

11. M. Koebel, Zum Austauschverhalten des Aquotisierten Silberions an Silber und Silberionen-Festelektrolyten. Die Gemischte Leitung von Silbersulfid bei Raumtemperatur; Diss. No. 4853, Eidgenössischen Technischen Hochschule, Zürich (1972).
12. K. Cammann, Untersuchungen zur Wirkungsweise Ionenselektiver Elektroden, Ludwig-Maximilians-Universität, München (1975).
13. M. M. Shul'ts, A. M. Pisarevskii, and I. P. Polozova, Oxidation Potential. Theory and Practice [in Russian], Khimiya, Leningrad (1984), p. 38.
14. A. Hulanicki and A. Lewenstam, Talanta, 23, 661 (1976).
15. M. A. Ilyushchenko and V. A. Mirkin, Electrode Processes in Aqueous Solutions, Tr. IOKE Akad. Nauk Kaz. SSR, Vol. 25, p. 160 (1981).
16. M. A. Ilyushchenko and V. A. Mirkin, Vestnik Akad. Nauk. Kaz. SSR, No. 4, 41 (1981).
17. V. A. Mirkin and M. A. Ilyushchenko, Potentiometric Sensors as Polyelectrodes [in Russian], Nauka, Alma-Ata (1983), 134 pp.
18. M. A. Ilyushchenko, Properties of Metal-Ion and Ion-Selective Electrodes and Their Interpretation Based on a Polyelectrode Model, Diss. Kand. Khim. Nauk, Kaz. Gos. Univ., Alma-Ata (1983), p. 68.

PHYSICO-CHEMICAL MECHANISM RESPONSIBLE FOR THE PARAMETERS OF GAS
SENSORS BASED ON OXIDE MATERIALS*

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Metal oxides are finding increasingly wide application in technology and electro-technology [1] in the form of ceramics, sintered layers, and films produced by various methods. Tin oxide doped with different additives in particular is widely used in sensors for different atmospheric gases [2]. At the same time, practical application of tin dioxide and other oxides is significantly restricted by the changes that occur in important parameters of sensing elements fabricated from them.

In the work reported here we investigated the reasons for changes in the adsorption properties of SnO_2 -Pd sensors in atmospheric air.

EXPERIMENTAL

The characteristics of the original and the annealed sensors were studied. Temperature, kinetic relationships, and the Hall coefficient were measured on samples having a contact geometry such as to prevent uncontrolled potentials from affecting the measured Hall emf. The Hall and electrical contact were fabricated from palladium annealed onto the surface of the layer. The measurements were made over 300-540 K in the presence of two polarized electrical and magnetic fields. From the sign of the Hall emf it was determined that the sensors were p-type conductors.

Immediately after fabrication, the resistance of the sensors at room temperature was $(1-4) \cdot 10^6$ ohm. The thickness of the layers from which they were made was approximately 50 μm . The measurements in the interelectrode gap ($l = 8$ mm) were made using a potential probe 0.01 mm in diameter that was moved by means of a microscrew. The potential was registered by an EM-0.5 electrometer.

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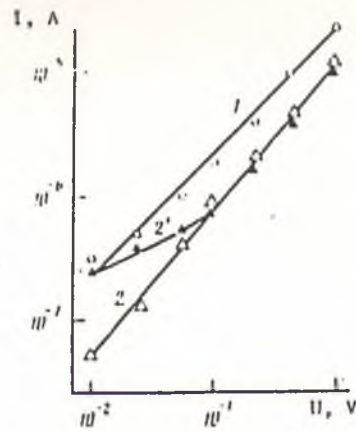


Fig. 1

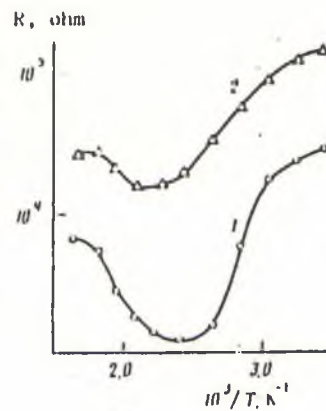


Fig. 2

Fig. 1. Current-voltage curves for the starting (1, 1') and annealed (540 K; 120 min) (2, 2') sensors: 1, 2) direct; 1', 2') reverse direction of current.

Fig. 2. Temperature dependence of the resistance of the starting (1) and annealed (540 K, 90 min) (2) sensors.

