defects, for example, often calls for an even larger unit cell because with too small a cell, the density of defects due to periodicity becomes too large. It seems that in the case of an SnO_2 (110) 1×1 surface, relaxation of the top layers is strong without bridge oxygen atoms, while with them it is negligible. This is a result which must be taken into account in future calculations, for example, with adsorbates.

3. Conclusions

Rate equation simulations predicted the balance between O_2^- and O^- ions at SnO_2 surfaces at different temperatures in agreement with some experimental findings. The diffusion of oxygen vacancies in oxide semiconductors seems to be a reality. This, taken into account in rate equation simulation, gave more realistic values for eV_s . The geometry of the grains has only relative significance with grain sizes below 10 nm. Even small neck contacts strongly decreased eV_s compared to that in open-grain contacts. According to the Monte Carlo calculations, the non-linearity in I – U characteristics increased with increasing scatter of the barrier heights between grains. It was possible to get some qualitative information on the electronic structure of SnO_2 (110) surface with some defects from the cluster approximation. It seems, however, that more precise information can be achieved using periodic slab models.

Acknowledgements

This work was supported by the Academy of Finland. We also thank the Center for Scientific Computing (CSC, Espoo, Finland).

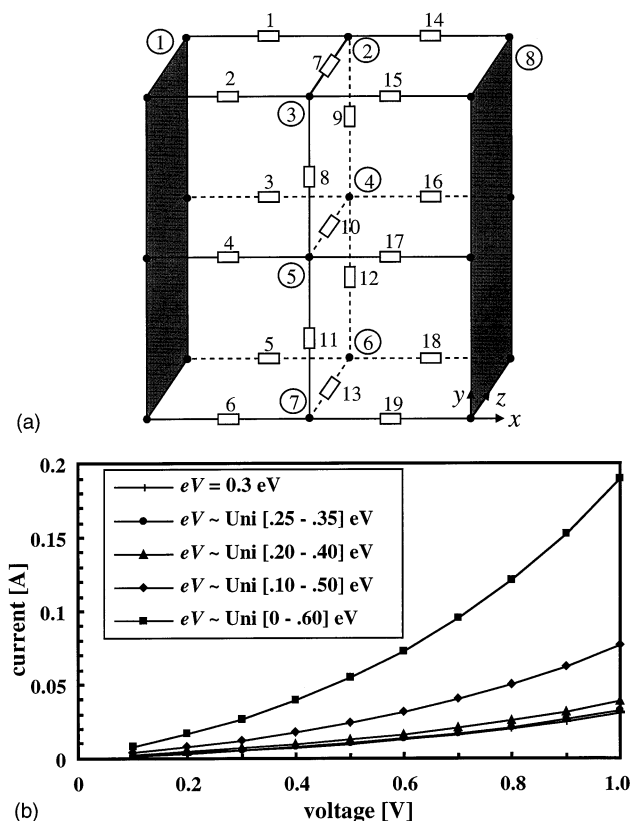


Fig. 5. (a) A schematic picture of a cubic-like network with dimensions 2, 2 and 1 in the x -, y - and z -directions, respectively. The voltage is connected between the conducting planes indicated by grey shading. (b) I – U curves simulated with different barrier distributions at 573 K [8].

