

# Characterization of Adsorption-Desorption Processes on Semiconductor Surfaces Using Nanocantilever Mass Sensors

Z.G. Djurić, K.T. Radulović, I.M. Jokić, M.P. Frantlović

**Abstract** – Characterization of adsorption-desorption (AD) processes of gas particles on semiconductors is necessary in order to investigate the influence of these processes on the micro/nanodevices performance. By applying a numerical computational method we determined the pressure dependence of the equilibrium coverage of the semiconductor surface by chemisorbed gas particles. We concluded that the pressure dependence of the total coverage of the surface by adparticles, and also of coverages by both the neutral and ionized adparticles, can be obtained by measuring the adsorbed mass. We propose the use of nanocantilever sensors for such extremely sensitive mass measurements. The obtained adsorption induced cantilever's resonant frequency shifts are higher than the detection threshold set by the termomechanical noise. This confirms the applicability of the used nanocantilever sensor for experimental characterization of AD processes at semiconductor surfaces.

## I. INTRODUCTION

Investigation of adsorption-desorption (AD) processes of particles from the environment on the surfaces of micro/nanostructures is important for development of devices whose principle of operation is based on these processes. Such devices are chemical and biological micro/nanocantilever based sensors, resistive thin film sensors, nanowire FET sensors, plasmonic sensors, etc., in which adsorption of target particles causes a measurable change of mechanical, electrical or optical parameters of the sensing element, but there are other kinds of micro/nanodevices whose operation and performance are also affected by AD processes. AD processes of particles from the gas or liquid phase occurring on a sensor's surface, as well as the generated AD noise, were analyzed in our previous works [1]-[4]. This paper considers the adsorption processes on the surface of semiconductors, which are specific since it is necessary to take into account a possible exchange of charge carriers between the adsorbed particles and the semiconductor, which can affect the performances of micro/nanodevices.

Due to participation of charge carriers from a semiconductor material in AD processes occurring on its

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surface, adsorbed particles can be converted from the electrically neutral to the charged (ionized) state and vice versa. In that case the binding energy (adsorption heat) varies with the degree of coverage of the surface by chemisorbed particles due to the strong electronic interaction between the adsorbate and the adsorbent. Such AD process in equilibrium can be described by Wolkenstein isotherm, which takes into account these electronic interactions and their effects on the adsorptivity of the semiconductor substrate [5].

In this paper we present the theoretical analysis of the Wolkenstein AD process. Based on the presented analysis we propose a method for characterization of AD processes on semiconductors using a nanocantilever mass sensor.

## II. THEORETICAL ANALYSIS

According to the Wolkenstein model of adsorption, a free particle (e.g. a gas atom or molecule) approaching the surface becomes adsorbed as electrically neutral. This is the neutral or weak form of chemisorption. In the case of an ideal crystalline surface, the weakly adsorbed particles act as surface impurities. Thus, if a free electron is available in the semiconductor, it may be captured by a neutral adsorbed particle which then becomes a negative adion (strong chemisorption). There is also a possibility for an adsorbed particle to act as a donor; however, in this paper the case of acceptor-like adsorbed particles will be analyzed. As a result of the process of electron transfer, the energy bands, which are assumed to be flat at the beginning of chemisorption, bend upward depending of chemisorption-induced surface potential barrier  $eV_s$ . In order for the ionized adsorbed gas particle to desorb and return back to the gas phase, it has to overcome the potential barrier. The potential barrier is a function of the surface coverage by chemisorbed anions, which depends on the semiconductor doping level, and at the same time it affects their binding and unbinding energy. Therefore, these energies of the charged form of chemisorption depend on the coverage of the surface by adions.

