Chemisorption of SO_2 on the Zn-modified In_2O_3 surface

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Chemisorption of SO_2 and O_2 on the In_2O_3 surface containing a zinc additive (0.4—2.7 at.%) was studied in a temperature range of 22—200 °C. At least three forms of sorbed SO_2 exist on the modified In_2O_3 surface. The temperature affects the contribution of single forms of SO_2 sorption and, hence, the change in the electric conductivity. The preliminary sorption of O_2 favors the formation of a donor form of chemisorbed SO_2.

Key words: chemisorption, conductivity, indium oxide, modification, sulfur dioxide.

Indium oxide is one of the promising materials for the development of gas-sensitive elements in sensors, whose operation is based on a change in the electric conductivity during gas chemisorption. We have previously[1] shown that the specific surface exerts a substantial effect on the electrophysical and sorption properties of the oxide. Indium oxide with a well developed specific surface has high conductivity and low activation energy of conductivity. An increase in the specific surface enhances the sensitivity of a sample to such a contaminator of the environment as SO_2. It is difficult to detect SO_2, because chemisorbed sulfur dioxide can manifest both the donor and acceptor properties. Both forms often coexist on the surface, and their ratio and, hence, the sensor response depend on the conductivity of a semiconductor. One of the most popular methods for affecting the electrophysical properties of semiconducting oxides, and, in particular, those of In_2O_3, is modification by metal ions.[2—4] It can be assumed that alloying indium oxide with additives with strong acceptor properties would decrease the fraction of the acceptor form of chemisorbed SO_2. In the present work, we studied the change in the electric conductivity of highly dispersed zinc-modified In_2O_3 during SO_2 chemisorption and the influence of preliminary O_2 sorption on this process.

Experimental

The chemisorption and conductivity of samples were measured under static conditions on a setup, which makes it possible to simultaneously detect the gas pressure in a reaction cell and the conductivity of a sample.[5] The amount of the adsorbed gas was determined from a decrease in the pressure in the cell. The conductivity of a sample (σ) was measured by the probe method with dc. The activation energy of conductivity (E_a) was found from the temperature plot of the conductivity of samples *in vacuo*. The measurement error of the pressure and conductivity was 3 and 2%, respectively. The specific surface (S_{sp}) was determined by the Brunauer—Emmett—Teller (BET) method from the low-temperature adsorption of Kr. The particle size was estimated from the data obtained by the BET method.

Samples of In_2O_3 containing Zn additives were prepared by coprecipitating the corresponding hydroxides with ammonia from a weakly acidic solution of indium and zinc chlorides.[6] The precipitates were washed by multiple decantation and then heated in air for 5 h at 150 °C and then *in vacuo* for 15 h at 225 °C. One sample was synthesized without additives, and two samples contained 0.4 and 2.7 at.% Zn. The samples were identified by chemical and X-ray diffraction analyses. According to the X-ray diffraction data, all samples contained only the In_2O_3 phase. The concentration of Cl^- ions in the precipitate did not exceed 0.01%.

Pelleted samples (2.0 g) were treated in the reaction cell *in vacuo* ($1 \cdot 10^{-5}$ Torr) for 20 h at 250 °C until constant conductivity values were achieved. After this treatment, the conductivity obeyed the Ohm law, which indicated no intergrain barriers for current. It was preliminarily determined (by the sign of thermal emf) that the samples under study were semiconductors of the n-type.

The chemisorption of O_2 and SO_2 was studied in a range of 22—200 °C. Prior to experiment, the samples were stored for 3 h in the reaction cell at a specified temperature, and then the sorbed gas was introduced at an initial pressure of 0.15—0.80 Torr. When the pressure became constant, the next gas portion was introduced. The overall amount of the gas adsorbed was found by the summation of particular portions. The amount of reversibly sorbed SO_2 at the experimental temperature was determined by its condensation for 1.5 h in a trap cooled with liquid nitrogen. The irreversibly sorbed gas was removed from the surface by heating the sample *in vacuo* for 2 h at 250 °C. After this treatment, the conductivity took the value characteristic of the sample before chemisorption.