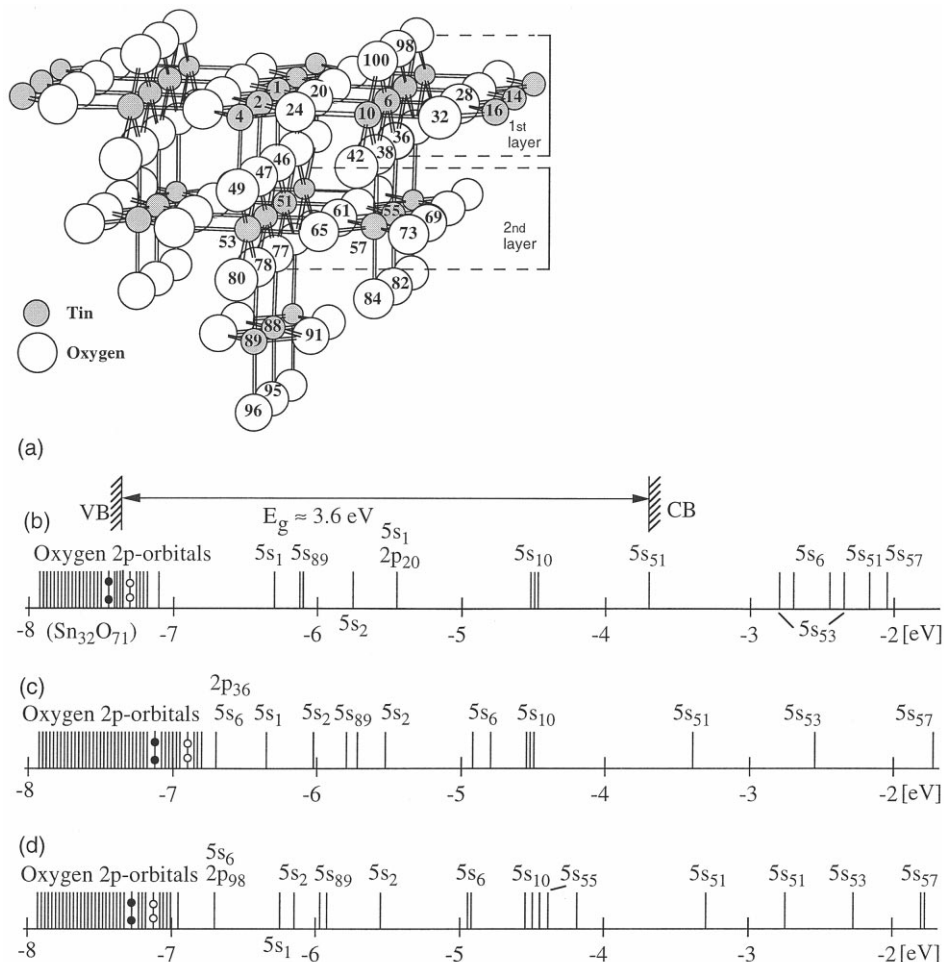


Fig. 6. (a) The cluster $\text{Sn}_{32}\text{O}_{71}$ containing six bridge-site oxygen atoms (98, 100 and their C_{2v} symmetry sites). The two topmost layers in the $[110]$ direction containing three atomic planes are also illustrated. Computed energy level diagrams around the 'band-gap' region ($E_g \approx 3.6$ eV) (b) of the cluster shown in (a) and of its two modifications: two oxygen vacancies at sites 98 and its C_{2v} symmetry site (c), and at sites 36 and its C_{2v} symmetry site (d) [9].

References

- [1] N. Yamazoe, New approaches for improving semiconductor gas sensors, *Sensors and Actuators B* 5 (1991) 7–19.
- [2] T.S. Rantala, Computational approaches to the chemical sensitivity of semiconducting tin dioxide, *Acta Universitatis Ouluensis C Technica* 96, University of Oulu, Oulu, Finland, 1997.
- [3] T.S. Rantala, V. Lantto, T.T. Rantala, Rate equation simulation of the height of Schottky barriers at the surface of oxides semiconductors, *Sensors and Actuators B* 13/14 (1993) 234–237.
- [4] H. Chon, J. Pajares, Hall effect studies on oxygen chemisorption on zinc oxide, *J. Catal.* 14 (1969) 257–260.
- [5] V. Lantto, T.S. Rantala, Computer simulation of the surface energy barrier of oxides semiconductors with mobile donors, *Sensors and Actuators B* 18/19 (1994) 711–715.
- [6] T.S. Rantala, V. Lantto, Some effects of mobile donors on electron trapping at semiconductor surface, *Surf. Sci.* 352/354 (1996) 765–770.
- [7] T.S. Rantala, V. Lantto, T.T. Rantala, Effects of mobile donors on potential distribution in grain contacts of sintered ceramic semiconductors, *J. Appl. Phys.* 79 (1996) 9206–9212.
- [8] J. Sinkkonen, DC conductivity of a random barrier network, *Phys. Status Solidi (b)* 102 (1980) 621–627.
- [9] T.S. Rantala, L. Pirttioho, V. Lantto, Simulation studies of non-ohmic conductance behaviour in SnO_2 thick-film gas sensors, *Sensors and Actuators B* 15/16 (1993) 323–327.
- [10] T.S. Rantala, V. Lantto, T.T. Rantala, A cluster approach for modelling of surface characteristics of stannic oxide, *Phys. Scr. T* 54 (1994) 252–255.
- [11] T.T. Rantala, T.S. Rantala, V. Lantto, J. Vaara, Surface relaxation of the $(10\bar{1}0)$ face of wurtzite CdS, *Surf. Sci.* 352/354 (1996) 77–82.

Biographies

Tuomo Rantala received his Diploma Engineer degree (M.Sc.) in electrical engineering in 1989 from the University of Oulu, Finland. He received his Licentiate of Technology and Doctorate degrees in material physics in 1993 and 1997, respectively, from the University of Oulu. He worked as a researcher in a EUREKA-project EU-94 dealing with metal oxide gas sensors until 1991. Between 1991 and 1994 he worked as a research

associate in the Microelectronics and Material Physics Laboratories of the University of Oulu. Since 1994 he has been a researcher in a project financed by the Finnish Academy, where he is working on surface effects of some compound semiconductors and oxidic semiconductor gas sensors.

Vilho Lantto received the B.Sc. and M.Sc. degrees in material engineering in 1965 and 1968, respectively, a Licentiate of Technology degree in solid-state physics in 1972 and his D.Sc. in 1975 from the University of Oulu, Finland. He worked as a research scientist at the Material Physics Laboratory of the University of Oulu until 1979, and since 1985, after working for a period of 5 years in industry, he has been at the Microelectronics Laboratory of the University of Oulu as an Associate Professor in solid-state physics and physical electronics.

His interests currently include surface effects, solid-state sensors, device simulation and modelling and different techniques for processing of different thin- and thick-film materials and devices.

Tapio T. Rantala is a docent of physics at the University of Oulu. He graduated in physics 1978, in electrical engineering in 1984 and received his Ph.D. degree in physics 1987. He has been a visiting scientist at the Chalmers University of Technology, Gothenburg, Sweden and the State University of New York at Buffalo, NY, USA, and a research fellow of the Academy of Finland. Presently, Tapio Rantala is involved in research in theoretical and computational physics on various topics from surface science and materials science to molecular physics. For more information see URL: <http://cc.oulu.fi/~trantala/>.