

The Kinetics of the Change of SnO_x Thin Films Conductivity during the Gas–Adsorptive Interaction

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The subjects of investigation are thin semiconductor SnO_x films received by thermal oxidation. The influence of gas environments on electrical conductivity of films were investigated by a static way by measurement of kinetic and equilibrium isotherm of adsorption of trimethylamine, alcohol, hydrogen sulfide and ammonia. The communication between a type isotherm of adsorption, chemical nature of gas and temperature is shown.

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1. Introduction

The majority of modern sensory converters are characterized by low selectivity. The problem of selectivity is solved by the choice of the type of semiconductor sorbent, doping and working temperature. However such an approach does not always permit to achieve the aims and get universal criteria for such a choice of selective sorbent.

The investigation of the kinetics of the change in the electrophysical properties of SnO_x films during the various gases adsorption on their surface permits to disclose general laws in the behavior of these films [1]. Obtained results may be used for the selective recognition of adsorbed gases on the surface of the sensitive elements of gas sensors.

The speed of the gas particle adsorption on the surface of the rigid body can obey the range of kinetic isotherms. The Langmuir isotherm is of the form

$$N(t) = \frac{N^*P}{P+b} [1 - \exp(-Kt)], \quad (1)$$

where N/N^* — the degree of the surface occupation, $N(t)$ — the number of the adsorbed to the moment of time t particles, N^* — the number of adsorption places, P — pressure in the gas phase, K and b — constants, depending on the particle mass, on the area, occupied by the particle, on the energy of adsorption, on its vibration frequency.

Adsorption interaction can obey the Roginsky–Elovich–Zeldovich kinetic isotherm

$$N(t) = A + B \ln(1 + t/t_0) \quad (2)$$

and the Benhem–Bart kinetic isotherm

$$N(t) = At^n - B, \quad (3)$$

where A , B , n , and t_0 — constants, depending on the nature of surface of the rigid body and on the nature of the adsorbable particles.

2. Experimental details and results

The subjects of this investigation are SnO_x films, 50 nm thin, received by thermal oxidation of the tin films. Deposition of the tin films was carried out on the vacuum universal post VUP-5M. As etchant gas was used argon, whose pressure was ≈ 0.1 – 1 Pa in the process of sputtering. The tin metal target mark “analytical grade” was used as the cathode. The target sputtering was carried out at an accelerating voltage of 0.5 kV, the discharge current was 0.15 A [2].

Obtained SnO_x films are characterized by the redundant oxygen content on the surface, conductivity is limited by high intergranular barriers, and they are sensitive to the gas-redundant [3]. These gases during the adsorption interact with the oxygen on the film surface, which leads to the increase in its conductivity at the expense of the decrease in the number of electron localization centers and the lowering of the intergranular barriers [4, 5]. In this research the interaction of the films with organic (trimethylamine, alcohol) and inorganic (hydrogen sulfide and ammonia) gases were investigated. During the investigation of the adsorption the change in the conductivity of the film in gas presence ($S = \sigma_{\text{gas}}/\sigma_{\text{air}}$) was measured.

During the interaction of the films with trimethylamine the changes in the conductivity at constant concentration rise at the increase of the temperature and then decrease (Fig. 1). The speed of the changes in the conductivity of the film also depends on the temperature, but less. At temperatures 200–250 °C the time of the adsorptive response amounts 180–160 s, at 300–350 °C — 100–80 s.

For the identification of the type of the kinetic isotherm, fitting the experimental data, it is necessary to approximate the kinetic curves of adsorptive responses with Eqs. (1), (2) and (3). As the change in the conductivity is proportional to the number of the particles adsorbable on the film surface, the quantity $N(t)$ in these equations can be replaced by the value S for the corresponding moment of time t .

