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Effect of antimony dopants on the sorption properties of SnO_2

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The effects of antimony modifying additive (0.15—0.50 at.% Sb) on the electrophysical and sorption properties of SnO_2 powders with a well developed specific surface were studied in the temperature range of 25—250 °C. Small amounts of antimony (0.15 at.%) increase the conductivity of SnO_2 containing SO_2 and CO chemisorbed in the temperature range of 25—100 °C. This makes this composition promising as a sensitive element of gas sensors.

Key words: chemisorption, conductivity, dopants, surface, sulfur dioxide, tin dioxide, antimony.

Tin dioxide is a promising material for the design of gas sensitive elements of semiconductor sensors whose operation is based on the dependence of the conductivity on the gas phase composition.[1—3]

Systematic research into the influence of doping on the electrophysical and sorption properties of semiconductor oxides showed that the introduction of dopants that change the electrophysical parameters of the oxide is accompanied by changes in the amount of chemisorbed gas and the types of bonding of sorbed molecules with the surface.[4—6] The observed features can be used in the development of highly sensitive detectors for some toxic gases.

In this work, we studied the effect of antimony additives on the chemisorption of CO and SO_2 and on the change in the conductivity of SnO_2 upon chemisorption.

Experimental

The chemisorption and conductivity measurements were carried out under static conditions using a setup with simultaneous recording of the gas pressure in the reaction cell and the conductivity of the specimen.[7] The amount of adsorbed gas was determined from the decrease in the pressure in the cell. The conductivity of the specimen was measured by the probe method using direct current. The activation energy for conduction was determined from the temperature dependence of the conductivity. The errors of pressure and conductivity measurements were 3 and 2%, respectively. The specific surface area was determined by the Brunauer—Emmett—Teller (BET) method on the basis of low-temperature adsorption of Kr.

Tin dioxide containing no dopants and SnO_2 specimens doped with antimony were prepared by co-precipitation of the corresponding hydroxides with ammonia from solutions of $SnCl_4$ and $SbCl_3$ in hydrochloric acid. The precipitates were washed by multiple decantation. The specimens were dehydrated in a measuring cell for 90 h at 300 °C *in vacuo* (10^{-5} Torr).[8] According to the data of chemical analysis, the resulting samples contained 0.15 (Sn-Sb1) and 0.50 (Sn-Sb2) at. % Sb and the concentration of the Cl^- ions did not exceed 0.01%. The specimens were identified by chemical and powder X-ray diffraction analyses.

Prior to the experiment, the specimens pressed to form pellets were evacuated in a measuring cell (10^{-5} Torr) at a specified temperature until a constant conductivity was attained. The linear dependence of the conductivity on the current strength was retained after this treatment, which is indicative of the absence of intergrain barriers hampering the passage of the current.

The chemisorption of CO and SO_2 was studied at 25—250 °C and an initial pressure of 0.2—0.3 Torr. After a constant pressure was established, the next portion of the gas was introduced into the reaction cell. The surface coverage of the gas absorbed over all admissions did not exceed 1% of a monolayer. When estimating the coverage, it was suggested that 1 m^2 of the surface contains ~10^{19} adsorption sites. Under these conditions, the competition for the active areas of the surface does not affect much the gas chemisorption.

The amount of reversibly sorbed sulfur dioxide was determined by condensing it in a trap with liquid nitrogen for 1.5 h at the experiment temperature. The gas sorbed irreversibly was removed from the surface by evacuation of the sample at 350 °C.

Results and Discussion

The physicochemical characteristics of the specimens are presented in Table 1. All specimens showed a well developed specific surface S_{sp} (particle size 8—12 nm), high conductivity σ, and low activation energy for conduction E_a.

The activation energies for conduction determined *in vacuo* are equal for SnO_2 and Sn-Sb1 specimens. The incorporation of 0.15% Sb into the SnO_2 lattice increases somewhat the conductivity. The increase in the Sb content in the specimen to 0.50% is accompanied by further increase in the conductivity and a decrease in the activation energy.

