

COMPUTATIONAL APPROACHES TO THE CHEMICAL SENSITIVITY OF SEMICONDUCTING TIN DIOXIDE

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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. 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. 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. 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.

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 phenomena in an n-type oxidic semiconductor.

In tin dioxide, which is a wide band-gap oxide semiconductor, oxygen vacancies behave as

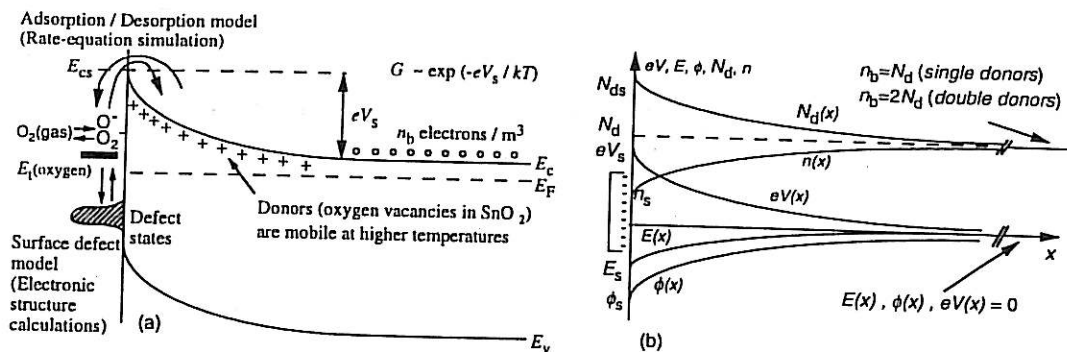


Figure 1: (a) A schematic drawing describing some possible surface and bulk phenomena in an n-type oxodic semiconductor. (b) A schematic drawing for the illustration of the electrical potential $\phi(x)$, the electric field $E(x)$, the potential energy of electrons $eV(x)$, the distribution of mobile 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].

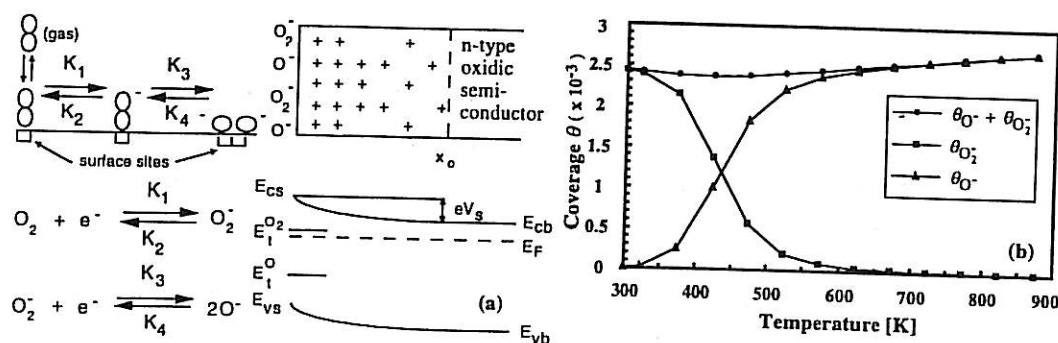


Figure 2: (a) A schematic illustration with rate equation constants K_i ($i=1,2,3,4$) of the ionosorption of oxygen on an n-type semiconductor surface with band bending. (b) Simulated coverage (per adsorption site) of O_2^- , O^- and $O_2^- + O^-$ as a function of temperature T in dry synthetic air with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

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.

Computational methods and results

A rate equation model has been constructed in the frame of the Shockley-Hall-Read generation-recombination model to describe the electronic exchange between adsorbed oxygen species and

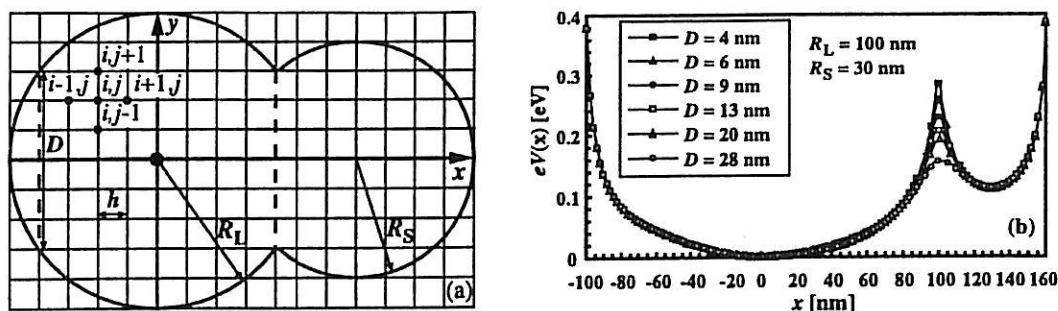


Figure 3: (a) Schematic illustrations of a contact between two grains with different radii R_L and R_S . D is the diameter of the contact circle in a neck and h is the mesh size used in the numerical solution. (b) Potential energies $eV(x)$ through various neck contacts between two spherical grains with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

