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To the theory of semiconductor gas sensors

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Abstract

Physical processes in semiconductor gas sensors and dependencies of the surface potential and concentration of charge carriers in the space charge region (SCR) of a semiconductor on the gas pressure contacting with a gas, are investigated. Corresponding sub-linear dependencies of the concentration of carriers on the pressure of an adsorbed gas are obtained in usual Langmuirian case and in the case when adsorption leads to a reduction in the heat of adsorption due to a charging of the semiconductor surface. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Gas adsorption; Surface conductivity; Semiconductor gas sensor

1. Introduction

In creating a semiconductor gas sensor it is essential to judge the degree of the gas semiconductor interaction by the change of electrical properties of the semiconductor (the electrical potential or surface conductivity). As the sensor should be reversible device gas molecules must be coupled retrievably on the surface in order to they can leave the surface. At the same time, for a change of the electrical properties of the semiconductor, it is essential that free charge carriers at the surface of the solid and sorbed particles create charged states on the surface. In this case a charge transfer between adparticles and the semiconductor takes place. The performance of a semiconductor gas sensor is determined by the charged (strong) form of chemisorption [1]. We do not consider bellow the cases of physisorption and neutral (weak) form of chemisorption and investigate theoretically sub-linear dependencies of the surface conductivity on the gas pressure.

2. Dependence of the surface conductivity on the pressure of an adsorbed gas

It is well known that chemisorption of a gas on a semiconductor, in particular, results in a change of the surface conductivity [1–3]. The potential in the space charge region (SCR), as usual, is determined by the Poisson equation

$$\Delta\varphi = \frac{4\pi}{\varepsilon}\rho, \tag{1}$$

where $\rho = (N_D - N_A + p - n)$ is the charge density in SCR arising due to the contact of the semiconductor with the gas, N_D and N_A are the concentration of ionized donors and acceptors, n and p are the concentration of free electrons and holes in SCR, respectively.

Taking in account that in the bulk of the semiconductor:

$$N_D - N_A + p_0 - n_0 = 0, \tag{2}$$

where n_0 and p_0 are the equilibrium concentrations of electrons and holes in bulk, respectively, and also that the charge carriers concentration changes only in a normal direction to the surface (the surface is located in $x = 0$, the semiconductor is placed at $x > 0$), where the Boltzmann distribution is realized, we have the following expression for the Poisson equation.

$$\frac{d^2 y}{dx^2} = \frac{1}{2L^2}[\gamma(1 - e^{-y}) + \gamma^{-1}(e^y - 1)], \tag{3}$$

where $y = e\varphi/kT$ is the dimensionless potential, $L = \sqrt{(\varepsilon kT/8\pi e^2 n_i)}$ is the screening length, $\gamma = n_0/n_i = (n_0/$

$p_0)^{1/2} = e^{\mu/kT}$, $n_i = (n_0 p_0)^{1/2}$ is the concentration of electrons and holes in the impurity semiconductor, μ is the chemical potential.

Under boundary conditions

$$\rho = 0, \quad y = 0, \quad dy/dx = 0 \quad \text{at } x \to \infty, \tag{4}$$

we obtain after integration of Eq. (3) the equation [2–4]

$$\frac{dy}{dx} = L^{-1}F(y, \gamma), \tag{5}$$

where

$$F(y, \gamma) = \pm\sqrt{(e^{-y} + y - 1)\gamma + (e^y + y^{-1} - 1)\gamma^{-1}}. \tag{6}$$

The sign of the function $F(y_s, \gamma)$ is determined as follows, the positive sign corresponds to the inequality $y_s > 0$, at $y_s < 0$ we have the negative sign. We remind that y_s is the magnitude of dimensionless potential on the surface of the semiconductor, the positive sign corresponds to the band bending upwards.

The surface concentrations of electrons Δn and holes Δp in SCR are determined by the following expressions

$$\Delta n = -n_0 L \varphi(y_s, \gamma), \Delta p = p_0 L \phi(y_s, \gamma), \tag{7}$$

where

$$\varphi(y_s, \gamma) = \int_0^{y_s} \frac{1 - e^{-y}}{F(y, \gamma)} \, dy, \quad \phi(y_s, \gamma) = \int_0^{y_s} \frac{e^y - 1}{F(y, \gamma)} \, dy. \tag{8}$$

The total charge in SCR is equal [3,4,5,6]

$$Q = 2n_i e L F(y_s, \gamma). \tag{9}$$

The charge in SCR is equal to the opposite sign charge located on the surface of the semiconductor (the electroneutrality condition). As this charge depends also on the concentration of the adsorbed ions of gas, the concentration of the surface charge should be a function of the gas pressure. Hence, the charge in SCR will be some function of the gas pressure P:

$$Q = -(Q_0 + eN_s(P)) = -Q_s(P). \tag{10}$$

Here $N_s(P)$ is the concentration of the adsorbed atoms on the surface, Q_0 is the charge density on the surface in the absence of adsorption.

