Effect of lithium oxide dopants on electrophysical and sorption properties of zinc oxide

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The effects of lithium oxide dopants (0.5—0.8 at. % Li) on the electrophysical and sorption properties of ZnO were studied in the temperature range from 150 °C to 410 °C. The introduction of lithium increases the activation energy of the conductivity of ZnO, decreases its conductivity, and increases the amount of SO_2 sorbed. Two forms of chemisorbed SO_2 (donor and acceptor) are observed on the surface.

Key words: sulfur dioxide, chemisorption; zinc oxide, conductivity, surface; lithium, dopants.

Doping by metal ions, in particular lithium ions, is one of the best known methods to affect electrophysical and sorption properties of semiconducting oxides.[1,2]

This work studied the effects of lithium oxide dopants on the electroconductivity of polycrystalline samples of ZnO and chemisorption of SO_2 on their surface.

Experimental

Samples of ZnO containing 0, 0.5, and 0.8 at. % Li were obtained by the addition of an aqueous solution of LiOH to $Zn(OH)_2$ freshly precipitated with ammonia. The resulting paste-like mixture was dried at 60 °C, grind, and calcined *in vacuo* for 40—50 h at 500 °C.

According to the literature data,[3] under the conditions indicated, Li_2O dissolves in ZnO to form a solid inclusion solution in the concentration range from 0 to 1.0 %.

The content of lithium in the samples was determined by the atomic absorption method. The X-ray diffraction analysis was carried out on a DRON-3 UM diffractometer. The specific surface was determined by the low-temperature adsorption of Kr by the BET method (Table 1).

Table 1. Physicochemical properties of the samples studied

Parameter	ZnO	ZnO + 0.5 % Li	ZnO + 0.8 % Li
$S_{sp}{}^{a}/m^2\ g^{-1}$	5.50	3.50	1.20
$\sigma_{250}{}^{b}$ /Ohm^{-1} cm^{-1}	9.00	$1.9 \cdot 10^{-3}$	$3.5 \cdot 10^{-5}$
$E_a(\sigma)^c$/eV:			
100—325 °C	0.05	—	1.70
325—500 °C	0.05	0.65	0.45

[a] Specific surface.
[b] Electroconductivity at 250 °C.
[c] Activation energy of the conductivity.

The chemisorption was measured by the vacuum static method, and the electroconductivity (σ) was measured by the probe method on a setup with automatic registration of the gas pressure and the conductivity of the sample. This setup was described previously.[4] A weighed sample (2.0 g) was molded under the pressure of 400 MPa, and the pellet was placed into a measuring cell and kept *in vacuo* (10^{-5} Torr) at 500 °C until a constant value of the electroconductivity was achieved. After this treatment, the conductivity of the samples obeyed Ohm's law.

Before the beginning of the experiment, the sample was exposed for 5—7 h at the temperature of the experiment, and a known amount of the gas purified by freezing—thawing out *in vacuo* was let into the cell. When constant pressure was established, the fraction of the reversibly sorbed gas was determined by its freezing with liquid nitrogen for 2 h at the temperature of the experiment. The reversibly sorbed gas was removed from the surface by heating of the sample *in vacuo* for 4—6 h at 500 °C.

The chemisorption of SO_2 was studied at 0.1—0.6 Torr in the temperature range from 150 °C to 410 °C. The composition of the products was analyzed by the thermodesorption method with programming heating on an MI-1201V mass spectrometer.[5]

Results and Discussion

According to the X-ray diffraction analysis data, all samples are single-phase ZnO. The dopants of 0.5 and 0.8 at. % Li exert no effect on the unit cell parameters of ZnO crystals. All samples are semiconductors of the n-type.[6]

The studies performed showed that doping of ZnO by lithium oxide results in a substantial increase in the activation energy of the conductivity and a decrease in

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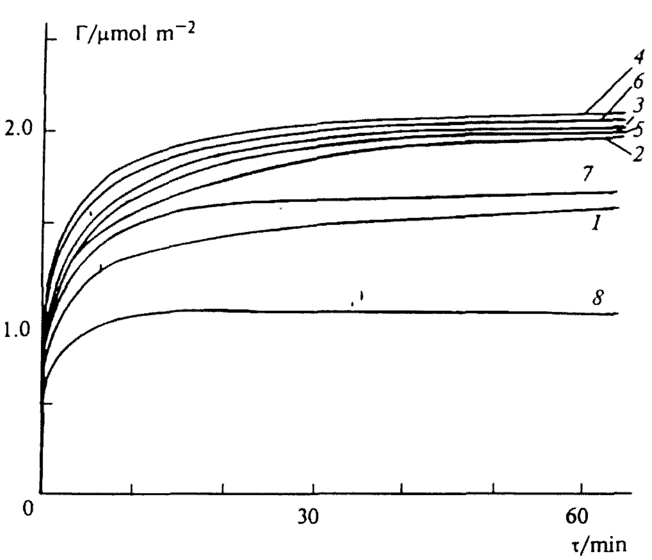

