

Rate equation simulation of the height of Schottky barriers at the surface of oxidic semiconductors

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Abstract

Rate equation simulation is used in the present computational approach in order to study the role of different adsorbed oxygen ions (O_2^- and O^-) in controlling the height of the Schottky barrier at the surface of SnO_2 , a key material in the field of semiconductor gas sensors. Computations are based on the adsorption/desorption model and consider the electron transfer between different oxygen species on the surface and the bulk conduction band. Different values have been tested for both the frequency factors and the activation energies of the rate constants in order to consider the relative population between the O^- and O_2^- ions on the surface at different temperatures, the dependence of the height of the surface Schottky barrier on temperature and oxygen partial pressure, and also the response and recovery times of the barrier heights as a consequence of rapid temperature changes. Comparisons of calculated barrier heights with some empirical values are also given at different temperatures and oxygen partial pressures.

1. Introduction

It is well known that negative charges accumulate on the surface of n-type semiconductor materials like ZnO , SnO_2 and $CdSe$ in an atmosphere containing oxygen. According to the general electronic theory of chemisorption, this is due to the discrete energy levels introduced by oxygen within the bandgap at the semiconductor surface. The situation is, to some extent, similar to the interface trapped charge in MOS structures [1], where the well-known dangling bond states inside the bandgap behave as electron traps on silicon surfaces (the optical bandgap of SnO_2 was found to be nearly free of surface states in ref. 2). Either capacitance measurement or conductance measurement can be used to evaluate electron transfer rates between the interface traps and the bulk conduction band in MOS diodes [3]. Expressions which are similar to those for the generation–recombination processes (Shockley–Hall–Read) can be used to describe the variation of measured electron transfer rates versus surface potential for MOS diodes [3]. In our simulation procedure we adopt similar expressions to describe electron capture rates from the bulk conduction band to oxygen surface species.

2. Surface reactions

The computer simulation is based on the rate equations:



where all species O_2 , O_2^- and O^- are considered to be adsorbed (on similar surface sites). Corresponding surface concentrations are denoted by $[O_2]$, $[O_2^-]$ and $[O^-]$. According to the concept of the capture cross section from the generation–recombination theory, the rate constants K_1 and K_3 are described by the following expressions:

$$K_1 = \nu_{01}(T) S_{O_2}(T) \sigma_{O_2} v_{th} n_s P_{O_2} (1 - \theta) / N_s \quad (3)$$

$$K_3 = \sigma_{O_2^-} v_{th} n_s \exp(-\Delta E_d / kT) \theta_{O_2^-} (1 - \theta) \quad (4)$$

where σ_{O_2} and $\sigma_{O_2^-}$ are the capture cross sections related to O_2 and O_2^- , respectively, v_{th} is the average thermal velocity $(3kT/m^*)^{1/2}$ (m^* is the effective mass of electrons) and the conduction electron concentration at the surface

$$n_s = n_b \exp(-eV_s / kT) \quad (5)$$

n_b being the bulk concentration and eV_s the height of the Schottky barrier at the surface. $\nu_{01}(T)$ describes the number of molecules colliding per unit surface area in unit time and can be expressed according to the kinetic gas theory as

$$\nu_{01}(T) = (N_A P / 4R) (8k / \pi m_{O_2})^{1/2} T^{-1/2} \quad (6)$$

where P is the total pressure, m_{O_2} the mass of O_2 , N_A Avogadro's number and R the gas constant. P_{O_2} in eqn. (3) is the partial pressure of oxygen and the number of adsorption sites per unit surface area $N_s \approx (\rho N_A / A)^{2/3}$ where ρ is the density and A the mass number. $S_{O_2}(T)$ is a sticking coefficient for O_2 describing the fraction of colliding O_2 molecules which are physisorbed, while t_{ph} is the average adsorption time of physisorbed oxygen molecules described by the expression:

$$t_{ph} = (\nu_{O_2})^{-1} \exp(\Delta E_{ph}/kT) \quad (7)$$

where ν_{O_2} is the vibration frequency of physisorbed O_2 and ΔE_{ph} the average energy of physisorption of O_2 . In addition to the electron capture to O_2^- , it is assumed in expression (4) that a vibration energy ΔE_d is also necessary for the dissociation reaction (2).