It is obvious from Eq. (9) and Eq. (10) that the surface potential becomes now some function of the gas pressure, analytical kind of the dependence of which in general case is impossible to obtain. It can be done in special cases only. In order to obtain an expression for the change of the surface conductivity $\Delta\sigma(P) = e(\Delta n \, \mu_{ns} + \Delta p \mu_{ps})$, it is necessary to solve the Eq. (5) and Eq. (9) which is possible to realize analytically again only in special cases [3,4,6].

In general case, the dependence of the surface conductivity on the pressure of the adsorbed gas can be determined using the values of the functions $F(y_s, \gamma)$, $\varphi(y_s, \gamma)$ and $\Phi(y_s, \gamma)$ tabulated in a certain range of the values of y_s and γ. These functions are represented in Refs. [5,6] as nomograms and in Ref. [3] as Tables.

3. The Langmuirian model

In this case the dependence of the concentration of adsorbed atoms isdetermined by the following equation:

$$N = N_i \frac{Pb}{Pb + 1} = N_t \frac{\Psi}{\Psi + 1}, \tag{11}$$

where b is the kinetic constant of adsorption, $\Psi = Pb$ is the normalized pressure, N_t is the number of adsorption centers per unit of the surface. Then, under condition (10), we have the following expression:

$$2n_i L F(y_s, \gamma) = -N_t \frac{\Psi}{\Psi + 1} - N_0, \tag{12}$$

whence it follows that

$$\Psi = \frac{f - 1}{\lambda - f - 1} \text{ or } f = 1 + \lambda \frac{\Psi}{\Psi + 1}, \tag{13}$$

where $f = (-2n_i L/N_0) F(y_s, \gamma)$, $\lambda = (N_t/N_0)$.

We have the following expression for a change of charge carriers concentration:

$$\Delta n = -n_0 L \varphi(y_s, \gamma) = \gamma \frac{Nt}{v} \varphi(y_s, \gamma),$$

$$\Delta p = p_0 L \Phi(y_s, \gamma) = \gamma^{-1} \frac{N_t}{v} \Phi(y_s, \gamma), \tag{14}$$

where $v = (N_t/n_i L)$.

From the tables of functions $F(y_s, \gamma)$, $\varphi(y_s, \gamma)$ and $\Phi(y_s, \gamma)$, given in Ref. [3],using expressions (13) and (14) at fixed value of γ, it is possible to find a range of values Δn, Δp, y_s and Ψ. Hence some relation between the concentration of charge carriers and pressure can be obtained.

It is necessary to define a sign of N_0 in Eq. (13). The sign is negative when, in the absence of the adsorption, electrons from the bulk of the semiconductor are captured by surface states. The sign is positive for the case of the hole capture by surface states. For definiteness, we took values for N_t, N_0, n_i and L characteristic for Si. We consider the case of the n-type semiconductor when $N_0 > 0$ and a donor-like adsorption of the gas takes place on the surface of the semiconductor: $F(y_s, \gamma) > 0$. Let $N_t = 10^{13}$ cm^{-2}, $N_{osi} = 10^{11}$ cm^{-2}, $n_{isi} = 1.4 \times 10^{10}$ cm^{-3}, $L = 2.2 \times 10^{-3}$ cm^{-1}. For γ we take the value 100 ($n_0 = 10^4 p_0$).

Values of Ψ, Δn, y_s and $F(y_s, \gamma)$ are resulted below in Table 1. They are calculated by the formulas (13) and (14) by the use of the Tables obtained in Ref. [3]. As

might be expected, values of Δp are insignificantly changed.

As follows from Eq. (9), at $\Psi = 0$, $F_0 = -1623.4$, $y_s \approx -10.2$. The value of F at $\Psi = 0$ (F_0) depends on N_0. It is obvious that the value of y_s depends on N_0

$$F_0 = -\frac{N_0}{2n_iL}. \tag{15}$$

When $\Psi \to \infty$, it follows from Eq. (9) that

$$F_\infty = -\frac{N_0}{2n_iL}(1 + \eta) = -\frac{N_0 + N_t}{2n_i L}, \tag{16}$$

which corresponds in our case $F_\infty = -163923$. This value, in turn, corresponds $y_s \approx -19.4$, $\Delta n_\infty = 10^{13}$ cm^{-2}, $\Delta p_\infty = 0.736 \times 10^5$ cm^{-2}. Certainly, at other values of N_0 and N_t other values of F_∞ and therefore $y_{s\infty}$, Δn_∞, Δp_∞ are obtained. As an illustration, let limit us by a case of a choosing one set of parameters only. It is necessary to note both F_0 and F_∞ depend also on n_i and L, i.e. on the type of the semiconductor.

