

UDC 537.222.22; 543.51; 54-183.544.723

INVESTIGATION OF A GAS LAYER FORMATION ON THE SURFACE OF THE ZnO AND Co₃O₄ SEMICONDUCTOR NANOPARTICLES

Corresponding Member of ANAS R.R.Huseynov, R.A.Alizade, V.S.Tagiyev, N.B.Mustafayev

Stages of the formation of adsorption gas layers on the surface of nanoparticles are determined. Process of the adsorption of gas molecules to the surface of nanoparticles is described using the diffusion equation. Expressions are obtained for dependences of the thickness and the rate of formation of the adsorption gas layer on time, the concentration and type of ambient gas, and the size of nanoparticles. The gas mass accumulated at the nanoparticle surface and the accumulation rate are calculated. From values of the adsorption layer thickness and the accumulated gas mass, the number and structure of layers are determined.

Keywords: adsorption gas layer, thickness of adsorption gas layer, accumulation of gas mass, adsorption kinetics, semiconductor nanoparticles

Introduction

Materials consisting of the semiconductor nanoparticles decorated with small clusters of metal oxides are widely used now for making devices that detect the presence of combustible, flammable and toxic gases in environment [1, 2]. The method for detecting such gases by these devices is based on a specific change in electrical conductivity of the material during gas adsorption. Detectors based on the semiconductor nanoparticles decorated with small clusters of metal oxides are very sensitive. They can detect a very small percentage of ambient gas. These detectors are economically inexpensive.

In this paper, the process of adsorption of gas molecules to the surface of semiconductor nanoparticles is described using the diffusion equation. Expressions are obtained for dependences of the thickness and the rate of formation of the adsorption gas layer on time, the concentration and molecular mass of the ambient gas, and on the concentration and size of nanoparticles. From values of the adsorption layer thickness and the accumulated gas mass, the number and structure of layers are determined.

Formation of multilayer gas adsorption on the surface of a nanoparticle

The formation of a gas layer on the surface of a semiconductor nanoparticle depends on the physical (electrical, magnetic, etc.) characteristics

of the nanoparticle and gas, the attractive force which acts between the gas molecule and nanoparticle, the attraction between molecules of the gas, the size of nanoparticle, the temperature and partial pressure of the gas, etc. A more or less close molecular packing in the adsorption gas layer can be realized: (a) molecules are located one above the other (Brunauer-Emmett-Teller theory) [3], or (b) molecules are located on the voids formed by the molecules of the previous layer [4].

Consider first the case (a) where, after the formation of the first adsorption layer, subsequent layers are formed by placing the gas molecules vertically over the molecules of the previous layer. Theory of such formation of the adsorption layers is given by Brunauer, Emmett and Teller (BET). Since the gas molecules of a given layer are located above the molecules of the previous layer, the thickness of the n -th adsorption layer will be determined as $d_n = 2mr$ (here r is the radius of the gas molecule). The distance between the gas molecules located radially in the same adsorption layer can be defined as the difference between the length of the side of a polygon inscribed in the circle with radius $R_0 + (2i - 1)r$ (here i is the number of a given layer) and the doubled radius of the gas molecule $a_i = 2 [R_0 + (2i - 1)r] \sin(\alpha/2) - 2r$. The polygon angle is defined as $\alpha = 2\pi/N$, where N is the number of gas molecules loca-

ted along a circle with radius $R_0 + r$. For small values of α , we can replace $\sin \alpha$ by α and get

$$a_i = 2 [R_0 + (2i - 1)r] \frac{r}{R_0 + r} - 2r.$$

For a gas molecule, the condition $a_i \geq 2r$ must be satisfied in order to get a position between radial located molecules. If $R_0 = 5$ nm and $r = 0.1$ nm, the number of adsorption layers should be more than 30. The number of layers can be determined using the following formula:

$$N_{L, \text{BET}} = \frac{d_{\max}}{2r} \quad (1)$$

where $d_{\max}$ is the thickness of adsorption layer. The density of the i -th gas layer is $\rho_i = iN/V_{\text{ads}, i}$ where $V_{\text{ads}, i} = 8\pi R_0^2 r i$ is the volume of the i -th layer, and N is determined by the formula:

$$N(R_0, r) = A(R_0) + B(R_0) \exp(-r/C) \quad (2)$$

here

$A(R_0) = 23.014 + 22.089 R_0 + 32.863 R_0^2$ and $B(R_0) = 913.227 + 18.09 R_0 + 1783.224 R_0^2$. Within the measurement error, the value of C can be assumed to be constant and equal to 0.0537 nm.

