

Interaction between collective and local subsystems in semiconductor surface-active structures

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Abstract

Two different mechanisms have been suggested to describe the interaction between the chemisorbed molecule and semiconductor surface during equilibrium disturbance. The correlation between the sorption subsystem, characterized by local quantum-mechanical parameters of a chemisorbed complex, and the electronic subsystem, described by collective characteristics of the crystal, has been analysed using the example of oxygen interaction with CdS and SnO₂ polycrystalline films.

Keywords: Gas sensors; Semiconductor surfaces

1. Introduction

For the improvement of the detection of molecules or ions by semiconductor solid-state sensors, a detailed understanding is required of the chemical composition and structure of the surface, together with the surface electronic properties of the materials involved.

Two different approaches are commonly discussed to explain the interaction between adsorbed particles and a semiconductor surface:

(i) a collective (electronic approach) within the range of the band scheme of the semiconductor, with special emphasis on the Fermi-level position in the band gap [1];

(ii) a local (chemical approach), based on a consideration of the concrete electronic structures of surface species and adsorbed molecules, using MO LCAO theories and the cluster approximation [2].

The collective approach allows a great number of theories and methods, well developed in semiconductor physics, to be applied. From the viewpoint of collective interactions, the entire individuality of a chemisorbed particle lies in a single parameter, the position of the local level of that particle. Thus, all chemical properties of the chemisorbed molecule are restricted by consideration of the affinity to the electrons or ionization energy, while all the chemical properties of the crystal depend on the position of the Fermi level in the band gap.

The local approach opens possibilities to use the methods of quantum chemistry, dealing with limited

molecular systems, considering the interaction between corresponding molecular fragments. The MO LCAO methods allow the electronic levels of the cluster to be projected onto the atomic basis functions, which are the most convenient in explaining adsorption processes in terms of atomic orbitals [3].

This paper deals with an attempt to apply interaction diagrams (model of external orbitals) within the band scheme of the semiconductor. In this case, the interaction between separate orbitals localized in space and the semiconductor surface should be considered, taking into account the energy position of the orbitals in the band gap of the semiconductor. Therefore, studies of chemisorption processes can be extended by considering the interaction between the sorption subsystem, characterized by the local quantum-mechanical parameters of a chemisorbed complex (e.g., configuration and location of external orbitals) and the electronic subsystem, described by the collective characteristics of the crystal (e.g., values of band bending ($e\Delta V_s$) and bulk position of the conduction-band edge relative to the Fermi level (ΔE_F)). The splitting of local energy levels, originating from the 'adsorbates', and their changes during an excitation can be computed using the cluster approach, based, for instance, on the local-density approximation and atomic orbitals as a basic set [3].

The different possibilities of the equilibrium disturbance are analysed in terms of the suggested model for the example of oxygen interaction with CdS and SnO₂ surfaces.

2. Theoretical treatment

Excitation of a surface-active system (e.g., by photons, applied electric field, changing partial pressure or temperature, etc.), breaks the equilibrium of both electron and sorption subsystems. Because of the interaction between these two subsystems, a fundamental question arises about the priority between the subsystems when the system is passing to a new steady state, which is not clear.

Two different mechanisms have been suggested to describe the interaction between the chemisorbed molecule and the semiconductor surface during equilibrium disturbance. The 'physical' channel transfers the energy to the electron subsystem, while the 'chemical' channel generates direct excitations of the chemisorbed complex, allowing the desorption of molecules through thermal vibration.

Predomination of the electron subsystem is considered in the framework of the widespread Volkenstein model, with a special role belonging to the Fermi energy, which determines the conductivity behaviour as well as the concentration of different adsorbed extrinsic species on the surface. In the case of temperature-stimulated desorption, the Fermi level is expected to be found at an energy distance $\approx kT$ from the level formed by the chemisorbed molecule in the semiconductor band gap. The thermal activation of an electron from the chemisorption state into the conduction band (in the case of an acceptor-type surface defect) is considered as the precursor for the desorption of the neutral molecule, since lifetimes in the physisorption state are usually negligible at higher temperatures. The rate constants for the injection of electrons from the extrinsic species are described by the expression [1]

$$K_1 = v_{th} \sigma_s N_c N_s^- \exp(-\Delta E_s/kT) \quad (1)$$

where v_{th} is the average thermal velocity $(3kT/m^*)^{1/2}$ (m^* is the effective mass of an electron), σ_s and N_s^- are the capture cross section and surface concentration of the chemisorbed molecules, ΔE_s is the surface-state energy of the chemisorbed molecule, relative to the conduction band edge and N_c is the effective density of states in the conduction band. The correlation between the concentration of donor-type defects (N_d) and adsorbed states, $N_d \geq N_s^-/d$ (where d is the grain size), will define the surface- or bulk-control mode of the dark conductivity behaviour. In this case, the intrinsic defects may pin the Fermi level and, hence, it does not essentially change position in the band gap.