By processing data represented in Table 1, we can convinced that the dependence of Δn on the gas pressure has sub-linear character and it may be written as

$$\ln|\Delta n(p)| = k \ln \Psi. \tag{17}$$

As Ψ increase, k increases from zero up to a maximal value of 0.4625. With further increase in Ψ, k consistently decreases gradually tending to zero. The case of $k = 0$ corresponds the saturation branch of the $\Psi(P)$ dependence.

4. The case of a reduction in the heat of adsorption

Above it was marked an charge transfer between of the gas molecules and semiconductor takes place that at the gas chemisorption on the semiconductor surface. The ions of the gas are linked near the surface (on the external part of the semiconductor). But, at the same time they can leave back in the gas phase and a dynamic balance should be achieved in a steady state condition. It is well known that in order to the gas molecule can leave the surface, it is necessary to overcome some potential barrier determined usually as the

heat of adsorption. The heat of adsorption usually depends on the temperature, a degree of filling of the surface states of the semiconductor by the gas molecules and other characteristics of system. Earlier [5,7–9] we have considered the case when the heat of adsorption can decrease on some quantity W with the increase in the gas ions number. For simplicity of calculation of the energy W, we assume that the surface of the semiconductor has a circular form. At first we will calculate the electric potential of the adsorption layer taking into account that the potential in the bulk of the semiconductor is equal zero. If the surface charge density σ is produced, in the ring dS on the surface of the sensor, the field

$$d\varphi = \frac{\sigma dS}{R} \tag{18}$$

affects on an ion positioned in a center of the ring. Here R is the distance between the ion and the ring. In the case of uniform charge distribution on the surface and 'one-electron' bond, it is easy to receive the following expression for the potential φ for a sensor having the radius A:

$$\varphi = 2\pi eNA. \tag{19}$$

For the energy W we have the expression

$$W = \eta N, \tag{20}$$

where

$$\eta = 2\pi e^2 A. \tag{21}$$

Here N is the quantity of adsorbed gas atoms per unit area of the surface of the adsorption layer. It is unlikely that the dependence of W on N is changed significantly for an other geometrical forms of the sensor.

Let consider the adsorption kinetic for the case of the charging of the surface by an 'one-electron' gas in the framework of usual theory. The kinetic equation in this case

$$\frac{dN}{dt} = \alpha P(N_t - N) - \beta'N \tag{22}$$

is well known [1]. Here P is the pressure,

Table 1

Ψ	0.04	0.06	0.08	0.1	0.12	0.15	0.18	0.22	0.24	0.3
$-F$	7867	10 812	13 645	16 377	19 012	22 792	26 380	30 890	33 035	39 077
$\Delta n*10^{12}$ cm^{-2}	0.5	0.675	0.825	1.01	1.232	1.36	1.66	1.83	2.03	2.46
$-y_s$	13.4	14	14.4	14.8	15.2	15.4	15.8	16	16.2	16.6
Ψ	0.6	0.8	1	1.2	1.5	1.97	2.77	4.35	8.95	206.85
$-F$	62 485	73 756	82 773	90 150	99 003	109 380	120 880	133 600	147 650	163 180
$\Delta n*10^{12}$ cm^{-2}	3.7	4.515	4.993	5.513	6.190	6.745	7.454	8.224	9.086	10.041
$-y_s$	17.4	17.8	18	18.2	18.4	18.6	18.8	19	19.2	19.4

Table 2

$-F$	2003	2447	2988	3650	4458	5446	6651	8124	9923	12 120
$-y_s$	10.6	11	11.4	11.8	12.2	12.6	13	13.4	13.8	14.2
ψ	0.0042	0.014	0.032	0.065	0.121	0.213	0.362	0.598	0.972	1.559
$-F$	14 800	18 080	22 080	29 810	36 410	44 470	54 320	66 340	81 030	98 970
$-y_s$	14.6	15	15.4	16	16.4	16.8	17.2	17.6	18	18.4
ψ	2.478	3.89	6.2	12.37	19.75	31.9	52.49	88.76	157.1	300.9

$$\alpha = \frac{\chi^S}{(2\pi m^* kT)^{\frac{1}{2}}}, \beta' = \beta_0 \exp\left(\frac{W-q}{kT}\right). \quad (23)$$