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Table 1. Physicochemical properties of the SnO_2, Sn-Sb1, and Sn-Sb2 specimens

Specimen	S_{sp} /m^2 g^{-1}	σ/Ω^{-1} cm^{-1}		E_a/eV
		25 °C	200 °C	
SnO_2	78	$4.6 \cdot 10^{-3}$	$4.0 \cdot 10^{-2}$	0.12
Sn-Sb1	92	$1.5 \cdot 10^{-2}$	$1.0 \cdot 10^{-1}$	0.11
Sn-Sb2	58	$2.9 \cdot 10^{-1}$	$6.9 \cdot 10^{-1}$	0.06

It was shown by preliminary experiments that the conductivity of the specimens decreases after chemisorption of O_2. This indicates that these materials are n-type semiconductors.

The regularities of the SO_2 chemisorption are similar for all specimens over the whole temperature range. Figure 1 shows the kinetic curves for SO_2 absorption and for the change in the conductivity of the Sn-Sb1 specimen induced by chemisorption. The major bulk of the gas is adsorbed during the first minute of the experiment, sorption kinetics being described by the Zel´dovich—Roginsky equation. A change in the temperature does not significantly affect the reaction rate or the amount of the absorbed gas, which may be due to low activation energy for chemisorption.

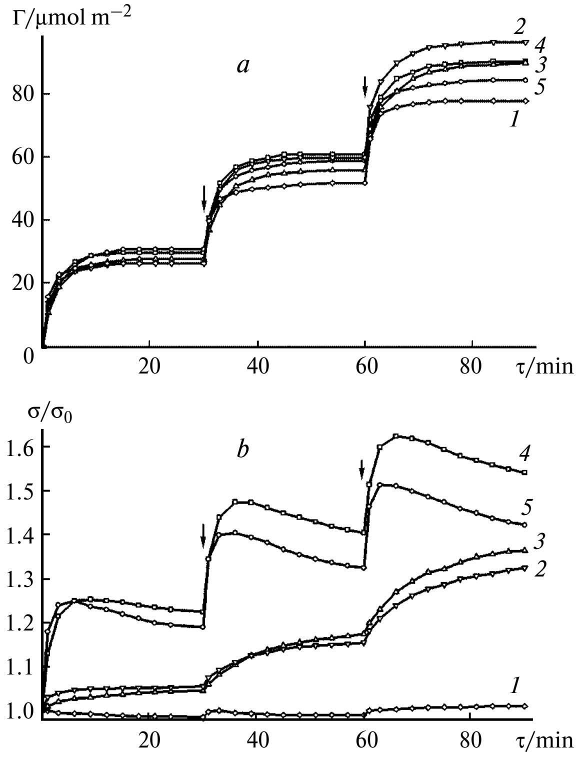

Fig. 1. Amount of SO_2 absorbed (Γ) (*a*) and relative conductivity (σ/σ_0) (*b*) of the SnO_2 specimen doped with 0.15% Sb (Sn-Sb1) at temperatures of 25 (*1*), 100 (*2*), 150 (*3*), 200 (*4*), and 250 °C (*5*) *vs*. time. The arrows mark the points where gas was admitted into the cell.

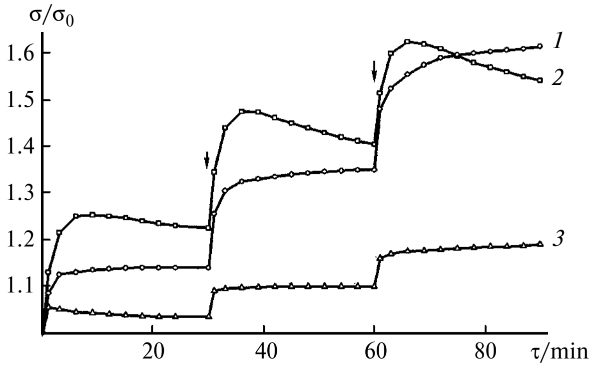

Fig. 2. Relative conductivity (σ/σ_0) of SnO_2 (*1*), Sn-Sb1 (*2*), and Sn-Sb2 (*3*) *vs*. time for SO_2 chemisorption at 200 °C.