In the coordinates $\ln(1 - S(t)/S_{\text{max}})-t$ the kinetic isotherm (1) is a straight line. The equation of kinetic

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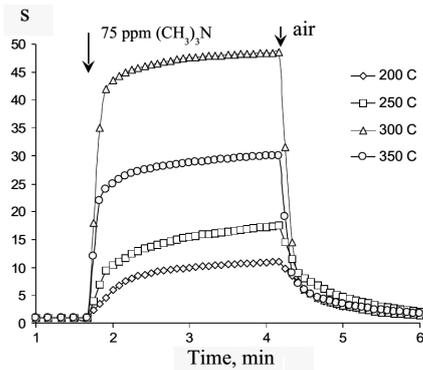


Fig. 1. Kinetics of the response of conductivity SnO_x thin films at the adsorptive interaction with the trimethylamine.

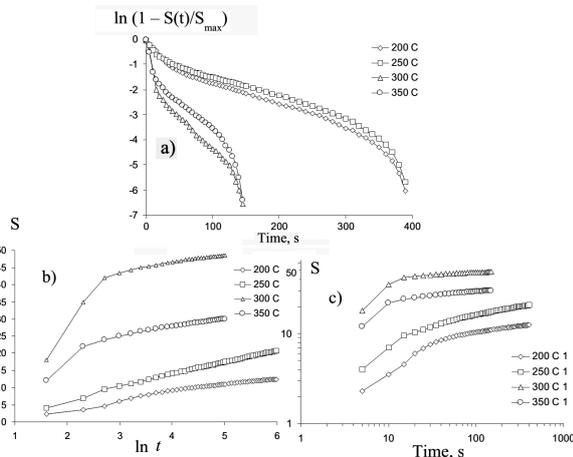


Fig. 2. Approximation of kinetic curves of adsorption trimethylamine by: (a) Langmuir's kinetic isotherm, (b) Roginsky-Elovich-Zeldovich kinetic isotherm, (c) Benhem-Bart kinetic isotherm.

isotherm (2) for the interpretation of the experimental results best of all is used in the differential form

$$\frac{dN}{dt} = A \exp(-BN). \quad (4)$$

The experimental data, represented after the differentiation in the coordinate's $\ln(dS/dt)-S$ are linear dependences. But, because of the fact that the number of experimental points is limited, the operation of numerical differentiation is not always correct. When $t \gg t_0$, the quantity $S(t)$ should be directly proportional to $\ln t$. That is why the linear dependence of the experimental data in coordinates $S(t)-\ln t$ should confirm the applicability of kinetic isotherm (2) for the process of gas adsorption.

The equation of kinetic isotherm (3) for the approximation of the experimental results is also best of all used in the differential form

$$\frac{dN}{dt} = t^{n-1} \quad (5)$$

and experimental data should be best of all represented in coordinates $\ln(dS/dt)-\ln t$. However, as in the pre-

vious case, the operation of the numerical differentiation cannot be correctly done. That is why in some approximation the linearity of the experimental curve in the coordinates $\ln S(t)-\ln t$ can serve as a confirmation of the applicability of kinetic isotherm (3) for the process of the gas adsorption.

The results of the approximation of the received kinetic curves of trimethylamine adsorption showed that the response curves of the SnO_x films in the coordinates $\ln(1-S(t)/S_{\max})-t$ do not linearize. Consequently, isotherm (1) cannot be appropriate only for the adsorption description. The response curves in coordinates $S-\ln t$ and $\ln S(t)-\ln t$ take almost a linear form. Exceptions are the initial parts of the curves (Fig. 2).

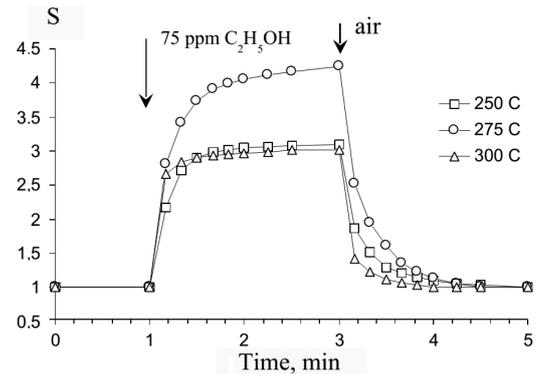


Fig. 3. Kinetics of the response of conductivity SnO_x thin films at the adsorptive interaction with the alcohol vapor.