In Eq. (23) χ is a probability of a holding of the adsorbed molecule on the adsorption center, m is the mass of the adsorbed molecule, k is the Boltzmann constant, t is a time, T is a temperature. Eq. (6) may be written in the form:

$$\frac{dN}{dt} = \alpha P(N_t - N) - N\beta \exp\left(\frac{\eta N}{kT}\right). \quad (24)$$

This equation indicates that a number of molecules, leaving the semiconductor surface and passing in the gas phase, increases in $\exp(W/kT)$ times in compare with usual case describing by the Langmuirian model (compare with Eq. (11)). It is impossible to solve this equation exactly. If $\eta N < kT$, we can expand the exponent in series. Limiting ourselves by first two terms of the expansion, we obtain for the steady state case [5,7,8] the following expression:

$$\Theta = \frac{N(t=\infty)}{N_t} = C(\Psi+1)\left[\sqrt{1 + \frac{2\Psi}{C(\Psi+1)^2}} - 1\right], \quad (25)$$

where,

$$C = \frac{kT}{2\eta N_t}. \quad (26)$$

If the term located adjacent to unit under root is small, it is an easy matter to obtain from Eq. (25) the Langmuirs' and Henry's isotherms. In the case when

$$2\Psi > C(\Psi+1)^2, \quad (27)$$

limiting ourselves again by two terms of the expansion, we obtain

$$\Theta(t=\infty) \cong \sqrt{2C\Psi} - C(\Psi+1). \quad (28)$$

Analysis of Eq. (27) and Eq. (28) show that at $C < 1$ a gas pressure range is possible where the adsorption isotherm prescribes mainly by the root dependence on the gas pressure. Such root dependence for one-electron system does not explain in the framework of the Langmuirian model. Here the square root dependence is possible in the event that a molecule dissociates on two ions each of which occupies its own adsorption center. Such dependencies are observed in series of experimental

investigations where an root dependencies of the surface concentration of adparticles on the gas pressure are detected (see [5,7–13]). Note that the dependence of the surface conductivity on the adsorbed gas pressure, observed in experiments, is mainly described by a power-law dependence, $\sigma(P) \propto P^k$, where $0 < k < 1$ [10–14]. For example, such dependence with power $k = 1/3$ for thin-film gas sensors is obtained in Ref. [14]. Such type dependencies predicted by the Langmuirs' theory only for many atomic gases [1].

In a case when the adsorption isotherm is given by the expression (25), an equation, corresponding Eq. (10), looks already like

$$N_t C(\Psi+1)\left[\sqrt{1 + \frac{2\Psi}{C(\Psi+1)^2}} - 1\right] + N_0$$
$$= -2n_i LF(y_s, \gamma). \quad (29)$$

After simple transformations we obtain from Eq. (29):

$$\Psi = \frac{(f-1)^2 + 2\lambda C(f-1)}{2\lambda C(\lambda - f + 1)} \quad (30a)$$

or

$$f = \lambda C(\Psi+1)\left[\sqrt{1 + \frac{2\Psi}{C(\Psi+1)^2}} - 1\right] + 1. \quad (30b)$$

From Eq. (30a) and Eq. (30b) it is an easy matter to obtain the Eq. (13) at $2\lambda C >> (f-1)$ in Eq. (30a) and $2\Psi << C(\Psi+1)^2$ in Eq. (30b). Using the Tables, given in Ref. [3], from eqns. 30 we can obtain values of Δn, y_s and $F(y_s, \gamma)$ and to establish some relation between Δn and Ψ. In Table 2 for an illustration some of these values at $C = 1.5 * 10^{-3}$ are presented.

The values of Δn and Δp are again obtained from the formulas (14). Value of Δp, as well as before, does not practically vary. By analyzing obtained values, it is possible to convince that the dependence of Δn on the pressure has sub-linear character and it can be presented as Eq. (17). In this case, as well as in the Langmuirian case, with the increase in Ψ, $k(k = \ln(|\Delta n|/\ln\Psi)$ at first increases, passes a maximum, then decreases, tends to zero. But in this case, as distinct from the Langmuirian case, k depends on C. For example, at $C = 1.5 \times 10^{-3}$, maximum k does not exceed 0.5, besides in a rather wide range Ψ (from 0.0465 up to 300) k changes from 0.3 till 0.45, testifying sub-linear dependence of Δn on the gas pressure.

5. Conclusion

It is shown that the surface conductivity dependence on the one-atomic gas pressure has sub-linear character both in the Langmuirian kinetics case and in the case of a charging of the surface. But in the second case there is a wide range of the gas pressure where the value of power k varies slowly ($k \propto 0.3/0.45$). This means that a form of the sub-linear dependence $\sigma(P)$ can be essentially affected when we are taking into account an interaction between adparticles.

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