At 25 °C, the chemisorption of SO_2 on any specimen does not induce a change in the conductivity. At higher temperatures, the pattern of variation of the conductivity depends on the concentration of the dopant. The conductivity of SnO_2 increases monotonically with temperature and with an increase in the amount of chemisorbed sulfur dioxide. The monotonic growth of the Sn-Sb1 conductivity following the absorption of SO_2 occurs in the temperature range of 100—150 °C. On further increase in the temperature (200—250 °C), the curves for the dependence of the conductivity on the sorption time pass through a maximum. After subsequent admissions of the gas, the pattern of variation of the conductivity remains the same. Under comparable conditions, the change in the conductivity of Sn-Sb1 during the chemisorption of SO_2 is greater than that observed for SnO_2 (Fig. 2). The initial growth of the conductivity of Sn-Sb1 at 200 °C is 25%, that for SnO_2 is 10—12%.

The increase in the conductivity of Sn-Sb2 induced by SO_2 chemisorption at 25—150 °C does not exceed 5%. At higher temperatures, the change in the conductivity becomes more pronounced; however, even at 200 °C, this change is amaller than those observed for the SnO_2 or Sn-Sb1 specimens under the same conditions.

Thus, the pattern of variation of the conductivity of specimens during SO_2 chemisorption depends not only on the sorption temperature but also on the amount of Sb in the SnO_2 lattice. The greatest conductivity increment is observed for the SnO_2 specimen containing 0.15% Sb, while the smallest increment corresponds to the specimen containing 0.50% Sb (see Fig. 2, curve *3*).

The kinetics of chemisorption and the conductivity growth of the specimens are virtually the same. At the experimental temperature, the initial increase in the conductivity for all specimens is nearly proportional to the amount of the absorbed gas. The dependence of the conductivity of Sn-Sb1 on the amount of the absorbed SO_2 at 100 °C is shown in Fig. 3.

The initial decrease in the conductivity of doped samples at 200—250 °C shows completion of sorption

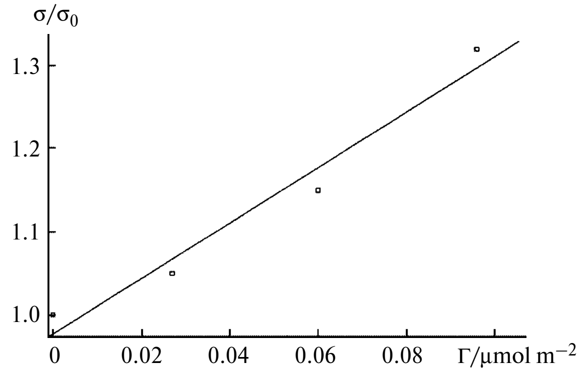

Fig. 3. Relative conductivity (σ/σ_0) of the Sn-Sb1 specimen *vs.* the amount of SO_2 absorbed (Γ) at 100 °C.

of SO_2. This shows that the decrease in the conductivity is due to some processes taking place in the chemisorbed layer, which are slower than sorption, rather than to the sorption kinetics. As the contact time increases, the variation of the conductivity slows down and 2 h after the start of the experiment, it virtually stops. The conductivity of the specimen recorded by this time remains higher than the initial value.

It is known that SO_2 can be sorbed in different ways on the surface of semiconductor oxides. The donor type of sorption is accompanied by electron transfer from the chemisorbed molecule to the conduction band of the semiconductor, while in the case of acceptor sorption, an electron passes from the solid surface to the chemisorbed molecule.[9,10] The donor chemisorption results in a higher conductivity of n-type semiconductors, while acceptor chemisorption decreases the conductivity. Both types can occur simultaneously on the same surface. Their ratio dictates the overall change in the conductivity of materials upon the chemisorption of SO_2.