In the second case (b), the adsorption of gas molecules on the surface of nanoparticles is similar to the close atomic packing in crystals [4]. The close packing AB model is mostly realized. In this arrangement, the spheres of the second layer (B) are above the voids of the first layer (A). The voids are surrounded by three spheres, and the lines connecting the centers of these spheres form a tetrahedron. This arrangement is repeated in other layers. Then the thickness of the second layer will be $d_2 = 2r + h$, and the thickness of the i -th layer will accordingly be $d_i = 2r + (i - 1)h$, where $h = 2\sqrt{2/3}r$ is the tetrahedron height. In this case, the number of layers can be determined using the following formula:

$$N_{L, 4\text{-sp}} = 1 + (d_{\max} - 2r)/h \quad (3)$$

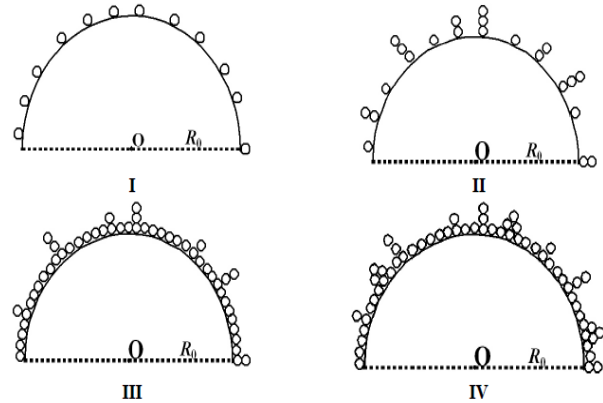


Fig.1. Stages of the formation of adsorption layer on the surface of a nanoparticle

Thus, based on the mentioned above, it can be concluded that the adsorption layer is formed in several steps. The formation stages are shown in Fig.1.

Description of the adsorption gas layer formation using the diffusion equation

The process of gas adsorption on the surface of a semiconductor nanoparticle can be considered as a change in the gas concentration at the surface of the nanoparticle. Assume that the change in the concentration of the gas adsorbed on the surface of the semiconductor nanoparticle does not change the concentration of ambient gas. Suppose that spontaneous desorption of gas molecules from the nanoparticle as well as chemical reaction between the gas molecules and nanoparticle do not exist. Let us describe the variation of the adsorbed gas concentration $n(d, t)$ with time using the diffusion equation

$$\frac{\partial n(d, t)}{\partial t} = D \nabla^2 n(d, t) - K n(d, t) \quad (4)$$

where D is the diffusion constant, and K is the reaction constant. Values of these constants are given in [3]. Suppose that the system is symmetric, there is no preferred direction of adsorption, and solve the last equation in a spherical coordinate system. We can introduce the dimensionless quantity $x = d/R_0$, and use the following initial and boundary conditions: $n(x, t)|_{t \rightarrow 0} = 0$, $n(x, t)|_{t \rightarrow \infty} = n_0$, $n(x, t)|_{x \rightarrow 0} = 0$

and $n(x, t)|_{x \rightarrow \infty} = n_0$ where n_0 is the ambient gas concentration.

