Chemisorption of SO₂ on the Zn-modified In₂O₃ surface

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Chemisorption of SO₂ and O₂ on the In₂O₃ 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 SO₂ exist on the modified In₂O₃ surface. The temperature affects the contribution of single forms of SO₂ sorption and, hence, the change in the electric conductivity. The preliminary sorption of O₂ favors the formation of a donor form of chemisorbed SO₂.

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 previously¹ 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 SO₂. It is difficult to detect SO₂, 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 In₂O₃, 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 SO₂. In the present work, we studied the change in the electric conductivity of highly dispersed zinc-modified In₂O₃ during SO₂ chemisorption and the influence of preliminary O₂ 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 (E₉) 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 (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 In₂O₃ 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 In₂O₃ 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 (1·10⁻⁵ Torr) for 2 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 O₂ and SO₂ 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 gas adsorbed was found by the summation of particular portions. The amount of reversibly sorbed SO₂ 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 (E₉) of the samples are similar to each other (Table 1) and...
Table 1. Properties of the In$_2$O$_3$ samples under study

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{sp}$ /m$^2$g$^{-1}$</th>
<th>Particle size /nm</th>
<th>$\sigma$ /S cm$^{-1}$</th>
<th>$E_a$ /eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>In$_2$O$_3$</td>
<td>45.5</td>
<td>20</td>
<td>0.7</td>
<td>0.038</td>
</tr>
<tr>
<td>In$_2$O$_3$ + 0.4 at.% Zn</td>
<td>69.0</td>
<td>12</td>
<td>3.7</td>
<td>0.031</td>
</tr>
<tr>
<td>In$_2$O$_3$ + 2.7 at.% Zn</td>
<td>64.0</td>
<td>13</td>
<td>2.3</td>
<td>0.033</td>
</tr>
</tbody>
</table>

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

much lower than the forbidden band width of In$_2$O$_3$ (2.3 eV). The specific surface of the modified samples and the conductivity ($\sigma$) 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$_2$O$_3$ 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$_2$O$_3$ 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:

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

where $\sigma/\sigma_0$ is the relative electric conductivity of a sample at the time $\tau$; $a$ 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$_2$O$_3$. 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 $\sigma/\sigma_0$ achieve the initial values in 3 h, which is a consequence, most likely, of oxygen desorption from the surface.

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, 3, and 1. 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