The results obtained showed that chemisorption of SO_2 on the surface of the undoped specimen is mainly of the donor type. The ratio of the donor to acceptor types of SO_2 sorption on the surface of doped samples depends on temperature and experiment duration. At temperatures above 100 °C, the donor chemisorption of SO_2 predominates at an initial stage of the process. At subsequent stages, the contribution of the acceptor type becomes more significant and, hence, the conductivity of specimens decreases.

The chemisorption of SO_2 on the specimen surface may be both reversible and irreversible, the ratio of these types being dependent on the sorption temperature. In the temperature range under study, the lowest fraction of the reversibly sorbed sulfur dioxide on the Sn-Sb1 specimen is found at 100 °C (4.2%), while the highest, at 250 °C (20.0%).

The lack of the change in the conductivity upon SO_2 chemisorption at 25 °C can be attributed to close concentrations of the donor and acceptor chemisorbed forms on the surface and to the fact that the greater part of sorbed SO_2 is noncharged. After removal of the reversibly sorbed species, the conductivity of the specimen increases, *i.e.*, at 25 °C, reversible sorption is predominantly of the acceptor type.

The removal of the reversibly sorbed gas at 100 °C is also accompanied by an increase in the conductivity. This means that, in the temperature range of 25—100 °C, the compounds formed upon reversible and irreversible types of SO_2 chemisorption carry opposite charges. The acceptor type species are more weakly bound to the surface, as they can be removed at the temperatures used in the experiments. With an increase in the temperature, the strength of bonding of the donor species decreases: the conductivity of samples decreases after freezing-out of the reversibly sorbed SO_2.

Chemisorption of CO was studied with two specimens, namely, SnO_2 and Sn-Sb1. At 25 °C, the chemisorption of CO on the undoped tin oxide does not induce a change in the conductivity, whereas in the case of Sn-Sb1, the conductivity increases under the same conditions. The most pronounced change in the conductivity was detected at the initial instant of the experiment (Fig. 4). At higher temperatures, CO chemisorption leads to an increase in the conductivity for both doped and undoped SnO_2 samples.

The chemisorption of CO on Sn-Sb1 is accompanied by partial reduction of the adsorbent surface even at 150 °C. As a consequence, the gas pressure in the measuring cell increases, CO_2 appears in the gas phase, and tin(II) appears in the condensed phase, its content being higher than 0.15%. The reduction of the undoped specimen takes place at 200 °C.

The preliminary chemisorption of SO_2 at 25 °C does not affect the subsequent sorption of CO on Sn-Sb1: the amount of the absorbed CO and the concomitant change in the conductivity for an SO_2-treated surface and an SO_2-free surface are nearly the same. This indicates that no competition for the adsorption sites is involved.

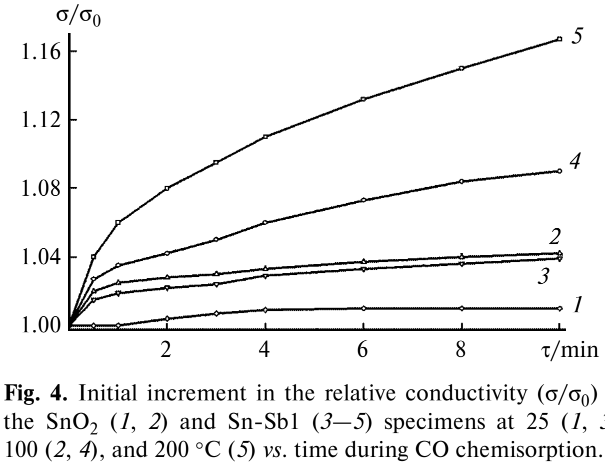

Fig. 4. Initial increment in the relative conductivity (σ/σ_0) of the SnO_2 (*1*, *2*) and Sn-Sb1 (*3*—*5*) specimens at 25 (*1*, *3*), 100 (*2*, *4*), and 200 °C (*5*) *vs.* time during CO chemisorption.