The total adsorbed oxygen coverage per adsorption site is

$$\theta = ([O_2] + [O_2^-] + [O^-])/N_s = \theta_{O_2} + \theta_{O_2^-} + \theta_{O^-} \quad (8)$$

In the case of constant donor concentration N_d (single donors) in the space charge region at the surface, the Schottky barrier has an expression:

$$eV_s = e^2 N_t^2 / (2\epsilon_s N_d) \quad (9)$$

where ϵ_s ($= \epsilon_r \epsilon_0$) is the permittivity of the semiconductor and N_t is the density of trapped electrons on the surface ($N_t = [O_2^-] + [O^-]$).

The rate constants for the injection rates of electrons from the O_2^- and O^- species are described by the expressions:

$$K_2 = \nu_{O_2} \exp(-\Delta E_{O_2}/kT) \theta_{O_2^-} \quad (10)$$

$$K_4 = \nu_{O_4} \exp(-\Delta E_O/kT) (\theta_{O^-})^2 \quad (11)$$

By depositing ferrocyanide on porous ZnO and measuring the surface potential in an oxygen atmosphere, Morrison [4] found Arrhenius plots with inverse temperature for the injection rates of both O_2^- and O^- . The Arrhenius slopes were 0.9 eV for O_2^- and 0.4 eV for O^- . The ion densities on the surface were very high (nearly a monolayer) in those experiments. It is believed that 0.9 eV represents the surface state energy $E_{t^{O_2}}$ of O_2^-/O_2 . The electron injection in the case of O^- is not a simple electron transfer, but must involve the chemical combination of two atoms, as is assumed in reaction (2). The experimental results in ref. 4 give low values for the frequency factors in expressions (10) and (11) (about 100 s^{-1} for ν_{O_4} and 10^7 s^{-1} for ν_{O_2}).

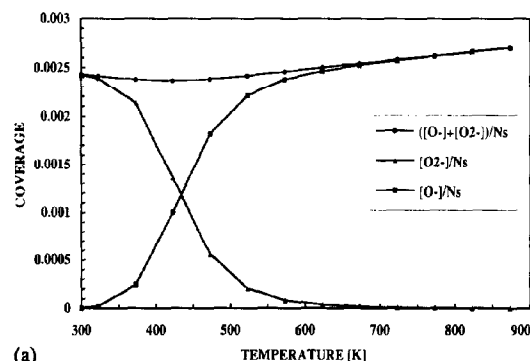
At equilibrium we have

$$d\theta_{O_2^-}/dt = K_1 + K_4 - K_2 - K_3 = 0 \quad (12)$$

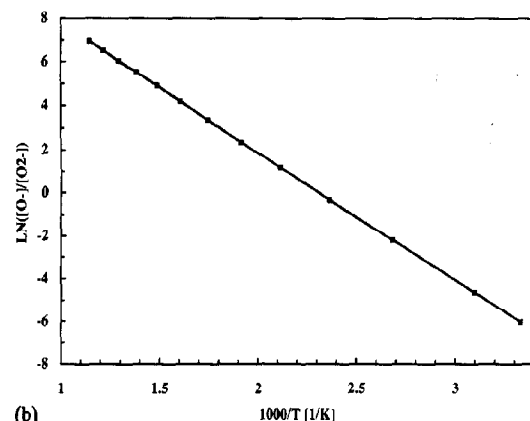
$$d\theta_{O^-}/dt = K_3 - K_4 = 0 \quad (13)$$