Fig. 1. Kinetics of the chemisorption of SO$_2$ on the surface of ZnO + 0.8 % Li at T/°C = 150 (*1*), 185 (*2*), 205 (*3*), 245 (*4*), 265 (*5*), 305 (*6*), 345 (*7*), and 410 (*8*). The initial pressure of the gas is 0.3 Torr.

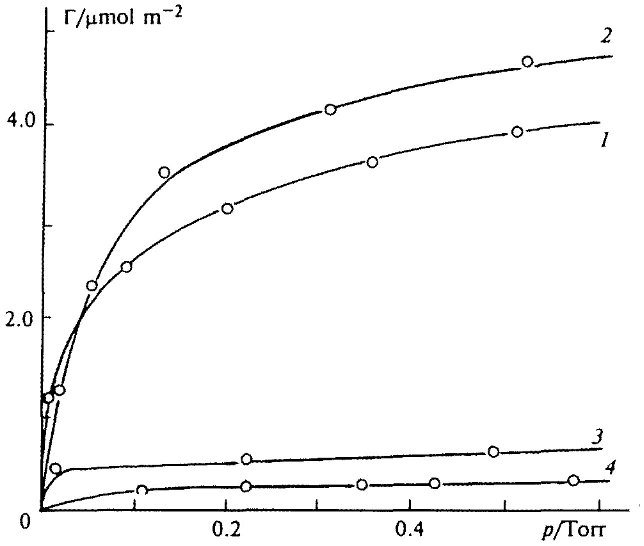

Fig. 2. Isotherms of chemisorption of SO$_2$ on the surface of ZnO + 0.8 % Li (*1*, *2*) and ZnO (*3*, *4*) at T/°C = 185 (*1*), 285 (*2*), 255 (*3*), and 345 (*4*).

the electroconductivity of the samples, which are likely caused by the localization of conductivity electrons on the dopant levels of lithium (see Table 1).

It is known that under various conditions of doping lithium can diffuse to both the nodes of the crystalline lattice of ZnO to form acceptor centers and to the internodes to form donor centers.[7,8] The observed decrease in the conductivity indicates that the dopant Li atoms occupy predominantly the nodes of the crystalline lattice of ZnO under the experimental conditions.

In the temperature range from 150 °C to 410 °C, the kinetics of chemisorption of SO$_2$ on the doped sample (Fig. 1) is described by the Zel'dovich—Roginskii equation:

$$\Gamma = a\ln\tau + b,$$

where Γ is the amount of the gas sorbed and τ is time.[9] It has been shown previously[4] that the chemisorption of SO$_2$ on ZnO that does not contain dopants obeys the same law. However, the rate of SO$_2$ chemisorption on the doped sample in almost an order of magnitude higher.

The reversible and irreversible forms of the chemisorption of SO$_2$ were observed in the temperature range studied. At 150—310 °C, the fraction of the reversible chemisorption is 20 %, and its contribution increases to 45 % as the temperature increases. This indicates that several forms of irreversibly sorbed SO$_2$ are present on the surface. Some of them become reversibly sorbed at the elevated temperatures.

The isotherms of the general chemisorption of SO$_2$ on the doped sample and ZnO without dopants (Fig. 2) are evidence that the filling of the surface of doped ZnO is considerably higher under comparable conditions. It can be calculated on the basis of the geometric sizes of the molecule and the assumption about the continuous covering of the surface that the irreversibly sorbed gas occupies 55 % of the monolayer in the temperature range from 200 °C to 310 °C.