Results and Discussion

The values of the activation energy of conductivity (E_a) of the samples are similar to each other (Table 1) and

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Table 1. Properties of the In_2O_3 samples under study

Sample	S_{sp} /$m^2 g^{-1}$	Particle size /nm	σ /S cm^{-1}	E_a /eV
In_2O_3	45.5	20	0.7	0.038
In_2O_3 + 0.4 at.% Zn	69.0	12	3.7	0.031
In_2O_3 + 2.7 at.% Zn	64.0	13	2.3	0.033

Note: S_{sp} is the specific surface, σ is the electric conductivity, and E_a is the activation energy of conductivity.

much lower than the forbidden band width of In_2O_3 (2.3 eV).[7] The specific surface of the modified samples and the conductivity (σ) at 22 °C are somewhat higher than those of the unmodified sample; however, the differences observed are not high. A plausible reason is that the introduction of zinc into the lattice of In_2O_3 exerts no substantial effect on the electrophysical properties of the oxide.

On all the samples under study the oxygen chemisorption is fast: a constant pressure in the cell is reached at 22 °C within 5—10 min and at 200 °C for somewhat longer period. The surface coverage with oxygen is small: at a residual pressure of 0.2 Torr, the coverage does not exceed 0.1% monolayer (Fig. 1, *a*). The surface coverages were calculated on the basis of an assumption that 1 m^2 of the surface contains 10^{19} adsorption sites. The amount of adsorbed oxygen increases with the temperature increase. Under comparable conditions, all samples adsorb similar amounts of oxygen.

The chemisorption of O_2 is accompanied by a decrease in the conductivity of the In_2O_3 samples under study (Fig. 1, *b*). The change in the conductivity is described by the kinetic equation similar to the Zel´dovich—Roginskii equation for a heterogeneous surface with a linear distribution of the activation energy among active sites[8]

$$\sigma/\sigma_0 = a\log\tau + b,$$

where σ/σ_0 is the relative electric conductivity of a sample at the time τ; *a* and *b* are constants.

The effect of decreasing conductivity with an increase in the surface coverage becomes more pronounced as the temperature increase. The results obtained for the alloyed samples are similar. A decrease in the conductivity of the alloyed samples with an increase in the surface coverage is more substantial than that for the unalloyed sample: at 200 °C the conductivity of the modified samples changes by three orders of magnitude, whereas for the sample without an additive the change is within one order of magnitude. Since the amount of O_2 sorbed per surface unit is approximately the same for all samples, the results show that the effective negative charge of the sorbed O_2 particles is higher on modified In_2O_3. The removal of oxygen from the reaction cell at 22—100 °C does not change the conductivity of the samples. An increase in the evacuation temperature to 200 °C induces the conductivity increase, and σ/σ_0 achieve the initial values in 3 h, which is a consequence, most likely, of oxygen desorption from the surface.