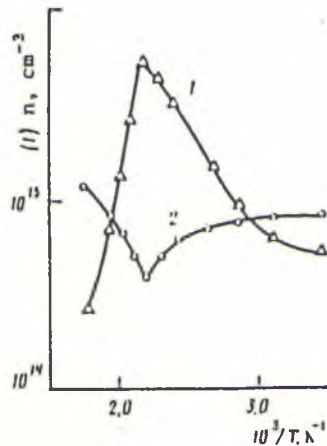


Fig. 3

Fig. 3. Temperature dependence of the concentration (1) and mobility (2) of free electrons.

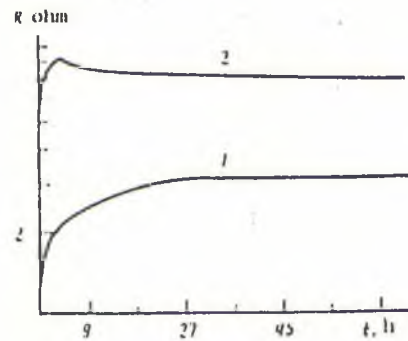


Fig. 4

Fig. 4. Sensor resistance as a function of annealing time in a mixture of $N_2 + O_2$. Oxygen concentration, vol. %: 1) 20; 2) 45.

RESULTS AND DISCUSSION

The current-voltage characteristics and the temperature dependences of the resistances of the sensors are illustrated in Figs. 1 and 2.

The temperature dependence of the resistance of the unannealed layers has the characteristic exponential appearance of a metal-oxide semiconductor (Fig. 2, curve 1) up to 420 K. The resistance of the layer decreases up to 320 K, and the exponent is equal to 0.2 eV, while between 330 K and 420 K it is 0.5 eV. The exponential nature of the dependence may be a result of electrons being released from the level of the donors [3], or it may be due to the conductivity barrier mechanism. In the latter case, the activation energies for the relationship $R = f(T)$ become multivalued, since the increase in R with temperature according to the exponential law may be appreciably affected by the average value of the intercrystallite barrier.

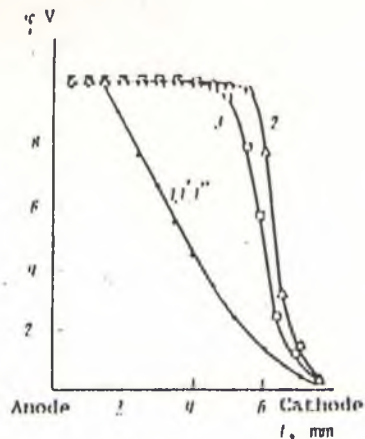


Fig. 5. Potential distribution between the electrodes. 1) Starting sensor, 1') after annealing at 540 K with no electrical field; 1'') after annealing at 540 K and with an alternating electrical field $U_{\perp} = 10$ V; 2) sensor after annealing at 540 K and $U_{\perp} = 10$ V; 3) annealed sensor after being stored in the dark for 8 days at room temperature and normal atmospheric pressure.

A study of the temperature dependence of the concentration (c) and the free-electron mobility (μ) due to the Hall effect showed that at room temperature the unannealed samples have relatively high values of these magnitudes: $c \approx 1 \cdot 10^{21} \text{ m}^{-3}$ and $\mu \approx 1 \cdot 10^{-2} \text{ m}^2 \cdot \text{R}^{-1} \cdot \text{sec}^{-1}$ (Fig. 3, curves 1 and 2). When the dependence of μ on T is weak (Fig. 3, curve 2), the concentration of free electrons as T rises from 300 to 450-460 K increases in the near-room-temperature region exponentially with an activation energy of ~ 0.2 eV. At higher temperatures, E_d is approximately 0.5 eV (Fig. 3, curve 1). By comparing curves No. 1 of Figs. 2 and 3 we see that the activation energy for $R \sim \exp(E_d/kT)$ is determined primarily by the depth of the energy well corresponding to localization of the matrix donors (E_d) in the forbidden band. Instead of the exponential decrease in R with temperature characteristic of semiconductors at $T > 420$ K, there is an increase in resistance (Fig. 2, curve 1). Measurements of the Hall emf show that in this temperature range, the concentration of free electrons decreases sharply, with exponents of 1.1-1.2 eV (Fig. 3, curve 1).