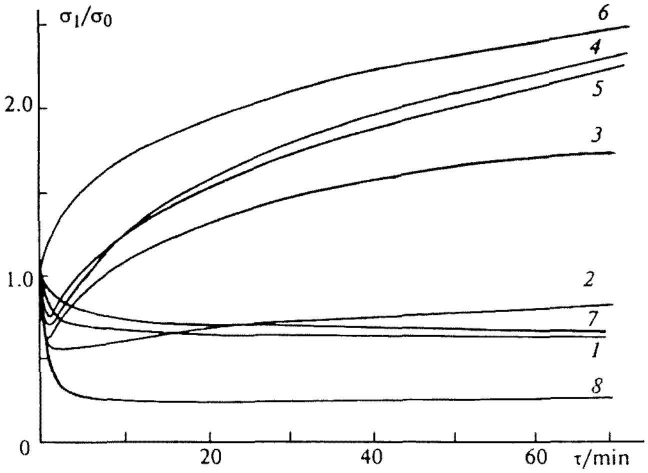

Fig. 3. Change in the electroconductivity (σ$_l$/σ$_0$) of the sample ZnO + 0.8 % Li upon the chemisorption of SO$_2$ at T/°C = 150 (*1*), 185 (*2*), 205 (*3*), 245 (*4*), 265 (*5*), 305 (*6*), 345 (*7*), and 410 (*8*).

The isotherms of adsorption of SO_2 are described by the Freundlich equation:

$$\Gamma = cp^n,$$

where p is the equilibrium gas pressure over the sample. This form of the isotherms corresponds to the adsorption on the heterogeneous surface with the uniform distribution of regions over adsorption heats.

As has been shown previously,[4] the chemisorption of SO_2 is accompanied by a monotonic decrease in the electroconductivity of ZnO. The time and temperature dependences of the change in the conductivity of ZnO containing lithium dopants have a complicated character (Fig. 3). The sorption of SO_2 at 150 °C, as on the undoped sample, results in a monotonic decrease in the conductivity, while at 185 °C the twofold decrease in the conductivity is observed only at the moment of the inlet of the gas, after which the σ value increases slowly. A similar situation is observed upon chemisorption in the temperature range from 200 °C to 310 °C, so that the electroconductivity of the doped ZnO sample is more than twice as large as the initial value after the cessation of the sorption of SO_2. Only a decrease in the electroconductivity is observed for the chemisorption at temperatures higher than 310 °C.

The amount of the sorbed gas and the conductivity of both undoped oxide and ZnO doped with lithium are not directly related, and the electroconductivity of the sample continues to change even after the cessation of the sorption of SO_2. This peculiarity can be explained by a lower rate of transformations in the surface reaction layer of the sample upon chemisorption.

The analysis of the thermodesorption products by mass spectrometry shows that SO_2 desorbs in the unchanged form at 100—750 °C. The absence of SO_3 attests to the fact that SO_2 does not reduce the sample surface under the experimental conditions.

It is noteworthy that the mass spectra of thermodesorption contain two groups of the SO_2^+ peaks: "low-temperature" and "high-temperature" peaks, whose properties differ strongly. The maxima of the high-temperature peaks of thermodesorption (580 and 660 °C) are independent of the temperature of the sorption of SO_2, while the low-temperature peak of SO_2^+ shifts to the high-temperature range as the temperature increases (Fig. 4). For example, in the spectrum obtained after the adsorption of SO_2 at 100 °C, the maximum of the low-temperature thermodesorption peak is observed at 190 °C, while it is observed at 440 °C in the case of the sorption at 350 °C.

The dependence of the form of the spectra on the sorption temperature is evidence of the presence on the sample surface of different types of adsorption centers, on which the substance adsorbed under different conditions can exist in different forms.[10] The desorption of "low-temperature" forms occurs at a temperature close to the adsorption temperature, and hence it is precisely these forms that are responsible for the increase in the fraction of the reversible sorption as the temperature increases.

It is known that the chemisorption of SO_2 can occur in both the acceptor and donor forms, depending on the state of the oxide surface, which is related to the ability of the SO_2 molecule to be coordinated in different ways.[11,12] SO_2 is sorbed in the acceptor form on the ZnO surface without dopants. This results in a decrease in the conductivity of the sample due to the localization of free electrons on sorbed particles. The introduction of modifying dopants, which affect the electrophysical properties of the oxide, into the sample results in a change in the form of the SO_2 sorption. For example, a decrease in the concentration of free electrons in the surface ZnO layer caused by the addition of lithium results in the appearance of the donor form of SO_2 on the surface, which is evidenced by the increase in the electroconductivity observed upon chemisorption.