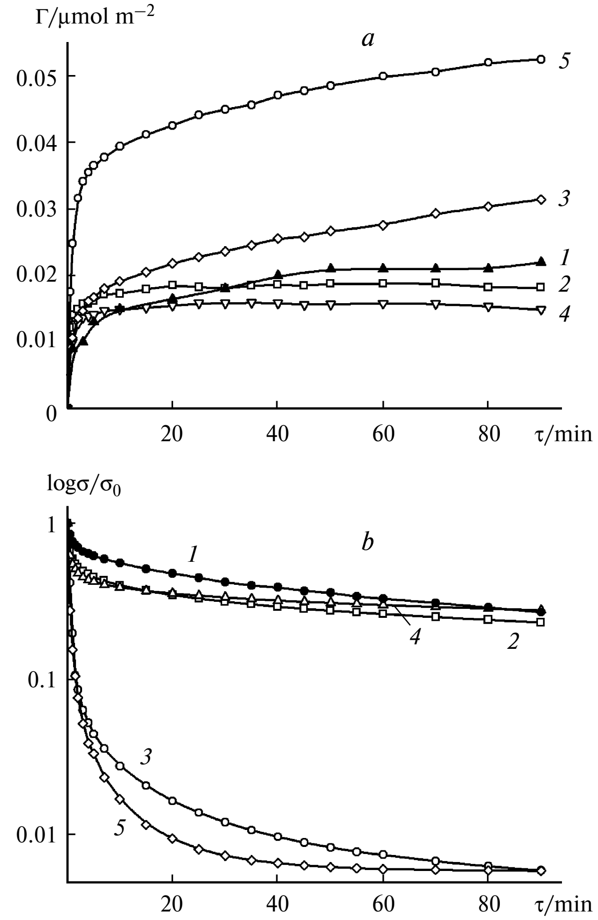

Fig. 1. Kinetics of O_2 chemisorption (Γ) (*a*) and the change in conductivity ($\log\sigma/\sigma_0$) (*b*) of In_2O_3 at 200 °C (*1*), In_2O_3 with an additive of 0.4 at.% Zn at 22 (*2*) and 200 °C (*3*), and In_2O_3 with an additive of 2.7 at.% Zn at 22 (*4*) and 200 °C (*5*).

The regularities of SO_2 chemisorption in the studied temperature range are the same for all samples. The kinetic curves describing SO_2 adsorption at 22 and 200 °C are shown in Figs 2, *a* and 3, *a*, respectively. The chemisorption of SO_2 is fast, and a constant pressure is settled already 5 min after the experiment onset. The change in the temperature exerts no substantial effect on the process rate. The amount of the chemisorbed gas decreases with an increase in the rate of chemisorption (Fig. 4). The Zn concentration in the sample has a weak effect on the amount of adsorbed SO_2. The most noticeable decrease in the amount of the chemisorbed gas under the action of an alloying additive is observed at 200 °C.

Although under the comparable conditions the fraction of surface covered with sulfur dioxide is higher than

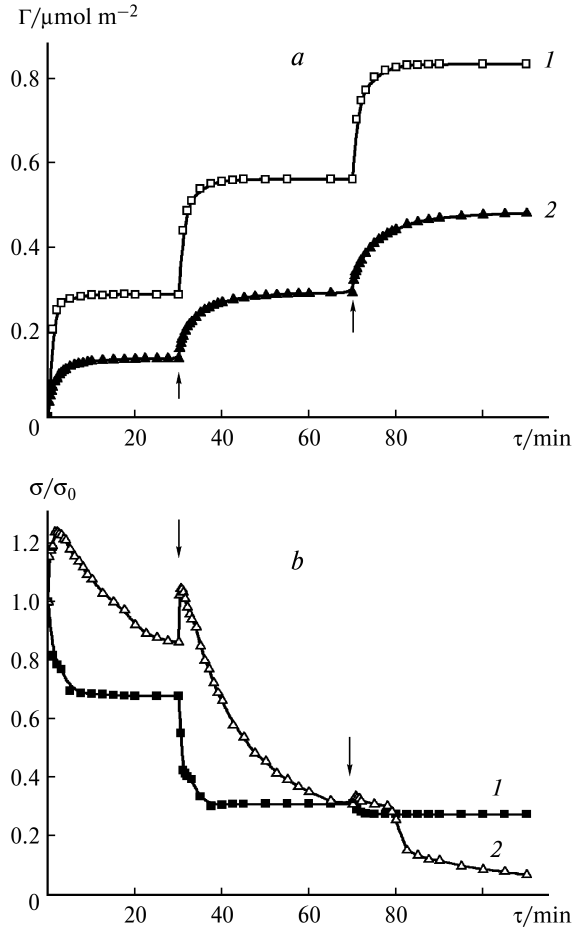

Fig. 2. Kinetics of SO_2 chemisorption (Γ) (*a*) and the change in the conductivity (σ/σ_0) (*b*) of In_2O_3 (*1*) and In_2O_3 with an additive of 2.7 at.% Zn (*2*) at 22 °C. Arrows show the moments of gas inlet.

that covered with oxygen, the sorption of SO_2 induces considerably lower changes in the conductivity.