Bad correspondence of the initial parts of the isotherm curves can be connected either with the two-stage process or with the applicability for the definition of these stages of Eq. (1), according to which the initial adsorption stage can obey the linear isotherm.

The curves of the relative change in the SnO_x film conductivity during the adsorption of the alcohol vapor at different film temperatures show that the sensitivity of the films also depends on the temperature with its maximum at 275 °C. However, the multiplicity of the change in the film conductivity at the work of the alcohol vapor is 10 times less than at the work of the trimethylamine of the same concentration (Fig. 3). It may be determined by the difference in the molecular structure of the gases. Obviously, one trimethylamine molecule with three CH_3 -groups is able to interact with greater amount of surface oxygen than the alcohol molecule. It may be determined either by the dissociation of the molecule during the adsorption into 4 "fragments", or by its oxidation by the surface oxygen or by the greater density of the occupation of the film surface by the trimethylamine during the adsorption.

The speed of the film conductivity at the influence of alcohol is much higher. The time of getting the response at the alcohol vapor is 20–40 s. It may be explained by the absence of some limiting stage during the alcohol adsorption (Fig. 3).

The results of the approximation of the kinetic curves of the absorption of the alcohol vapor on the SnO_x film surface showed that the response curves of the films in coordinates of Eq. (1) do not linearize (Fig. 4a).

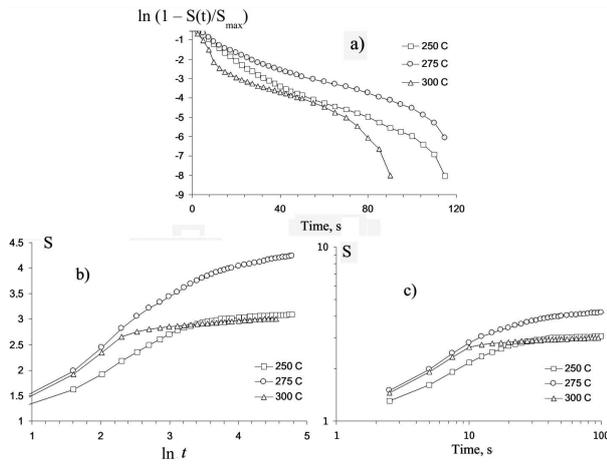


Fig. 4. Approximation of kinetic curves of adsorption alcohol vapor by: (a) Langmuir's kinetic isotherm, (b) Roginsky-Elovich-Zeldovich kinetic isotherm, (c) Benhem-Bart kinetic isotherm.

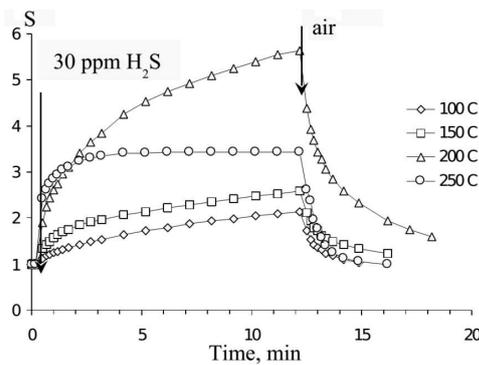


Fig. 5. Kinetics of the response of conductivity SnO_x thin films at the adsorptive interaction with the hydrogen sulfide.

Kinetic isotherms (2) and (3) for the alcohol adsorption, as in the case of trimethylamine, correspond to the experimental results quite well (Fig. 4b,c). The curves of the relative change in the SnO_x film conductivity linearize in the coordinates of these equations. But not all the received dependences have the break, splitting the first and the last stages of the process. It has not been noticed in the case of trimethylamine.