3. Rate equation simulation of eV_s

A value of 10^{-17} cm^2 was used for both capture cross sections σ_{O_2} and $\sigma_{O_2^-}$ (for the interface trap states of MOS diodes the values are of the order of 10^{-16} cm^2 [3]) together with a value 0.01 for $S_{O_2}(T)$ (independent of temperature) in the calculation of the values of the surface barrier eV_s on SnO_2 . The other necessary assumptions in the calculation were 10^{12} s^{-1} for ν_{O_2} , 0.1 eV for ΔE_{ph} and 0.4 eV for ΔE_d , while the empirical results of Morrison [4] were used for the rate constants K_2 and K_4 in expressions (10) and (11). The coverage of different oxygen ions $\theta_{O_2^-}$ and θ_{O^-} together with total coverage $\theta_{O_2^-} + \theta_{O^-}$ on SnO_2 , with the bulk electron concentration of $4.5 \times 10^{17} \text{ cm}^{-3}$, in dry synthetic air (20% O_2) from the simulation calculation are shown in Fig. 1(a). An analytical expression is given by Morrison [5] for the ratio



(a)



(b)

Fig. 1. (a) Calculated coverage (per adsorption site) of O_2^- , O^- and $O_2^- + O^-$ as a function of temperature in dry synthetic air. (b) Natural logarithm of the ratio $[O^-]/[O_2^-]$ as a function of inverse temperature from a rate equation simulation (■) together with fitting to eqn. (14) (—).

$$[O^-]/[O_2^-] = (K/[O_2])^{1/2} \exp[(E_t^{O_2} - E_t^{O^-} - \Delta G/2)/kT] \quad (14)$$

where ΔG is the free-energy change of the dissociation of an oxygen molecule and $E_t^{O_2}$ and $E_t^{O^-}$ are the surface state energies for O_2^- and O^- . The logarithm of the ratio $[O^-]/[O_2^-]$ from the results in Fig. 1(a) is plotted as a function of inverse temperature in Fig. 1(b). It is possible to calculate from the slope of this curve a value 0.51 eV for $(E_t^{O^-} - E_t^{O_2} + \Delta G/2)$.

Figure 2 shows calculated values of eV_s as a function of oxygen partial pressure at temperatures of 373, 573 and 773 K. A value $2.25 \times 10^{17} \text{ cm}^{-3}$ was used for the concentration of double donors (oxygen vacancies) in SnO_2 . eV_s is found to be proportional to the logarithm of oxygen partial pressure at all three temperatures. The influence of doping on eV_s at temperatures between 300 and 873 K is shown in Fig. 3 where calculated values of eV_s in synthetic air are given at five different constant concentrations of double donors. The surface barrier is shown to increase with increasing constant donor concentration at all temperatures. It is also shown

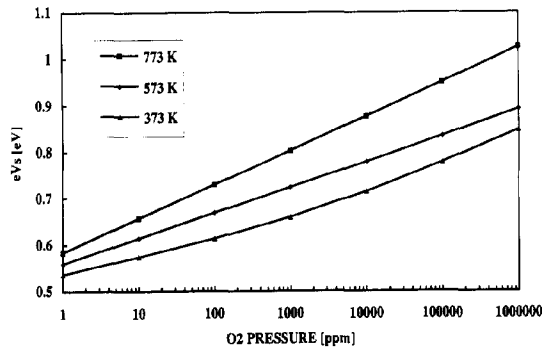


Fig. 2. Calculated surface barriers eV_s as a function of oxygen partial pressure at temperatures of 373, 573 and 773 K.