The character of charging the In_2O_3 surface during SO_2 adsorption depends on the temperature and also on the presence of an alloying additive. The chemisorption of SO_2 on the unalloyed sample at 22 °C is accompanied by a monotonic decrease in the conductivity (Fig. 2, *b*). The change in the conductivity decreases with an increase in the coverage. As the temperature increases, the decrease in the conductivity becomes less substantial. At 200 °C (Fig. 3, *b*), the character of changing the conductivity changes with an increase in the surface coverage. The curves describing the conductivity as a function of the sorption time show a minimum. The initial decrease in the conductivity gives gradually a way to an increase that persists after the termination of SO_2 sorption on the sample. This shows that an increase in the conductivity is caused by the processes occurring in the chemisorption layer, whose rate is lower than the chemisorption rate, rather than by the kinetics of gas sorption. This pattern of variation of the conductivity is retained after each next admittance of gas.

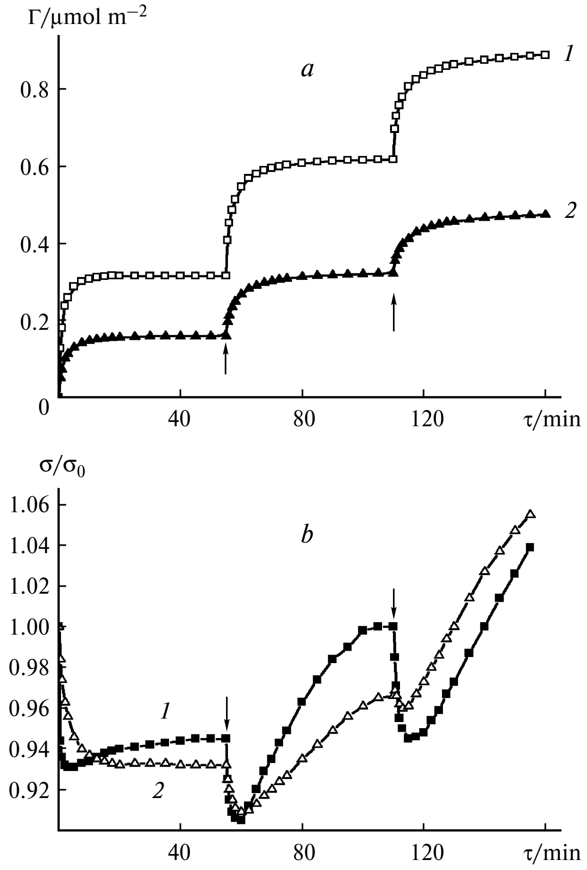

Fig. 3. Kinetics of SO_2 chemisorption (Γ) (*a*) and the change in the conductivity (σ/σ_0) (*b*) of In_2O_3 (*1*) and In_2O_3 with an additive of 2.7 at.% Zn (*2*) at 200 °C.