The equation which describes the kinetics of an adsorption process, i.e. the change of the total number of adsorbed particles ( $N$ ) in time, is

$$\frac{dN}{dt} = \alpha p(N^* - N) - \nu^0 N^0 e^{-\frac{q^0}{k_B T}} - \frac{dN^-}{dt} \quad (1)$$

In this equation,  $N^0$  is the number of neutral adsorbate particles,  $N^-$  is the number of negative adions and  $N^*$  is the total number of adsorption sites (all the values are per unit area),  $q^0$  is the heat of adsorption,  $\nu^0$  is the thermal oscillation frequency of the neutral adsorbed species,  $k_B$  is the Boltzmann constant, and  $T$  is the temperature. The coefficient  $\alpha$  is given by

$$\alpha = \frac{\chi / N^*}{\sqrt{2\pi M_a k_B T}} \quad (2)$$

where  $\chi$  is the sticking probability and  $M_a$  is the mass of a gas particle. The following relations are valid

$$N^- = f^- N, \quad N^0 = (1 - f^-) N \quad (3)$$

in which  $f^-$  is the occupation probability of the chemisorption-induced surface state in the thermal equilibrium given by the Fermi-Dirac distribution function.

In the steady state, the adsorption process is described by the Wolkenstein isotherm [5], [6] which represents the relationship between the degree of surface coverage by chemisorbed particles ( $\theta$ ) and the pressure of the surrounding adsorbate ( $p$ )

$$\theta(p) = \frac{N}{N^*} = \frac{\beta p}{1 + \beta p} = \theta^0 + \theta^- \quad (4)$$

Here,  $\beta$  is the adsorption coefficient which depends on the energy level of the chemisorption-induced states and the heat of adsorption of the neutral chemisorbed state. The equilibrium coverages corresponding to the neutral and ionized particles are  $\theta^0 = N^0/N^*$  and  $\theta^- = N^-/N^*$ , respectively. Obviously, the equilibrium adsorbed mass is

$$\Delta m = M_a \theta N^* A \quad (5)$$

where  $A$  is the area of the adsorbent.

The Wolkenstein isotherm is given as an implicit function of  $\theta$ , Eq. 4. It cannot be solved explicitly for  $\theta(p, T)$  since the adsorption coefficient  $\beta$  is a nonlinear function of  $\theta$  (i.e. it is the function of potential barrier  $eV_s$ ) [6].

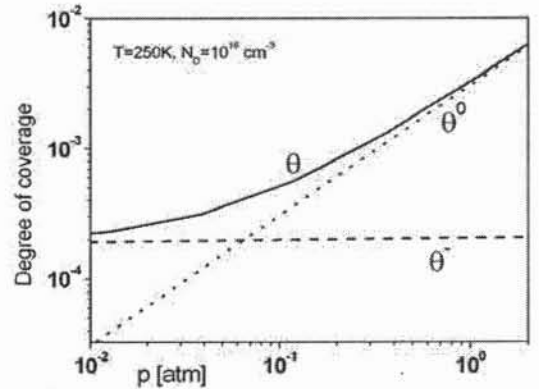
In order to obtain the dependences of coverages  $\theta$ ,  $\theta^0$  and  $\theta^-$  on the gas pressure for a constant temperature, which characterize the AD processes in equilibrium on the semiconductor surface, Eq. 1, Eq. 3 and Eq. 4, and the charge balance equation, must be solved simultaneously. This can be done by using a numerical method.

### III. NUMERICAL COMPUTATION

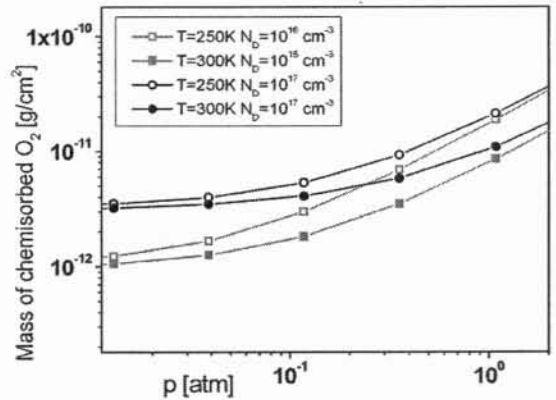
A computational method is applied in order to simulate the equilibrium chemisorption of gas particles on the

semiconductor surface. Fig. 1 shows the results of the numerical simulation performed for adsorption of oxygen on the  $n$ -type CdS. As it is known from the literature [7], the electrical conductivity of CdS decreases under the influence of an oxygen atmosphere.