On the other hand, in thin-film or polycrystalline materials, with thicknesses or grain sizes below the Debye length, ΔE_F essentially depends on the concentration of chemisorbed species, which in turn is changing during the excitation of the system. The application of the Volkenstein model is restricted, for this reason, by

consideration of different charged surface states with a constant concentration on the surface [4], i.e., the difference between extrinsic and intrinsic surface species disappears.

It was found at special operating conditions (direct excitation of chemisorbed complex) [5], the 'chemical' channel of energy transfer became significantly important and activation of electrons to the conduction band took place through the determining role of local subsystem excitations. In this case, the rate of electron injection to the conduction band will be given by

$$K_2 = \nu N_s^- \exp(-\Delta E_s/kT) \quad (2)$$

where ν is the vibration frequency of the chemisorbed molecule.

The comparison of Eqs. (1) and (2) gives simple criteria of realization of one of the possible mechanisms of desorption. The relation $v_{th} \sigma_s N_c > \nu$ describes the predominance of the electron subsystem. Conversely, $v_{th} \sigma_s N_c < \nu$ allows the thermal vibration desorption mechanism to take place. In this case, collective electronic parameters, e.g., the position of the Fermi level in the band gap, become functionally dependent on the local characteristics of the sorption subsystem, resulting in the recompensation of the sample. Since the disturbance of the equilibrium took place through the prevalence of the local excitation mechanism, the Fermi-level position in the band gap, calculated in accordance with Fermi-Dirac statistics, may be found $\approx kT$ from the corresponding intrinsic defects, while the Arrhenius slope with inverse temperature is determined by thermal activation of an electron from the chemisorbed species.

It must be noted that the Volkenstein model, based on Fermi-Dirac statistics, enables us to describe the equilibrium states of the system at different operating temperatures. At the same time, it could not be used for the consideration of equilibrium disturbance and transition to the new steady state for a system with predominance of the 'chemical' mechanism of excitation. The behaviour of the system with a changeable concentration of surface defects should be considered in terms of the general Gibbs distribution. However, with definite simplifications, it is possible to describe it by analytical equations.

Fig. 1 illustrates the schematic interaction steps used for the computation. In this model, changes in conductivity are due to electron capture by a physisorbed molecule and intrinsic donor-type defects shown respectively in reactions 1 and 5. Thermal activation of an electron from the intrinsic donors is indicated by reaction 4. The two different mechanisms suggested for energy transfer to the surface states are shown in reactions 3 and 2, which are related respectively to the activation of the electron subsystem and direct extinction of the chemisorbed complex. The corresponding rates

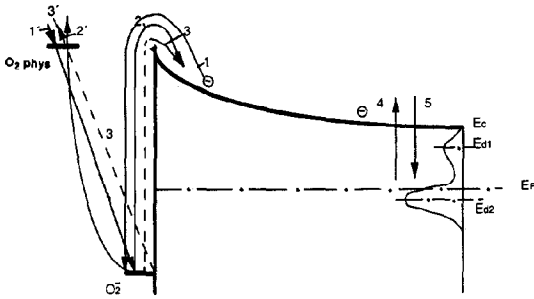


Fig. 1. Different steps of system activation during chemisorption.

of adsorption and desorption processes are shown by reactions 1', 2' and 3'.

The equilibrium of the sorption subsystem is described by the expression

$$\alpha P(N^* - N) = \nu_0 N_s^0 \exp(-q^0/kT) + \nu V_s^- \times \exp[-(\Delta E_s + q^0)/kT] \quad (3)$$

where $\alpha = \kappa/N^*(2\pi M kT)^{1/2}$, κ is the probability of a particle being captured by the surface, N and N^* are the surface concentration of adsorbed particles and adsorption centres, respectively, P is the pressure of the gas, M the adsorbed particle mass, ν_0 and ν are the vibration frequency factors, related to the physisorbed and chemisorbed states of the particle and q^0 is the binding energy of the physisorbed molecule.