We seek a solution of the diffusion equation in the form of product of two functions $n(x, t) = p(t) \cdot q(x)$ [5]. Substituting the latter into equation (4) and dividing the variables, we obtain two equations. Taking into account the initial conditions, the solution of the first equation can be written in the form $p(t) = 1 - \exp(-\lambda t)$. To solve the second equation, we introduce new variables, and obtain an equation of the Riccati type [5]. Finally, we get

$$n(x, t) = (1 - e^{-\lambda t}) \frac{n_0}{x} \coth(\sqrt{\lambda} x r_0 + n_0 \gamma r_0) \quad (5)$$

where $\gamma = (\lambda - K)/D$. For the adsorption layer thickness $d(t)$ and the accumulated gas mass $m(t)$, we find:

$$d(t) = R_0 \ln \frac{1 + f(t)}{1 - f(t)}$$

$$m(t) = \frac{4}{3} \pi R_0^3 \rho \left\{ 1 - \left[1 - \ln \frac{1 + f(t)}{1 - f(t)} \right]^3 \right\}$$

where

$$f(t) = \tan \left[K \frac{n_0}{6\rho\lambda} (1 - e^{-\lambda t}) \sqrt{\gamma} R_0 \right].$$

Differentiating $d(t)$ and $m(t)$ with respect to time, we obtain expressions for the rate of layer formation $v_d(t)$ and the rate of mass accumulation $v_m(t)$. Fig. 2 shows the time dependence of the gas mass accumulated at the surface of 20-nm-size ZnO and Co₃O₄ semiconductor nanoparticles. As can be seen in Fig. 2, after a certain time, the accumulation of mass stops and reaches its maximum value. The mass of the adsorption layer can also be defined as $M = N m_0$ where m_0 is the mass of gas molecule. We have determined the number of adsorption layers of known thickness using formulas (1) and (3). The number of gas molecules adsorbed on the nanoparticle surface has been calculated by formula (2). Calculations show that the number of adsorbed gas molecules found by the 4-step adsorption is closer to the value determined from the accumulated mass. Therefore, the

adsorption of gas on the nanoparticle surface occurs in four steps. However, for a large number of layers, there is a significant discrepancy between the values found by the 4-step adsorption and the values determined from the accumulated mass. This discrepancy indicates a random packing (a loose structure) of gas molecules on the surface of semiconductor nanoparticle. For large numbers of layers, the number of adsorbed gas molecules calculated by the BET packing model is closer to the value determined from the accumulated mass.

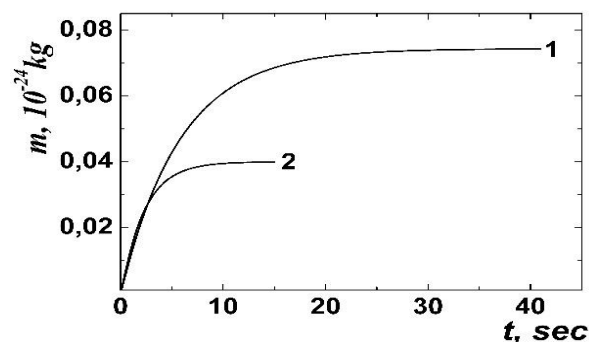


Fig. 2. Time dependence of the gas mass accumulated at the surface of 20-nm-size ZnO (curve 1) and Co₃O₄ (curve 2) semiconductor nanoparticles

Conclusion

The mechanism for the formation of adsorption layer is the diffusion of gas molecules from medium to a nanoparticle. Basically, the adsorption layer has a close packing structure. Starting with a certain value of the layer number, the adsorbed layer has a loose structure corresponding to the random packing of gas molecules. It follows from simple considerations that the values of filling factor for the first, second, third and the next layers should differ and satisfy the following relationship: $\theta_1 > \theta_2 > \theta_3 > \dots > \theta_n > \theta_{n+1} = 0$. This explains the formation of loose structure, starting with a certain value of the layer number. The density of the first adsorption layer depends on the molecular weight of gas, the size of gas molecule, the filling factor, and does not depend on the size of semiconductor nanoparticle, i.e. it is the same for surfaces of nanoparticles in all size range. Hence, the filling factor θ will not depend on the size of semiconductor nanoparticle.

The number of adsorption layers increases with the nanoparticle size. With increase in the number of adsorption layers, the operating efficiency of gas detector decreases. Therefore, in order to increase the efficiency of the detector operation, it is desirable to synthesize semiconductor nanoparticles with an average radius of 2-5 nm.