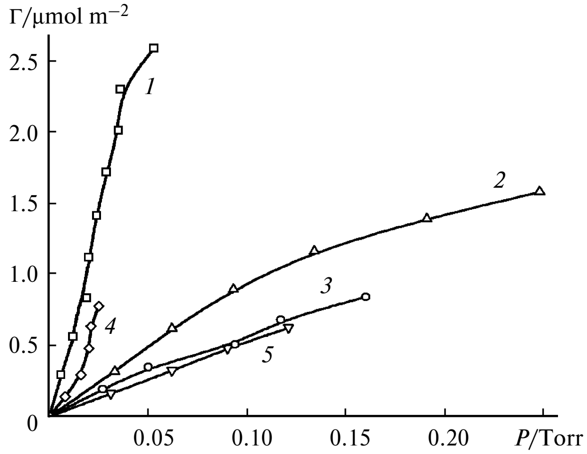

Fig. 4. Isotherms of SO_2 chemisorption on In_2O_3 at 22 (*1*) and 200 °C (*2*), In_2O_3 with an additive of 0.4 at.% Zn at 200 °C (*3*), and In_2O_3 with an additive of 2.7 at.% Zn at 22 (*4*) and 200 °C (*5*).

On the modified In_2O_3 (2.7 at.% Zn), SO_2 sorption at 22 °C results in a sharp initial increase in the conductivity (by 25%), which is followed by the fast decrease (see Fig. 2, *b*). With an increase in the surface coverage, the initial increase in the conductivity becomes less pronounced, and the conductivity only decreases at a coverage of 0.4 μmol m^{-2}. The monotonic decrease in the conductivity shown in Fig. 2, *b* for 22 °C is also evident for SO_2 chemisorption in a range of 100—150 °C. At 200 °C the conductivity decreases monotonically only for the first inlet of SO_2. With an increase in the coverage (repeated introductions of SO_2), the change in the conductivity of modified In_2O_3 in time has extremes: the step of decreasing the conductivity is followed by its increase (see Fig. 3, *b*).

The chemisorption of SO_2 occurs in both the reversible and irreversible forms. The fraction of the reversible form of sorption increases with temperature: for all samples at 22 °C it is 1.0—2.5%, and at 200 °C it reaches 26.1% for the sample containing no additive and ~40% for the sample containing 2.7 at.% Zn. In an interval of 22—100 °C, the highest portion of the gas is desorbed from the surface when the duration of freezing is 1.5 h. At 200 °C an increase in the freezing duration by a factor of two results in the corresponding increase in the amount of the desorbed gas. During desorption at 22 °C the conductivity of the samples remains virtually unchanged, *i.e.*, the uncharged form of SO_2 is reversible. When the desorption temperature increases to 200 °C, the conductivity of the samples decreases (within 15—17%). Evidently, a certain part of SO_2 is sorbed reversibly in the donor form.

The results obtained show that on all the samples the chemisorbed SO_2 exists in at least three forms: donor, acceptor, and electrically neutral. The first form induces an increase in the conductivity of the samples, while the second form decreases the conductivity. Their relation determines the character of the charged surface.[9]

At 22 °C the sorption of SO_2 on In_2O_3 results in the formation of the predominantly acceptor form. However, the contribution of this form decreases with the temperature increase. The initial decrease in the conductivity of the sample at 200 °C indicates that SO_2 is also chemisorbed in the acceptor form immediately after the gas was introduced into the cell. However, the processes of rearrangement of the chemisorbed layer produce the donor form of SO_2, which is present on the sample surface along with the acceptor form.

On the modified samples, the sorption of SO_2 at 22 °C at the initial moment gives the donor form, which is gradually transformed into the acceptor form. An opposite phenomenon is observed at 200 °C: the donor form, which was first prevailing, is replaced by the acceptor form.