Perhaps, in this case we deal with two stages of adsorption, that obey Eqs. (4) and (5) with different value of the constants in the equations. Two stages can be connected either with differences in the behavior of the processes on the surface and in the volume of the film, or with the presence of two types of sorption centers, for example, of the ions O²⁻ and O⁻.

The investigation of the relative change in the SnO_x film conductivity during the adsorption of hydrogen sul-

fide on its surface showed that the sensitivity of the films to hydrogen sulfide has its maximum at 200 °C, which is less than in the case of organic gases. During longer interaction with hydrogen sulfide the time of getting the adsorption responses is longer, perhaps because of the low temperature, at which kinetic processes are slower. At temperatures 100 °C and 150 °C a full response is achieved in more than 20 min, at 200 °C — in 10 min, at 250 °C — in 2 min (Fig. 5).

The results of the analysis of the SnO_x film response curves at hydrogen sulfide showed that the curves in coordinates of Eq. (1) are linear at the first stages. Consequently, isotherm (1) can be appropriate for the description of the quick first stage of the adsorption responses (Fig. 6a).

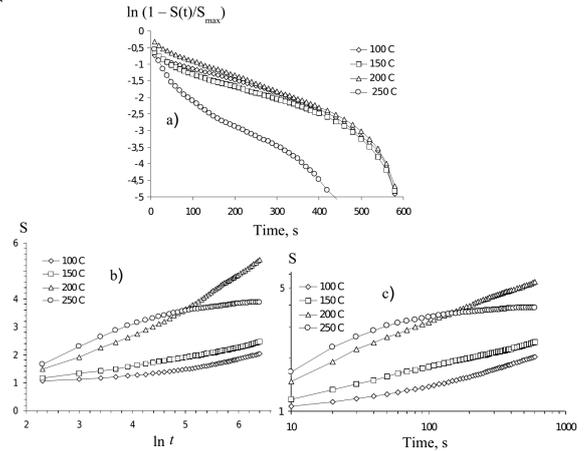


Fig. 6. Approximation of kinetic curves of adsorption hydrogen sulfide by: (a) Langmuir's kinetic isotherm, (b) Roginsky-Elovich-Zeldovich kinetic isotherm, (c) Benhem-Bart kinetic isotherm.

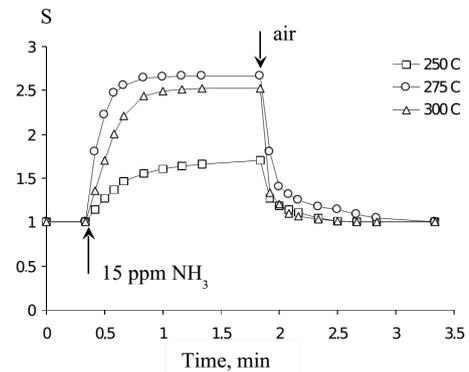


Fig. 7. Kinetics of the response of conductivity SnO_x thin films at the adsorptive interaction with the ammonia.

In the coordinates of isotherm (2) kinetic curves represent the lines with a break, and in the logarithmical coordinates of Eq. (3) they do not have a break. Consequently, it is better to use kinetic isotherm (3) for the description of the film response to hydrogen sulfide (Fig. 6b,c).

The investigation of the adsorption SnO_x film responses at ammonia showed that in contrast to hydrogen sulfide the greater sensitivity is achieved at higher temperatures, it has its maximum at 275 °C. Also unlike hydrogen sulfide the speed of the ammonia adsorption at the SnO_x film surface is considerably higher and the responses are achieved in 15–25 s (Fig. 7). However, the multiplicity (S) of the changes in conductivity is practically the same as at the interaction with hydrogen sulfide.