If $\nu < \nu_{th} \sigma_s N_c$, the thermal vibration mechanism of desorption is negligible (reactions 2 and 2', Fig. 1) and from Eq. (3) we have

$$\alpha P(N^* - N) \approx \nu_0 N_s^0 \exp(-q^0/kT) \quad (4)$$

The equilibrium for the electron subsystem in the case of constant donor concentration N_d (single donors) can be expressed as

$$\nu_{th} \sigma_d N_c n_d \exp(-\Delta E_d/kT) + d \nu_{th} \sigma_s N_c N_s^- \times \exp(-\Delta E_s/kT) = \nu_{th} \sigma_d N_d^+ n_b + d \nu_{th} \sigma_s N_s^0 n_s \quad (5)$$

where $n_s = n_b \exp(-e\Delta V_s/kT)$, ΔE_d is the bulk donor state energy relative to the conductance band edge, σ_d is the capture cross section related to the donors and N_d^+ and n_d are the concentrations of ionized and neutral donors, respectively.

An aim of this study was to consider the conductivity behaviour in the case of chemisorbed surface states ($\Delta E_s > \Delta E_F \sim \Delta E_d$) deeply situated in the band gap, which caused a strong depletion mode of the grains, and how it takes place, e.g., for oxygen chemisorption on CdS and SnO₂ [6,8].

The current through the sample can be described by

$$I(T) = e \mu_b n_b \exp(-e\Delta V_s/kT) ES \quad (6)$$

were E is the applied electric field, S is the cross section of the sample and μ_b is the bulk mobility of the free carriers. Starting from the equation

$$N_d = n_d + dN_s^- \quad (7)$$

and using Eqs. (5)-(7), we can write

$$I(T) = b(T) N_c \left[\left(\frac{N_d}{dN_s^-} - 1 \right) \exp(-\Delta E_d/kT) + \frac{\sigma_s}{\sigma_d} \exp(-\Delta E_s/kT) \right] \quad (8)$$

where $b(T) = e \mu \exp(-e\Delta V_s/kT) ES$.

The results presented in Refs. [1,7,11] give different values for the frequency factors in expression (3): about 10^{12} - 10^{16} s⁻¹ for ν_0 and 10^7 - 10^{16} s⁻¹ for ν . The effective cross section for electron capture of O₂phys and the value of ΔE_s are thus in the range 10^{-20} - 10^{-24} m² and 0.8-1.1 eV [1,8,10]. Fitting $\Delta E_d = 0.2$ eV from Ref. [10], it is easy to see that the first term in Eq. (8) predominates. Taking into account the low value of the band bending in the case of the strong depletion regime (see Section 4), we can conclude that the activation energy is determined by the bulk donor species, crossed by the Fermi level. The probability of the thermal activation of an electron from the surface states (reaction 3, Fig. 1) depends on the relation between ΔE_s and ΔE_F and is negligible for $\Delta E_s > \Delta E_F$.

The ratio between charged and neutral forms of chemisorbed species is also determined by ΔE_F :

$$N_s^- / N_s^0 = \exp[(\Delta E_s - \Delta E_F)/kT] \quad (9)$$

This is in accordance with Volkenstein theory. From these estimations, it follows that in the case of predomination of the electron subsystem, desorption of extrinsic species requires the relation $\Delta E_s \sim \Delta E_F$, which cannot easily be achieved. For instance, location of the Fermi level at 1.3 eV in the band gap of CdS should cause p-type conductivity behaviour, which has never been observed in such structures.

On the other hand, when $\nu > \nu_{th} \sigma_s N_c$ (reactions 1 and 1' (Fig. 1) are negligible), the equilibrium of the sorption subsystem is described by

$$\alpha P(N^* - N) \approx \nu N_s^- \exp[-(\Delta E_s + q^0)/kT] \quad (10)$$

and using Eqs. (5)-(7) for the current through the sample we have

$$I(T) = b(T) N_c \left[\left(\frac{N_d}{dN_s^-} - 1 \right) \exp(-\Delta E_d/kT) + \frac{\nu}{2\nu_{th}\sigma_s} \exp(-\Delta E_s/kT) \right] \quad (11)$$

If

$$N_c \left(\frac{N_d}{dN_s^-} - 1 \right) \exp(-\Delta E_d/kT) > \frac{\nu}{2\nu_{th}\sigma_s} \exp(-\Delta E_s/kT)$$

the thermal activation of electrons from the intrinsic donor defects takes place (reaction 4, Fig. 1) and the Arrhenius slope is determined by the Fermi-level position. Increase of the temperature leads to the relation

$$N_c \left(\frac{N_d}{dN_s^-} - 1 \right) \exp(-\Delta E_d/kT) < \frac{\nu}{2\nu_{th}\sigma_s} \exp(-\Delta E_s/kT)$$

and causes predomination of the thermal vibration desorption mechanism.