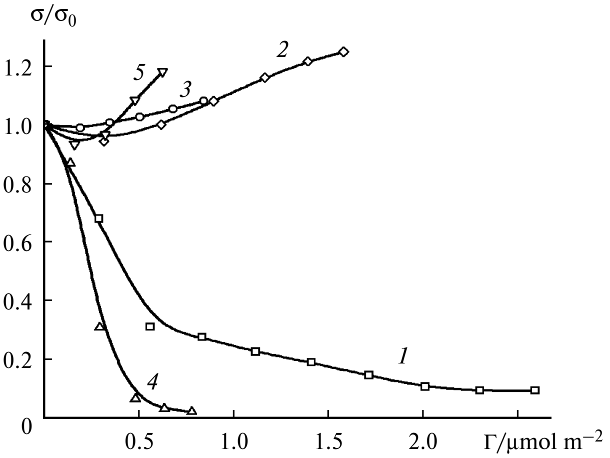

Fig. 5. Dependence of the change in the conductivity (σ/σ_0) on the surface coverage with sorbed sulfur dioxide (Γ) for In_2O_3 at 22 (*1*) and 200 °C (*2*), In_2O_3 with an additive of 0.4 at.% Zn at 200 °C (*3*), and In_2O_3 with an additive of 2.7 at.% Zn at 22 (*4*) and 200 °C (*5*).

The dependence of the change in the relative conductivity of the samples on the amount of sorbed SO_2 is shown in Fig. 5. At 22 °C the acceptor form of SO_2 sorption predominates on the surface of all samples, while at 200 °C the donor form is prevailing. At 22 °C the conductivity of modified In_2O_3 decreases more strongly than that of the unmodified sample, and at 200 °C the greater increase in the conductivity is observed for the samples with additives. Nevertheless, the difference between the conductivity values does not exceed 30%.

Thus, the introduction of zinc (up to 2.7 at.%) into the bulk of nanocrystalline indium oxide exerts a substantial effect on both the electrophysical properties of the sample and the character of surface charging during sulfur dioxide chemisorption. The decisive significance belongs to the presence of the developed surface caused by a small size of crystallites rather than to the introduction of an additive.[1]

It has previously[10,11] been shown that the modification of the oxide surface during chemisorption of acceptor gases significantly affects the charge distribution on its surface during the subsequent sorption of SO_2. This influence can be more significant than that observed upon the introduction of an alloying additive. Oxygen is a typical gas acceptor that is sorbed on active metallic sites of the surface.

The preliminary sorption of O_2 on all samples (the surface coverage is 0.03—0.05 μmol m^{-2}) does not substantially change the kinetics of the subsequent sorption of SO_2, the amount of adsorbed SO_2, and the fraction of the reversibly adsorbed gas. In this case, the pattern of changes in the conductivity of alloyed In_2O_3 is temperature-dependent. The chemisorption of SO_2 at 22—100 °C on the surface containing oxygen is accompanied by a monotonic decrease in the conductivity (Fig. 6), and the change in the conductivity of In_2O_3 during the adsorption of first oxygen and then SO_2 is somewhat less than that for the chemisorption of the gas on the oxygen-free surface.

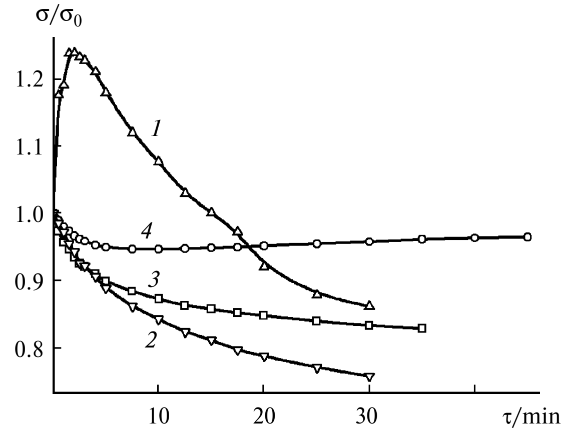

Fig. 6. Change in the conductivity (σ/σ_0) of In_2O_3 with an additive of 2.7 at.% Zn at 22 (*1*, *3*) and 100 °C (*2*, *4*) in the case of SO_2 chemisorption on the surface containing no sorbed O_2 (*1*, *2*) and on the surface subjected to preliminary sorption of O_2 (*3*, *4*).