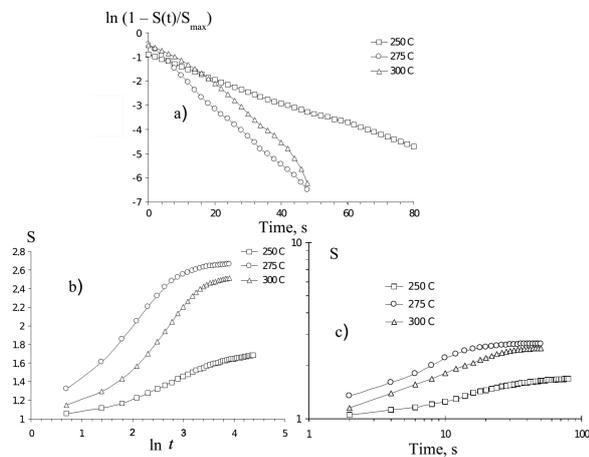


Fig. 8. Approximation of kinetic curves of adsorption ammonia by: (a) Langmuir's kinetic isotherm; (b) Roginsky–Elovich–Zeldovich kinetic isotherm, (c) Benhem–Bart kinetic isotherm.

The results of the approximation of the received film response curves by isotherms showed that the system of Eq. (1) coordinates linearizes the experimental curves well, consequently Langmuir isotherm suits well for the description of the kinetics of the adsorption interaction of the SnO_x films with ammonia (Fig. 8a). The suitability of isotherm (1) is also confirmed by the fact that in the coordinates of Eqs. (2) and (3) the response curves are not linear (Fig. 8b,c).

Thus, the considerable difference between the interaction of SnO_x films with gases of organic and inorganic nature has not been detected. The sensitivity of the film to all the examined gases depends on the temperature with its maximum. The presence of the maximum can be explained in the following way. At the rise of the temperature the number of the adsorbable particles rises too at the expense of the growth of the sticking coefficient, i.e. it is easier for the particles to get over the barrier in the form of the energy of adsorption activation. With the rise of temperature the vibration frequency of the adsorbable particle rise and the time of its stay on the film surface decreases, i.e. desorption increases. At the definite temperature and its further rising the desorption processes begin to prevail.

Investigation of the equilibrium isotherm of gas adsorption in the large ranges of concentration showed that the interaction of the films with organic gases obeys the Freundlich isotherm, and interaction with inorganic gases

may obey the Frumkin and Langmuir isotherms. It may be determined by the dissociation of the organic gases during the adsorption, which leads to the significant inhomogeneity of the distribution of the adsorption places for the various types of fragments by their energies. During the adsorption of inorganic gases the influence of such a distribution is not so important even during the molecular dissociation, that is why isotherms realize themselves, which describe homogeneous adsorption. The coefficient value in the equations of the equilibrium isotherms is stated to depend on the temperature, and if the isotherm types also coincide, the value depends on the chemical nature of the gas as well. It may be determined by the quantitative characteristics of the adsorption processes: the degree of the occupation of the surface and the quantitative interaction of the adsorbable gas with the oxygen of the SnO_x film surface.

3. Conclusion

The kinetics of the adsorption interaction of the SnO_x films with the gases is determined not only by the nature of the gas, but by the temperature as well. This applies not only to the change in speed of adsorption, but also to the change in the character of interaction, i.e. the changes of the kinetic isotherm, that describes the process.

In practice the results of the investigation of the adsorption isotherms and the choice of approximate equations with correspondent characteristic coefficients may be used for the recognizing of the gas type, adsorbing on the film surface. Thus, the information about the kinetics of the adsorption interaction may let conduct qualitative gas detection.

The obtained results may be used to create highly sensitive and selective sensors for detecting gas mixtures containing trimethylamine, alcohol, hydrogen sulfide, and ammonia. For example, created sensors can be used for the diagnostics of the quality of perishable raw products, such as fish, and meat, and also alcohol-containing products [6, 7].

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