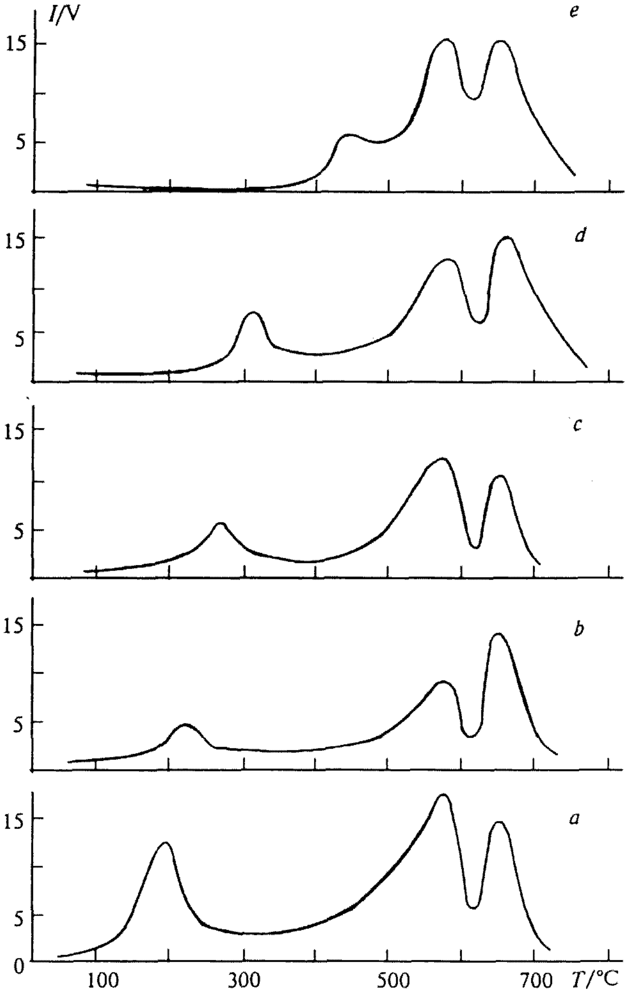

Fig. 4. Spectra of thermodesorption of SO_2 from the surface of ZnO + 0.8 % Li. Temperature of the sorption, T/°C = 100 (*a*), 150 (*b*), 200 (*c*), 250 (*d*), and 350 (*e*).

Table 2. Change in the surface properties of the sample ZnO + 0.8 % Li upon the sorption and desorption of SO_2 at different temperatures

Parameter	150 °C	265 °C	410 °C
σ_0[a]/Ohm^{-1} cm^{-1}	$8.33 \cdot 10^{-6}$	$8.21 \cdot 10^{-4}$	$3.74 \cdot 10^{-1}$
σ_1[b]/Ohm^{-1} cm^{-1}	$5.12 \cdot 10^{-6}$	$10.74 \cdot 10^{-4}$	$0.93 \cdot 10^{-1}$
Predominant form of sorption[c]	A	D	A
$(\Delta\sigma)_{1-0}/\sigma_0 \cdot 100$[d] (%)	38.5	30.8	75.5
σ_2[e]/Ohm^{-1} cm^{-1}	$4.75 \cdot 10^{-6}$	$9,92 \cdot 10^{-4}$	$1.72 \cdot 10^{-1}$
Predominant form of desorption	A	D	A
$(\Delta\sigma)_{2-1}/\sigma_1 \cdot 100$[f] (%)	7.2	7.6	84.9
Fraction of the reversible form of sorption (%)	21.0	22.4	38.5

[a] Initial electroconductivity.

[b] Electroconductivity after the sorption.

[c] A is the acceptor form, D is the donor form.

[d] Relative change in the conductivity upon the sorption.

[e] Electroconductivity after the desorption.

[f] Relative change in the conductivity upon the desorption.

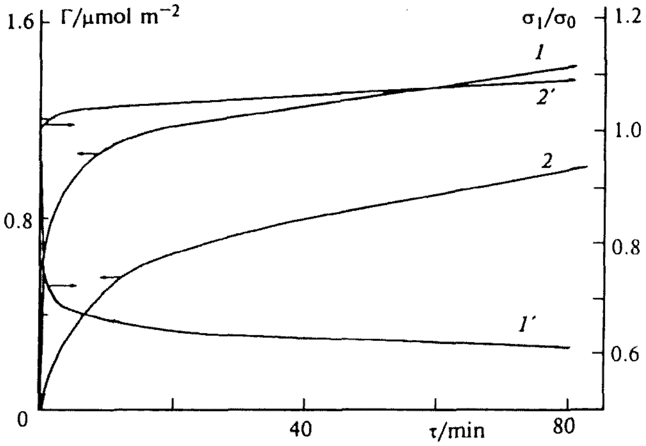

Fig. 5. Kinetics of the chemisorption of SO_2 (*1*, *2*) and the change in the electroconductivity of the sample ZnO + 0.8 % Li (*1′*, *2′*) at 150 °C: *1*, "clean" surface; *2*, surface containing sorbed Cl_2.