The detailed balance principle requires Eq. (9) to be satisfied at the equilibrium of the system. Hence, from Eqs. (9) and (11) we can conclude that the ratio between different charged forms of chemisorption does not depend on the position of the Fermi level and is determined by parameters of the local subsystem:

$$\frac{N_s^-}{N_s^0} \approx \frac{\nu}{2\nu_{th}\sigma_s N_c} \quad (12)$$

The charged and neutral forms leave the surface simultaneously and in such a way that their fractions do not vary with changing operating temperature, thus retaining their relative value all through the desorption process. Here, the shift of Fermi level in the band gap also depends on the characteristics of the sorption subsystem:

$$\Delta(\Delta E_F) = -k \ln \left[\frac{\nu}{\nu_{th}\sigma_s N_c} \right] \Delta T \quad (13)$$

while the activation energy corresponds to ΔE_s .

The value of ΔE_F calculated from Eq. (11) is shown in Fig. 4 (solid line). Fitting of the ratio (12) to the expression (3) leads to

$$\alpha P(N - N^*) = \nu_0 N_s^0 \exp(-q^0/kT) + \frac{N_s^0 \nu^2}{2\nu_{th}\sigma_s N_c} \exp \left[-\frac{(\Delta E_s + q^0)}{kT} \right] \quad (14)$$

The comparison of the terms in Eq. (14) gives the effective temperature

$$T^* = \frac{\Delta E_s}{k} \left[\ln \left(\frac{\nu^2}{2\nu_0 \nu_{th} \sigma_s N_c} \right) \right]^{-1} \quad (15)$$

which characterizes the peculiarity in exchanging chemisorbed particles with the gas phase. If $T < T^*$, we have

$$\alpha P(N^* - N) \approx \nu_0 N_s^0 \exp(-q^0/kT) \quad (16)$$

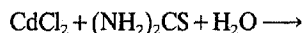
and the Volkenstein model may be applied. Conversely, if $T > T^*$

$$\alpha P(N^* - N) \approx \nu N_s^- \exp \left[-\frac{(\Delta E_s + q^0)}{kT} \right] \quad (17)$$

and the 'local excitation' mechanism of the desorption process predominates.

3. Experimental

The sensors were deposited by electrohydrodynamic spraying of 0.01–0.06 mole solutions of CdCl_2 and $(\text{NH}_2)_2\text{CS}$ on a glass substrate heated at 670–750 K in air, by the chemical reaction



The concentrations of CdCl_2 and $(\text{NH}_2)_2\text{CS}$ in solution were chosen in such a way that the Cd/S ratio in the spray-deposited films was equal to one. The resistivity of the films was in the range 10^8 – $10^{12} \Omega \text{ cm}$. The average grain size of the films, from SEM observations (about 100 nm), was comparable with the thicknesses of the samples (d), thus the deposited films represent a monolayer of crystals on the substrate. Film thicknesses were comparable to the Debye length for conduction electrons in order to avoid shunting of the surface of the sample by its volume. Evaporated indium was used for the contacts. All the contacts used were found to be ohmic.

The sensors were mounted in a test chamber and dry gas mixtures were allowed to flow through the chamber at a fixed flow rate. The desired temperature (300–500 K) for the sensor was obtained by heating in an oven. Temperature-stimulated current measurements were performed with a heating and cooling rate of 2 K min^{-1} in a dry gas mixture containing 2×10^5 ppm of oxygen in nitrogen.

XPS analysis of the oxygen interaction with CdS film surfaces was performed using a VG Escalab Mk II spectrometer.