In addition, the adsorption layer thickness depends on the type of semiconductor nanoparticle. For example, the thickness of gas layer adsorbed on the surface of Co_3O_4 nanoparticles is small. From this point of view, gas detectors based on Co_3O_4 nanoparticles would be preferable. However, the rate of accumulation of the adsorption mass on the surface of Co_3O_4 nanoparticles is less than that on the surface of ZnO nanoparticles. It means that ZnO nanoparticles will adsorb and detect the ambient gas faster. Therefore, in order to make the efficient and

sensitive gas detectors, it is necessary to determine optimal values of the adsorption layer thickness and the maximum rate of their formation for semiconductor nanoparticles.

REFERENCES

1. Rumyantseva M.N., Kovalenko V.V., Gas'kov A.M., Pagnier T. // Russian Journal of General Chemistry, 2008, v. 78, No. 5, pp. 1081-1084.
2. Trakhtenberg L.I., Gerasimov G.N., Gromov V.F., Belysheva T.V., Ilegbusi O.J. // Journal of Materials Science Research, 2012, v. 1, No. 2, pp. 56-68.
3. Physical Chemistry, Vol. 2 / Gerasimov Y. (Editor), Leib G. (Translator), Moscow: Mir, 1974. Original Russian book: Kurs Fizicheskoi Khimii, Tom 2 / Pod red. Gerasimova Ya. I., Moskva: Khimiya, 1973, 624 p.
4. Shaskol'skaya M.P. Crystallography (in Russian). Moscow: Vyssaya skola, 1978, 385 p.
5. Stepanov V.V. Course of Differential Equations (in Russian). Moscow: Fizmatlit, 1959, 468 p.

Institute of Physics of ANAS
alizade_r2@mail.ru

YARIMKEÇİRİCİ ZnO VƏ Co_3O_4 NANOHISSƏCİKLƏRİNİN SƏTHİNDƏ QAZ LAYININ ƏMƏLƏ GƏLMƏSİNİN TƏDQİQI

R.R.Hüseynov, R.Ə.Əlizadə, V.S.Tağıyev, N.B.Mustafayev

Nanohissəciklərin səthində qaz adsorbsiya layının əmələgəlmə mərhələləri təyin olunmuşdur. Qaz molekullarının nanohissəciklərin səthinə adsorbsiyası diffuziya tənliyi vasitəsilə ifadə edilmişdir. Adsorbsiya layının qalınlığının və əmələgəlmə sürətinin zamandan, qazın tipi və konsentrasiyasından, nanohissəciyin tipi və ölçüsündən asılılıqları üçün riyazi ifadələr alınmışdır. Adsorbsiya layının kütləsinin və onun əmələgəlmə sürətinin zamandan asılılığı hesablanmışdır. Adsorbsiya layının qalınlığı ilə kütləsinin qiyməti əsasında layların sayı və strukturu təyin edilmişdir.

Açar sözlər: qaz adsorbsiya layı, adsorbsiya layının qalınlığı, qaz kütləsinin yığılması, adsorbsiya prosesinin kinetikasi, yarımkeçirici nanohissəciklər

ИССЛЕДОВАНИЕ ОБРАЗОВАНИЯ ГАЗОВОГО СЛОЯ НА ПОВЕРХНОСТИ ПОЛУПРОВОДНИКОВЫХ НАНОЧАСТИЦ ZnO И Co_3O_4

Р.Р.Гусейнов, Р.А.Ализаде, В.С.Тагиев, Н.Б.Мустафаев

Определены этапы образования адсорбционных слоев на поверхности наночастиц. Процесс адсорбции молекул газов на поверхность полупроводниковых наночастиц описан с помощью уравнения диффузии. Получены выражения для зависимости толщины и скорости образования газового адсорбционного слоя от времени, концентрации и типа газа, размера наночастицы. Вычислены значения накопленной массы газа и скорость его накопления на поверхности наночастиц. По значениям толщины адсорбционного слоя газа и накопленной массы определялось количество и структура слоев.

Ключевые слова: адсорбционный слой газа, толщина адсорбционного слоя, накопление массы газа, кинетика адсорбции, полупроводниковые наночастицы