The Wolkenstein isotherm, i.e. the pressure dependence of the total coverage of the surface by chemisorbed particles, calculated for  $T=250$  K and the semiconductor doping level  $N_D=10^{16}$  cm $^{-3}$ , is presented in Fig. 1a (solid line). The dependencies  $\theta^0(p)$  (dotted line) and  $\theta^-(p)$  (dashed line) are also shown. The diagram shows that, with the decrease of the pressure,  $\theta(p)$  becomes dominantly determined by the dependence  $\theta^-(p)$ , which means that the majority of the adsorbed particles are ionized. At higher pressures,  $\theta^0(p)$ , being a constantly increasing function of pressure, starts to dominate. Therefore,  $\theta(p)$  asymptotically reaches the function  $\theta^0(p)$ .



(a)



(b)

Fig. 1. (a) The total coverage ( $\theta$ ) of the surface by chemisorbed oxygen particles vs. oxygen pressure at the doping level  $N_D$  and temperature  $T$  ( $\theta^-$  and  $\theta^0$  are the surface coverages by charged and neutral adsorbate particles, respectively). (b) The adsorbed oxygen mass per unit area for two different temperatures and two different doping levels.

Fig. 1b shows the adsorbed oxygen mass per unit area for two different temperatures and two different doping levels, as a function of the oxygen pressure. According to

Eq. 5 the adsorbed mass is proportional to  $\theta$ . Thus, based on Fig. 1b, conclusions about the dependence  $\theta(p)$  can be drawn. At a higher doping level, more free electrons are available for the process of strong chemisorption, and  $\theta$  increases. At the same time,  $\theta^0$  is independent of  $N_D$ . Therefore, at pressures where  $\theta^-(p)$  is dominated,  $\theta(p)$  is higher for a higher doping level, while at higher pressures,  $\theta(p)$  does not depend on the value of  $N_D$ . The temperature dependence of  $\theta(p)$  is significant only in the pressure range where  $\theta^0(p)$  dominates, for both doping levels.

The diagrams presented in Fig. 1 suggest that it is possible to obtain the dependences  $\theta(p)$ ,  $\theta^-(p)$  and  $\theta^0(p)$  by measuring the pressure dependence of the equilibrium adsorbed mass at a constant temperature. However, equilibrium coverages at pressures below 1 atm are low in a majority of practical cases of adsorption of gases on semiconductor surfaces, thus the adsorbed mass per unit area is small. Therefore, an extremely sensitive mass sensor should be used for characterization of AD processes on semiconductor surfaces. A semiconductor nanocantilever sensor operating in the resonant mode is convenient for this purpose, due to its extremely high sensitivity to adsorbed mass. Assuming that the adsorbed mass is distributed over the entire resonator surface, it can be calculated (assuming that there is no cantilever's stiffness change) using

$$\Delta m = -2 \frac{m_0}{f_0} \Delta f \quad (6)$$

where  $m_0$  and  $f_0$  are the cantilever's mass and resonant frequency, respectively, and  $\Delta f$  is the resonant frequency shift due to the added mass. Therefore, it is possible to determine  $\Delta m(p)$ , and thus  $\theta(p)$ , by measuring the dependence  $\Delta f(p)$ .

We found an absolute frequency shift due to the Wolkenstein adsorption process of oxygen for a CdS microcantilever whose resonant frequency is 0.5 MHz (Fig. 2a) and for a CdS nanocantilever whose resonant frequency is 6.74 MHz (Fig. 2b). The minimal detectable frequency values, which are limited by the thermomechanical noise that manifests as the Brownian motion of the cantilever, are shown in the same diagrams, for each cantilever. The spectral density of the thermomechanical noise [8]

$$\sqrt{\Delta f^2} = \sqrt{\frac{f_0 k_B T}{2\pi k Q \langle z_{osc}^2 \rangle}} \quad (7)$$

depends on the cantilever spring constant  $k$ , the resonant frequency  $f_0$ , the temperature  $T$ , the mean squared oscillation amplitude  $\langle z_{osc}^2 \rangle$ , and the quality factor  $Q$ . Although there are analytical models that predict the cantilever size dependence of  $k$  and  $f_0$ , the quality factor cannot be readily predicted.