When oxygen interacts with different kinds of semiconductors [4], including metal-oxide semiconductors, the oxygen molecules chemisorbed on the semiconductor surface dissociate to atoms at elevated temperatures. The chemisorbed oxygen atoms create new electron capture sites that are deeper than those formed by chemisorbed O_2^- ions. In most cases, the oxygen atoms create electron capture sites at $E_c = 1.1-1.4$ eV from the conduction band, with E_c being weakly dependent on the nature of the semiconductors and weakly determined by the electronegativity of the oxygen atoms (~ 1.4 eV [5]). From this it follows that the anomalous increase observed in R as the temperature increases (Fig. 3, curve 1) is due to the transition from the molecular to the atomic form of chemisorbed oxygen.

After the temperature stabilizes at 540 K, R continues to increase for a considerable time if the sensor is held at the same conditions. R attains a constant value only after 24 h of annealing (Fig. 4, curve 1). Such long stabilization times for R are characteristic of diffusion processes. From this it also follows that the appearance of a region of anomalous increase on the curve $R = f(T)$ may be associated with processes involving the diffusion of oxygen into the body of the sensor as well as with the localization of electrons at the surface levels.

Since chemisorbed oxygen atoms have an effective negative charge $\text{O}^{\delta-}$ (where δ is the degree of charge transfer in the chemisorbed complex consisting of the adsorption site and the chemisorbed species), it is possible for the $\text{O}^{\delta-}$ quasi-ions to diffuse over the surface of the sensor and accumulate at the anode. In this case, the increase of resistance with annealing structure will also be due to the formation of regions of high resistance at the anode; it is also possible for a barrier to arise between the high-ohmic region and the

rest of the interelectrode gap, i.e., close to the anode. In fact, the post-annealing current-voltage curves of the sensors demonstrate the existence of a rectification effect (Fig. 1, curves 2 and 2'), which, as can be seen from the relationship $I = f(U)$, in the region of low concentrations is the result of a Schottky barrier (Fig. 1, curve 2') forming at the cathode rather than the anode.

It is known that electrical heterogeneities near the electrical contacts with the semiconductors may form as a result of diffusion in an electrical field of positive and negative ions [6]. Positive ions accumulate at the cathode and form a region of lowered resistance, and negative ions form a high-ohmic region at the anode due to drift. These traditional mechanisms do not account for the formation of a barrier and a high-ohmic region at the cathode (Fig. 1).

The formation of a high-ohmic region at one of the contacts is supported by the results of direct measurements of the resistance distribution between the sensor electrodes, which leads to a corresponding potential distribution in this region. In the original state, the potential distribution is linear, and is evidence of the absence of macroheterogeneities between the electrodes (Fig. 5, curve 1), but after annealing, practically all of the voltage applied to the sample is concentrated in a narrow high-ohmic layer in the region of the cathode (Fig. 5, curve 2). The observed diffusion smearing of the boundary of the concentration of elevated resistance at the anode may be evidence that an acceptor-type contaminant enters the sample from the cathode and diffuses further toward the anode under the influence of the electric field.

From curve 1 in Fig. 2 it follows that, for $T > 420$ K, R increases with an activation energy $\sim 1.2-1.4$ eV, which is characteristic of processes accompanied by the formation of the chemisorbed species $O^{\delta-}$ [7]. Based on this an hypothesis was formulated to account for the process whereby oxygen molecules dissociate at the palladium electrode. The boundary palladium atoms have unsaturated bonds and serve to catalyze the dissociation of oxygen into atoms. This is confirmed by the independence of the described processes of the oxygen concentration in the atmosphere. Increasing the amount of oxygen in the oxygen-nitrogen mixture from 20% (Fig. 4, curve 1) to 45% (curve 2) reduces the time required for the resistance to stabilize due to the formation of an electrical heterogeneity at the cathode from 24 to 15 h. The formation of such an heterogeneity was not observed in an atmosphere of pure nitrogen at the selected annealing temperature.

A diffusion mechanism for the development of a high-ohmic heterogeneity and changes in resistance resulting from the field drift toward the anode of the $O^{\delta-}$ quasi-ion formed at the boundary of the palladium cathode is also substantiated by the fact that after the original sample is annealed under the same conditions as used for the measurements illustrated in curve 1 of Fig. 4 (but in the absence of an electrical field), the potential distribution remains linear, as it does for the original sample (Fig. 5, curve 1). This follows from the fact that the formation of a heterogeneity in the resistance distribution, and thus in the potential distribution, is not observed if an alternating electrical field with $U_{eff} = 10$ V (Fig. 5, curve 1) is applied during the annealing process and the other conditions remain unchanged.