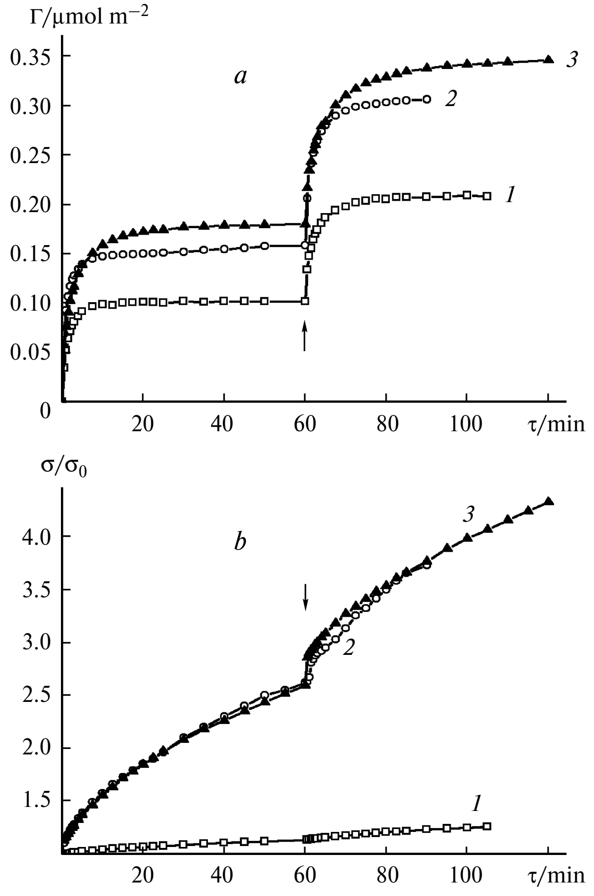

Fig. 7. Kinetics of SO_2 chemisorption (Γ) (*a*) and the change in the conductivity (σ/σ_0) (*b*) of In_2O_3 (*1*), In_2O_3 with an additive of 0.4 at.% Zn (*2*), and In_2O_3 with an additive of 2.7 at.% Zn (*3*) at 200 °C for the surface containing preliminarily sorbed O_2.

This suggests that the acceptor form of SO_2 is sorbed on the same sites as oxygen.

At 200 °C the preliminarily chemisorbed oxygen occupies the most part of active acceptor sites of In_2O_3. As a result, SO_2 chemisorption on the surface containing preadsorbed oxygen is accompanied at 200 °C by a monotonic increase in the conductivity of all samples (Fig. 7). The unmodified sample exhibits an insignificant increase in the conductivity (within 10%), and for the modified samples this increase is much higher and independent of the amount of introduced Zn. A sharp decrease in the concentration of free electrons caused by oxygen chemisorption on the surface of the modified samples results in the subsequent sorption of SO_2 in the donor form: the conductivity of the both samples increases by ~2.5 times.

The observed regularities are completely retained for the repeated introductions of SO_2. The kinetics of the conductivity change is described by the equation similar to the Zel´dovich—Roginskii equation, and the rate of an increase in the conductivity of the samples is much lower than the rate of SO_2 chemisorption. This shows that the formation of a positive charge on the alloyed sample surface due to the transition of electrons of sorbed molecules to the conductivity band of the oxide is an activation process that occurs in the chemisorption layer.

An increase in the conductivity of the In_2O_3 samples with a Zn additive is by an order of magnitude higher than that for In_2O_3 without an additive under the same conditions. Similar "double modification" of In_2O_3 (volume modification by zinc and surface modification by oxygen) favors the suppression of the acceptor form and a substantial increase in the contribution of the donor form of SO_2 chemisorption, which is responsible for the conductivity increase.

Thus, the change in the conductivity of In_2O_3 with Zn additives is determined by the relation of forms of sorbed SO_2, which depends on the sorption temperature. The use of zinc-modified In_2O_3 as a sensor for SO_2 is most promising at elevated temperatures when a considerable monotonic increase in the conductivity is observed during SO_2 chemisorption in the presence of oxygen.

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