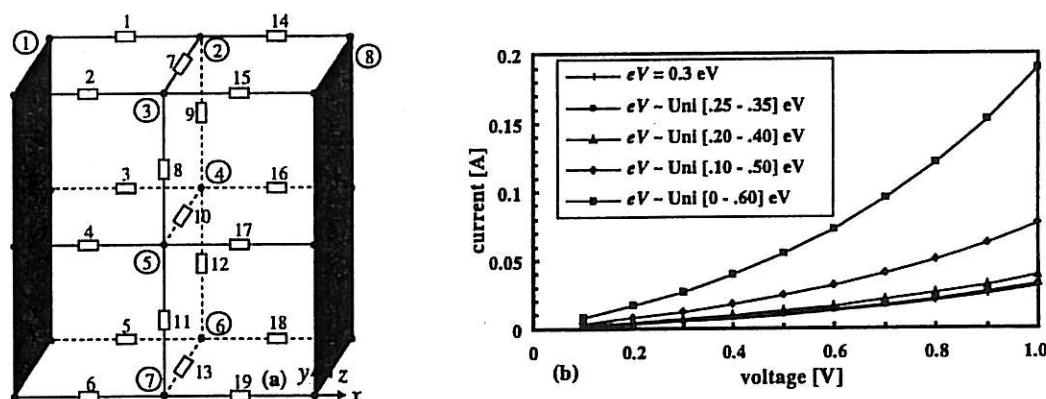


Figure 4: (a) A schematic picture of a cubic-like network with dimensions 2, 2 and 1 in the x , y and z directions, respectively. The voltage is connected between the conducting planes indicated by grey shading. (b) I - U curves simulated with different barrier distributions at $T = 573$ K [5].

the bulk conduction band of a semiconductor. Fig. 2(a) describes schematically the model, which with four rate constants are described in detail elsewhere [3]. 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.

Fig. 3(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 finite difference method [4]. The symbol D is the diameter of the contact circle in the neck between the grains. Fig. 3(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 of D on the energy barrier between the grains affects strongly also the electrical conductance between the grains.

Fig. 4(a) illustrates a small cubic-like network modelling a polycrystalline semiconductor. The

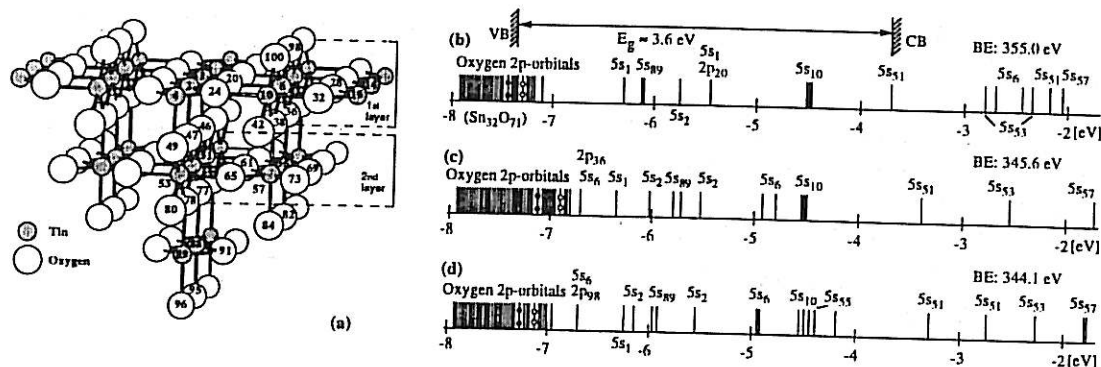


Figure 5: (a) The cluster $\text{Sn}_{32}\text{O}_{71}$ containing six bridge-site oxygen atoms (98, 100 and their C_{2v} symmetry sites). The two topmost layers in the $[110]$ direction containing three atomic planes are also illustrated. Computed energy level diagrams around the "band-gap" region ($E_g \approx 3.6$ 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) [6].

resistive components obey nonlinear I - U characteristic, which is reality in grain contacts at higher voltages. The potential energy barriers for different components are taken randomly from a uniform distribution. The results in Fig. 4(b) (in arbitrary units) are from a simulation with different widths of the barrier distributions with a network containing 420 resistive components. The nonlinearity of the network increases with increasing width of the barrier distributions. A detailed description and more results are given in Ref. [5].

Fig. 5(a) illustrates the cluster $\text{Sn}_{32}\text{O}_{71}$ modelling the unrelaxed $\text{SnO}_2(110)1 \times 1$ 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 (b), (c) and (d). The symbols above the energy levels indicate the strongest atomic-orbital component in that molecular orbital with a 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 [6].

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