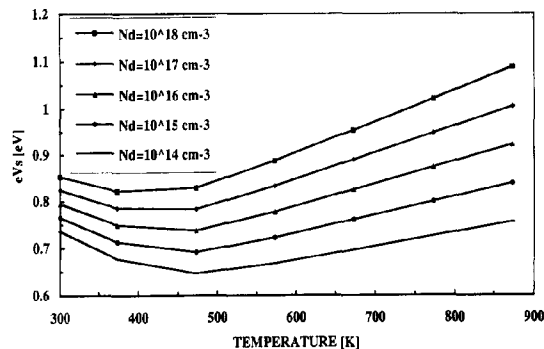
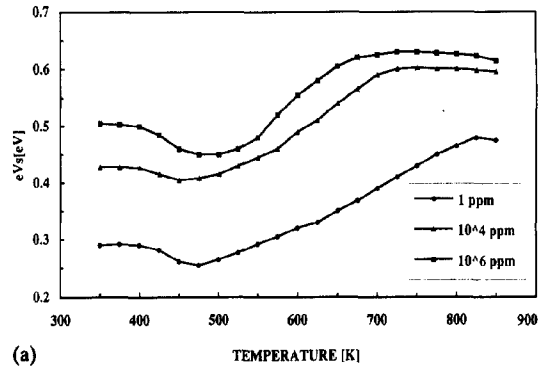
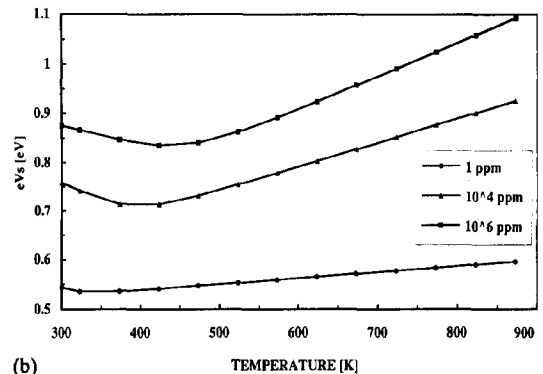


Fig. 3. Calculated surface barriers eV_s as a function of temperature in SnO_2 with donor concentrations (double donors) of 10^{14} , 10^{15} , 10^{16} , 10^{17} and 10^{18} cm^{-3} .



(a)



(b)

Fig. 4. (a) Empirical values of eV_s of a TGS 812 sensor as a function of temperature calculated from the measured conductance data at O_2 partial pressures of 10^6 , 10^4 and 1 ppm in N_2 [6]. (b) Calculated surface barriers eV_s as a function of temperature at the same O_2 partial pressures as in (a).

in Fig. 3 that eV_s increases with increasing temperature above about 200 °C (473 K).

A comparison of the present simulation results with some empirical values of eV_s is shown in Fig. 4. Figure 4(a) shows values of eV_s calculated from the measured conductance values of a commercial SnO_2 sensor (TGS 812) at different dry oxygen partial pressures (10^6 , 10^4 and 1 ppm O_2 in N_2 , humidity less than 5 ppm) between 350 and 850 K [6]. The increase of the activation energy of conductance eV_s ($G = G_0 \exp(-eV_s/kT)$ for sintered samples) above about 500 K in Fig. 4(a) is a peculiar property of sintered SnO_2 samples. This increase was related to the dissociation of O_2^- to the O^- form in ref. 6. The values of eV_s on SnO_2 from the simulation calculation at the same oxygen partial pressures between 300 and 873 K are shown in Fig. 4(b). The constant concentration of double donors was $2.25 \times 10^{17} \text{ cm}^{-3}$ in the calculation.

4. Conclusions

The values of the many entities in the expressions for K_1 , K_2 , K_3 and K_4 are not accurately known for the

case of SnO_2 (some cluster calculations based on both LDA-SCF and LDA-APA (atomic potential approximation) approaches were made in order to assign some of these entities). A variation between different alternatives may, however, give some information on how far the adsorption/desorption mechanism alone is capable of explaining the response characteristics of semiconductor gas sensors. A comparison of Figs. 4(a) and (b), for instance, on the basis of the results in Fig. 1, shows that the dissociation reaction (2) is capable of explaining the observed increase of activation energy with increasing temperature in SnO_2 gas sensors. The border temperature of about 170 °C between O_2^- and O^- ions in Fig. 1 is also in good agreement with some Hall effect measurements [7].

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