4. Results and discussion

Results from temperature-stimulated current measurements as a function of inverse temperature are shown in Fig. 2. Similar behaviour of conductivity for CdS analysed films and SnO_2 polycrystalline films was found [6], which allows us to assume the community of proceeding processes. Curve 1 represents the current response of freshly deposited films in pure nitrogen. Exposure of the films to oxygen at 300 K for 2 h led to a decrease of the current and to a sigmoid behaviour of dark conductivity during heating of the film (curve 2). Cooling back to 300 K caused a considerable decrease of the current (curve 3), and the form of curve 3 was reproducible during heating and cooling cycles in an oxygen atmosphere. The Arrhenius slopes corresponding to the activation energy of conductance are 0.2 eV

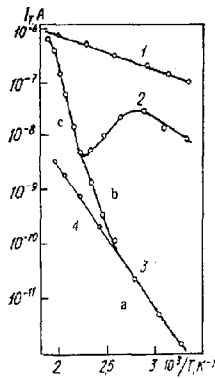


Fig. 2. Current through the CdS sensor as a function of inverse temperature, measured in (1) pure N₂ and after exposure to a dry gas mixture containing 2 × 10⁵ ppm O₂ in N₂ at heating (2) and cooling (3) rates of 2 K min⁻¹. Curve (4) was measured while the surface of the film has been coated by a thermostable paste, preventing chemisorption processes.

for curve 1 and 0.6, 0.9 and 1.3 eV for the three parts a, b and c of curve 3, respectively. The initial low-resistive state of the film could be restored by annealing at 500 K in pure nitrogen.

Mass-spectroscopy observations from CdS thin films during thermodesorption of oxygen [9] show two temperature ranges for oxygen desorption; a low-temperature range (300–400 K) with an activation energy of 0.9 eV and a high-temperature range (400–500 K) with an activation energy of 1.3 eV, related to O₂⁻ and O⁻ oxygen species, respectively. The Arrhenius slopes in Fig. 2 give similar activation energies for conductance of about the same temperature ranges, while part a of curve 3 (Fig. 2) may be connected with thermal activation of electrons from some native defects (reaction 4, Fig. 2).

XPS measurements combined with etching of the surface of analysed films confirm the presence of spatially separated populations of <O₂⁻>_{ad} and <O⁻>_{ad} complexes on the outer film surface and in the intergranular layers, respectively, with O 1s electron energies E_{O₂⁻} = 531.8 eV and E_{O⁻} = 531.1 eV.

The obtained experimental results may support an interpretation that above 360 K (curve 2, Fig. 2) the dissociation of molecular oxygen takes place together with a subsequent diffusion of atomic oxygen at grain boundaries of the film. This is in agreement with the observed hysteresis of conductance after the heating-cooling cycle of the sample (curves 2 and 3, Fig. 2).

The non-monotonic behaviour of the response times (τ_{a(d)}) of the CdS-based sensors on changing the partial pressure of oxygen from 0 to 2 × 10⁵ ppm at different operating temperatures is shown in Fig. 3 and can also be explained on the basis of the considered model. In the temperature interval 290–340 K, oxygen adsorbed

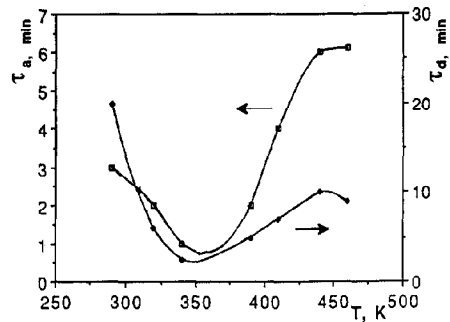


Fig. 3. Temperature dependence of adsorption (τ_a) and desorption (τ_d) response times on changing the oxygen partial pressure.

mainly on the surface of the film. Decrease of temperature in this case led to an increase of τ_{a(d)}, reducing the intensity of the sorption processes, which are the rate-determining step in this temperature interval. The increase of τ_{a(d)} at temperatures above 360–370 K is related to the domination of the diffusion of the oxygen species by the grain boundaries.

Increase of the Arrhenius slopes from 0.1 eV (curve 1, Fig. 2) to 0.6 eV (curve 3, Fig. 2) with an increase of concentration of elemental oxygen in the grain boundaries can be explained by changing eΔV_s as well as ΔE_F. To illustrate their role in influencing the dark-conductivity behaviour at different concentrations of the ionosorbed species, the values eΔV_s and ΔE_F were calculated from the temperature-stimulated measurements on the basis of the modified grain-boundary model, involving electron transfer between different adsorbed oxygen ions.