Figs. 2a and 2b illustrate that by using a smaller cantilever, a higher resonant frequency shift can be

obtained under the same conditions, and that the frequency detection threshold is lower for the smaller cantilever. In order for the minimal detectable frequency shift to be lower, a higher Q-factor value is required for both cantilevers. In the given oxygen pressure range the dominant source of dissipation is the viscous damping, so the Q-factor for  $n$ -th vibrational mode at a resonant frequency  $f_n = \omega_n / (2\pi)$  can be calculated as  $Q_n = \rho \omega_n S / \gamma$  [9], where  $\rho$  and  $S$  are the density and the cross-section area of the cantilever, respectively, and  $\gamma$  is the damping parameter. It can be concluded that for this application the cantilever must be of a very high resonant frequency and of a high Q-factor. Such cantilevers are those of submicrometer dimensions, i.e. the nanocantilevers [10], like the one used for calculations shown in Fig. 2b.

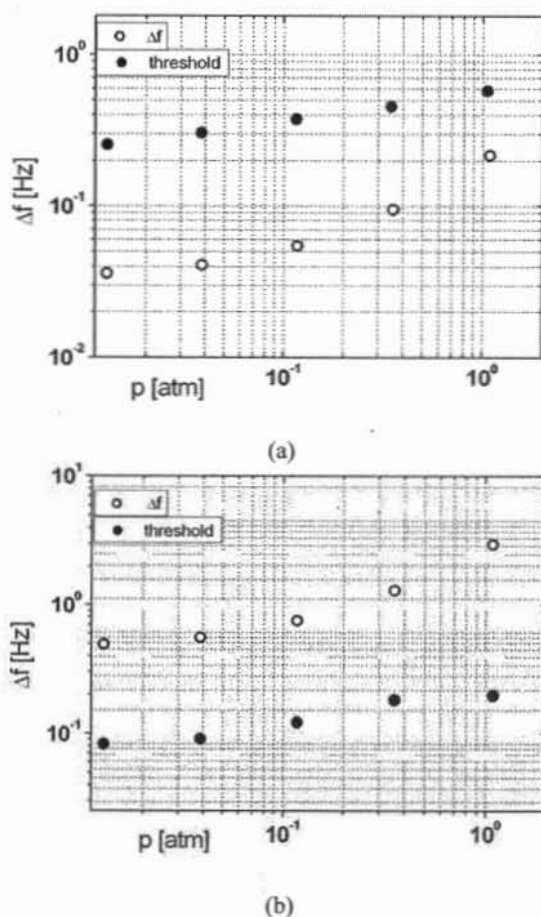


Fig. 2. The oxygen chemisorption induced cantilever resonant frequency shift vs. gas pressure ( $N_D = 10^{16} \text{ cm}^{-3}$ ,  $T = 250 \text{ K}$ ): (a) for the microcantilever,  $f_0 = 0.5 \text{ MHz}$ , (b) for the nanocantilever,  $f_0 = 6.74 \text{ MHz}$ . The detection threshold limited by the thermomechanical noise is also shown.

Fig. 2b illustrates that the obtained resonant frequency shifts are higher than the detection threshold (i.e. the minimal detectable frequency shift), which confirms the applicability of the used nanocantilever sensor for

experimental characterization of AD processes on semiconductor surfaces.

#### IV. CONCLUSION

In this paper, based on the theoretical analysis of the Wolkenstein AD processes on semiconductor surfaces, a method for characterization of such processes in equilibrium by using a nanocantilever mass sensor is proposed.

The presented work is significant in a fundamental sense, because it enables both the characterization of AD processes on semiconductors and the analysis of the influence of AD processes on semiconductor properties. It is also significant in a practical sense, because it enables the analysis of the influence of AD processes, particularly the presence of charged adsorbed particles (whose number is  $N^* \theta^-$ ), on the change of conductivity of semiconductor, and thus on the performance of resistive thin film and nanowire FET chemical and biological sensors.

#### ACKNOWLEDGEMENT

This work was funded by the European Commission 7<sup>th</sup> Framework Programme through the project REGMINA, grant 205533, and by the Serbian Ministry of Education and Science through the project TR 32008.

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