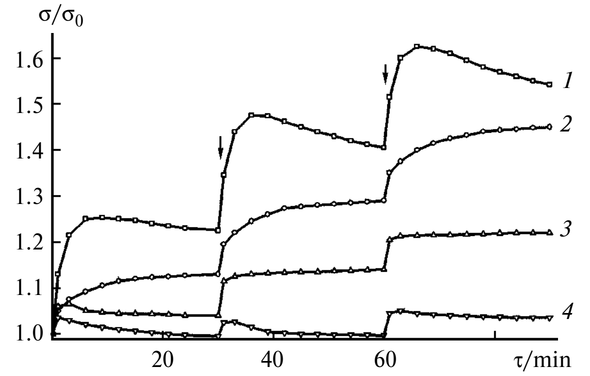

Fig. 5. Relative conductivity (σ/σ_0) of Sn-Sb1 (*1*, *2*) at 200 °C and Sn-Sb2 (*3*, *4*) at 150 °C *vs.* time during SO_2 chemisorption on a surface devoid of Cl_2 (*1*, *4*) and a surface subjected to presorption of Cl_2 (*2*, *3*).

The presence of the dopant results in an increase in the concentration of active sites on the SnO_2 surface responsible for both donor and acceptor types of sorption. Chlorine gas is known to be a typical acceptor sorbed on the metallic active sites of the surface. The preliminary sorption of Cl_2 carried out on Sn-Sb1 at 200 °C has a substantial influence on the pattern of variation of the conductivity, in particular, the step of decrease in the conductivity during the subsequent sorption of SO_2 is missing in this case (Fig. 5, curve *2*). Hence, blocking of the acceptor sorption sites prevents chemisorption of some of the SO_2 molecules in the acceptor form.

For the Sn-Sb2 sample, the growth of the conductivity during SO_2 chemisorption is less pronounced than for Sn-Sb1 under comparable conditions. Apparently, this is due to a greater contribution of the acceptor type sorption. In this case, blocking of the acceptor sites should entail an increase in the conductivity of Sn-Sb2 upon SO_2 chemisorption. Indeed, during chemisorption of SO_2 on the Sn-Sb2 specimen containing pre-sorbed Cl_2, the conductivity increases more appreciably than in the case of sorption on a chlorine-free surface (see Fig. 5, curve *3*).

Thus, the introduction of the Sb dopant in SnO_2 gives rise to additional donor and acceptor sorption sites on the modified surface and the competition between these sites governs the type of bonding of the chemisorbed molecules to the surface.

The donor type sorption of SO_2 on the surface of doped specimens is faster than the acceptor sorption. This results in a rapid initial increase in the conductivity. The strength of bonding of the donor species to the surface is maximum at temperatures of 25—100 °C. In this temperature range, the increase in the concentration of the donor adsorption sites facilitates chemisorption of SO_2 and CO and induces a more pronounced growth of the conductivity than in the case of the undoped specimen. At higher temperatures, the strength of binding of the donor species diminishes and the acceptor type sorption starts to predominate on the surface; hence, the conductivity decreases. The presence of different types of chemisorbed SO_2 with different bond strengths results in the apparent activation energy of chemisorption being close to zero and the chemisorption rate being virtually independent of temperature.

The fraction of the acceptor type species of SO_2 also increases upon an increase in the Sb dopant content from 0.15 to 0.50%, which is confirmed by the less pronounced growth of the conductivity during sorption. This may be due to both the appearance of additional sites for the acceptor sorption and an increase in the concentration of free electrons in the near-surface layer of the specimen.

Thus, the change in the conductivity of the specimens is fully dictated by the ratio of types of SO_2 sorption, which depends on the sorption temperature and on the amount of antimony added. The use of antimony-doped SnO_2 ($\leq$0.15 Sb) as a gas sensitive cell is practicable at temperatures of 25—100 °C. Under these conditions, the initial increment in the conductivity of the specimen is the highest and the dependence of the conductivity on the surface coverage by a chemisorbed gas is linear.

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