It is likely that the acceptor and donor forms exist simultaneously on the surface. Their ratio determines what charge predominates on the surface and depends on the duration of the experiment and temperature. At the moment of the gas inlet, SO_2 is sorbed in the acceptor form, which is indicated by the initial decrease in the electroconductivity. Blocking of active sorption centers and a sharp decrease in the concentration of free electrons result in the fact that at 185—310 °C the subsequent sorption occurs in the donor form and is accompanied by an increase in the surface conductivity. It also cannot be excluded that the acceptor form transforms into the donor form as the chemisorption occurs.

As shown above, the chemisorption of SO_2 at 150 °C occurs predominantly in the acceptor form and is accompanied by a monotonous decrease in the conductivity. The measurement of the electroconductivity performed after freezing out of the reversibly sorbed form of SO_2 showed that the conductivity of the sample continues to decrease during the desorption (Table 2). In the case of the chemisorption of SO_2 at 265 °C, a substantial increase in the electroconductivity is observed. However, after the desorption of the reversible form, the σ value also somewhat decreases, which is likely explained by the desorption of the donor form of SO_2 from the surface.

The chemisorption of SO_2 at 410 °C has a predominantly acceptor character. The desorption of the reversible form results in a noticeable growth in the conductivity, and this indicates that the acceptor form is reversible in the given temperature range.

The results confirm the supposition about the simultaneous existence of the donor and acceptor forms of SO_2 on the surface. The character of the change in the electroconductivity of the sample during the chemisorption at different temperatures allows one to conclude that the acceptor form of the sorption predominates on the surface at temperatures lower than 200 °C. When the temperature increases, the amount of the donor form increases rapidly and exceeds the amount of the acceptor form at 200—310 °C. It should be mentioned that at temperatures lower than 310 °C, the donor form is reversible. The monotonic decrease in the electroconductivity at a temperature higher than 310 °C attests to the predominant sorption of the acceptor form, but it also becomes reversible in this temperature range.

The studies performed show that control of the concentration of free electrons in the surface ZnO layer by the introduction of the dopants into the solid phase favors the appearance of the new form of the sorption of SO_2 on the surface. However, the preliminary chemisorption of the gas also can affect the concentration of electrons.

The chemisorption of Cl_2 (typical gas-acceptor) on the ZnO sample containing lithium dopants is completely irreversible at 100 °C. The filling of the surface reaches 45 % of the monolayer. The decrease in the electroconductivity that accompanies the sorption is 60 %.

The subsequent sorption of SO_2 (without removal of irreversibly sorbed Cl_2) was performed at 150 °C. Under these conditions, the amount of sorbed SO_2 decreases by 30 % compared to the sample whose surface does not contain chlorine. At the same time, unlike the sorption of SO_2 on the free surface, the conductivity of this sample increases slowly (Fig. 5).

These data are evidence that the ratio of the forms of the sorption of SO_2 is determined by the concentration of free electrons in the surface layer of the oxide. The acceptor form of SO_2 predominates in the absence of preliminary sorbed Cl_2 on the surface of the doped sample. Blocking of acceptor sorption centers (metal atoms[13]) and a decrease in the concentration of free electrons upon the sorption of Cl_2 results in the suppression of the acceptor form of SO_2 and an increase in the contribution of the donor form, which is responsible for the growth of the electroconductivity.

Thus, the character of the change in the electrophysical and sorption properties of ZnO upon the modification of its surface by the addition of Li_2O and chemisorption of Cl_2 is the same. The decrease in the initial electroconductivity of the oxide and the increase in the activation energy of the conductivity in both cases result in a change in the form of the sorption of SO_2. Unlike undoped ZnO, on which only the acceptor form of SO_2 was observed, both the acceptor and donor forms of SO_2 are present on the doped sample. The donor form is reversible at temperatures lower than 310 °C, and the acceptor form also becomes reversible at the temperatures higher than 310 °C. The ratio of the sorption forms depends on the concentration of electrons in the surface layer of the oxide.

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