The electric potential eΔV(x) in the surface region can be solved from Poisson's equation

$$\frac{d^2[e\Delta V(x)]}{dx^2} = -\frac{2e}{\epsilon_s} \int_0^{d/2} \left\{ N_d^+(x) - N_c \exp\left[-\frac{\Delta E_F - e\Delta V(x)}{kT} \right] \right\} dx \quad (18)$$

where

$$N_d^+(x) = \int_{E_v}^{E_c} \left\{ g_1 \exp\left[-\frac{(E_{d1} - E)^2}{kT_1^2} \right] + g_2 \exp\left[-\frac{(E_{d2} - E)^2}{kT_2^2} \right] \right\} \times \frac{dE}{1 + \exp\left[\frac{E - \Delta E_F - e\Delta V(x)}{kT} \right]}$$

ε_s (= ε_rε₀). Computer simulation of the surface energy barrier and Fermi energy is based on the solution of Eqs. (6), (7) and (18). The band scheme of pure CdS used for the computations is shown in Fig. 1. Ionization energies of intrinsic donor-type defects on investigated films were derived from Ref. [10].

It was found that the diverse types of dark-conductivity behaviour under the control of the Schottky barriers and the Fermi energy depend on the different concentrations of ionosorbed oxygen species. Freshly sputtered low-resistive films exhibit grain-boundary-limited mobility behaviour with $e\Delta V_s = 0.2$ eV and $\Delta E_F = 0.1$ eV (curve 2, Fig. 2). Exposure of the samples to an oxygen atmosphere at 500 K for 0.5 h and then cooling to 300 K led to a considerable decrease of the band bending and Fermi energy (e.g., for plot a, (curve 3, Fig. 2) at 300 K $e\Delta V_s = 0.03$ eV and $\Delta E_F = 0.6$ eV). In this high-resistive state a strong depletion regime of the grains was obtained and free-carrier concentration controls the chemiresistive behaviour of the film.

The calculated value of the Fermi energy as a function of operating temperature is shown in Fig. 4 (open circles). The ΔE_F was not essentially changed in the low-temperature interval (300–370 K), which corresponds to the prevalence of the electronic subsystem. The considerable shift of the Fermi level at 370–500 K characterizes the predomination of a local mechanism of oxygen desorption.

We can see that the empirical values of ΔE_F as a function of temperature, obtained from the measured conductance on a concrete semiconductor structure, are in good agreement with the analytical interpretation of the suggested model (solid line in Fig. 4).

It is also anticipated that reducing the intensity of the sorption processes in the system with a prevalent 'local excitation' mechanism should transfer the control of conductivity to the electron subsystem. Indeed, coating the film surface at room temperature with a commercial thermostable paste, preventing the sorption processes, led to the disappearing of plots b and c (curve 4, Fig. 2) attributed to the desorption of molecular and atomic oxygen. At the same time, the Arrhenius slope was found to be similar to the value of ΔE_F (curve 3, Fig. 2) that corresponded to the thermal

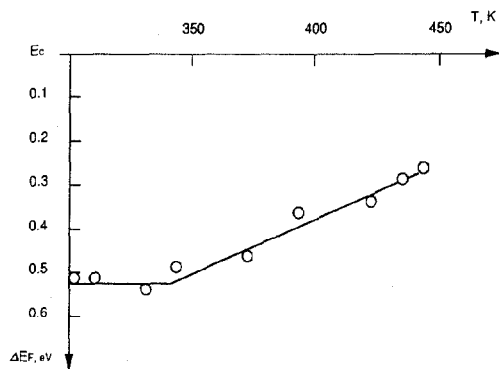


Fig. 4. Position of Fermi level in the band gap of CdS films, as a function of temperature calculated from analytical equation (—) and obtained from temperature-stimulated measurements of the dark conductivity (O) on CdS films.

activation of electrons from the bulk intrinsic defects crossed by the Fermi level. Such a behaviour is described by Eq. (8), which characterizes the predomination of the electron subsystem.

5. Conclusions

The dual mechanism of energy transfer on excitation of semiconductor surface-active structures allows the lifetimes of a conductance electron, captured by an extrinsic surface species ($\tau_c = 1/\nu_{th}\sigma_s N_c$) and a charged chemisorbed particle at the semiconductor surface ($\tau_s = 1/\nu$) to be distinguished. This has proved to be useful for the understanding of low-temperature desorption of molecules, which form deep energy levels in the band gap of a semiconductor. The verification of the suggested model displayed the correlation of the analytical results with the dark-conductivity behaviour for the example of oxygen interaction with a CdS surface.

The development of the atomistic understanding of the sensing mechanism allows the response characteristics of comparatively poorly understood but widely used devices to be predicted and should open possibilities for improving their sensitivity and selectivity to the analysed gas.

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