CONCLUSIONS

The stabilization of the parameters of gas sensors fabricated from oxides is a multi-step physicochemical process that concludes with the formation of a high-ohmic region at the cathode. The high working temperatures stimulate the breakdown of chemisorbed $O_2^{\delta-}$ into atoms at the palladium electrode which is apparently what catalyzes this process. Under the action of the electrical field, the chemisorbed $O^{\delta-}$ atoms diffuse from the cathode to the anode. The resulting high-resistance region thus determines not only the resistance of the sensor, but its sensitivity to the chemisorption of donor gases.

LITERATURE CITED

1. V. M. Baikovskii, K. B. Arutyunov, A. S. Egorova, et al., Current State and Trends in the Development of Sensors Based on TS-4 Microelectronic Technology: Review Inf., TsNITEM of Instrument Making, No. 5, 1987.
2. A. I. Buturlin, T. A. Gabuzyan, N. A. Golovanov, et al., Zarubezh. Elektron. Tekh., No. 10 (269), 10, 1983.
3. R. H. Bube, Photoconductivity of Solids, John Wiley & Sons, 1960.

4. V. F. Kiselev and O. V. Krylov, *Electronic Phenomena in Adsorption and Catalysis on Semiconductors and Insulators* [in Russian], Nauka, Moscow (1979).
5. V. I. Vedenev, L. V. Gurvich, V. H. Kondrat'ev, et al., *Bond-Breaking Energy of Chemical Bonds* [in Russian], Izd. Akad. Nauk SSSR, 1962.
6. B. I. Boltak, *Diffusion in Semiconductors* [in Russian], Fizmatgiz, Moscow (1961).
7. V. A. Smytyna, *Fiz. Tekh. Poluprovod.*, 21, No. 9, 1690, 1987.

PROOF OF ACCEPTABLE RELIABILITY OF REFERENCE DATA
FOR CHROMATOGRAPHIC RETENTION

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Literature data on retention values are widely used in the chromatographic identification of materials. The significance of the reliability of these data increases as the importance of the results of identification for assuring ecological safety, for industrial hygiene, and for other purposes increases. Unfortunately, it often turns out to be problematic [1-4] as a consequence of which work has begun whose task is to obtain critically evaluated values in order to officially certify them as standard reference data in the future. However, estimation of acceptable (allowable) errors (including systematic ones) of similar data turned out to be beyond consideration. The unsatisfactory nature of such an approach was discussed in article [5].

A more inclusive analysis of the task of assuring reliability of the information necessary for creating and using a data base on chromatographic retention was undertaken in [6]. This study [6] noted that the optimum approach to the solution of this problem should include: well founded choice of values of acceptable errors for each group of data; execution of a carefully planned experiment for obtaining the data; critical analysis of the results directed most of all at exposing unaccounted for systematic errors; a metrologically correct approach to excluding errors that might arise in the utilization phase of the data.

In this communication the task of validating acceptable errors in the data on chromatographic retention (in literature and especially standard reference data) is considered in more detail. Hereinafter all similar data will be called correlated reference data.

THE PRINCIPLE OF VALIDATION OF ACCEPTABLE ERRORS OF REFERENCE DATA.

MODE IDENTIFICATION TASKS.

The error δ° for reference data is a portion of the total error Δ of the result of the experiment carried out for identifying a substance (for more detail see [6]). Taking this into account it is first appropriate to consider approaches to the establishment of an acceptable value for Δ and then for δ° that will be applicable to the features of each of the model identification tasks. A summary of such tasks as well as the conditions and methods of their resolution are given in tabular form (Table 1). In this table and in the text the term substance is used in the general sense. In real situations one can speak of a representative of a class of substances, a subclass, or a narrower unit of classification down to, for example, an isomer. Understanding of adaptive and specialized experiments is used in the sense discussed in article [7]: an adaptive experiment is an experiment that can be carried out under conditions where a priori information about the composition of the object being analyzed is insufficient and a specialized one can be carried out under conditions where an object is analyzed in which only the determined components may or may not be present. The term recalculation in the table and the text refers to a procedure that leads to certain corrections characterizing a change in the retention values of an individual substance under concrete experimental conditions carried out for identification as compared to the initial reference data.

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