

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

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The effect of gallium oxide dopants (0.1–0.3 at.% Ga) on the electrophysical and sorption properties of ZnO was studied in the temperature range from 19 to 350 °C. The introduction of the dopant increasing the conductivity of ZnO is accompanied by a change in the amounts of SO₂ and Cl₂ sorbed and the reactivity of zinc oxide.

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

The study of the doping effect on the electrophysical and sorption properties of ZnO has shown that the introduction of iron(III) and lithium dopants results in a change in the electrophysical parameters of the oxide. This is accompanied by a change not only in the amounts of SO₂ and Cl₂ but also in the forms of bonding of the SO₂ and Cl₂ sorbed with the surface.^{1,2}

In this work, we studied the effect of gallium on the electroconductivity of polycrystalline ZnO samples and the chemisorption of SO₂ and Cl₂ on their surface.

Experimental

ZnO samples containing 0.1 and 0.3 at.% Ga were obtained by co-precipitation of hydroxides with ammonia from aqueous solutions followed by calcination at 500 °C in air (4 h) and *in vacuo* (2 h). According to the published data,³ under these conditions gallium is dissolved in ZnO to form a solid substitution solution in the 0–2.0 at.% concentration range.

The concentration of gallium in the samples was determined by the atomic-absorption method. X-ray phase analysis (XPA) of the samples was performed on a DRON-3 UM diffractometer.

The specific surface was determined from the low-temperature adsorption of Kr by the BET method (Table 1).

Chemisorption was measured by the vacuum static method, and electroconductivity was measured by the probe method on an installation with automated recording of the gas pressure and the conductivity of the sample described previously.⁴ The results obtained were processed on a PC-AT computer.

The weighed sample (0.2 g) was molded into a pellet under 400 MPa, placed into a measuring cell, and stored for 10–12 h under 10^{–5} Torr at the temperature of the experiment until a constant value of electroconductivity was achieved. Then a known amount of the gas (purified by freezing–thawing out *in vacuo*) was admitted to the cell with the simultaneous detection of its pressure and electroconductivity of the sample.

The next portion of the gas (0.10–1.00 Torr) was admitted upon isothermic saturation of the sample surface after a constant pressure has been established in the cell. The procedure was repeated to almost complete cessation of gas adsorption by the sample.

The fraction of the reversibly sorbed gas was determined by its condensation in a trap with liquid nitrogen at the temperature of the experiment for 2 h. The gas sorbed irreversibly was removed from the surface by heating the sample *in vacuo* at 500 °C for 2 h.

Table 1. Physicochemical properties of samples

Sample	S_{sp}^a /m ² g ^{–1}	Unit cell parameters/Å		σ^b /Ohm ^{–1} cm ^{–1}		E_a^c /eV
		$a \pm 0.001$	$c \pm 0.002$	20 °C	250 °C	
ZnO	1.5	3.249	5.205	—	$9.0 \cdot 10^{-4}$	0.15
ZnO+0.1% Ga	4.6	3.246	5.213	$1.3 \cdot 10^{-3}$	$6.1 \cdot 10^{-3}$	0.14
ZnO+0.3% Ga	3.7	3.249	5.209	$6.3 \cdot 10^{-2}$	$1.3 \cdot 10^{-1}$	0.04

^a S_{sp} is the specific surface of samples.

^b σ is electroconductivity.

^c E_a is the activation energy of conductivity.

Table 2. Chemisorption properties of samples

Sample	Gas	T/°C	Q _{tot} ^a /μmol m ⁻²	Q _{irrev} ^b		σ/σ ₀ ^c	
				μmol m ⁻²	% of Q _{tot}	sorption	desorption
ZnO	SO ₂	250	0.87	0.60	69.0	0.083	1.10
		350	0.41	0.20	48.8	0.127	1.10
	Cl ₂	19	0.30	—	—	0.036	—
		250	2.34	—	—	5 · 10 ⁻⁴	—
ZnO+0.1% Ga	SO ₂	19	0.61	0.23	37.7	0.88	1.02
		100	0.60	0.28	46.6	0.97	1.03
		250	0.38	0.20	52.8	2.25	1.31
		350	0.15	0.09	58.2	1.30	0.77
ZnO+0.3% Ga	SO ₂	19	0.42	0.02	4.0	0.99	0.97
		100	0.40	0.12	30.5	0.87	0.95
		250	0.29	0.13	43.8	0.70	0.86
		350	0.17	0.16	93.0	0.66	0.93
	Cl ₂	19	13.73	13.73	100.0	0.09	—
		250	17.57	17.57	100.0	0.17	—

^a Q_{tot} is the total amount of the absorbed gas.

^b Q_{irrev} is the amount of the irreversibly sorbed gas.

^c σ/σ₀ is the relative change in electroconductivity (σ₀ is the initial electroconductivity of the sample before sorption).

Chemisorption of SO₂ and Cl₂ was studied in the 19–350 °C temperature region.

Results and Discussion

According to the XPA data, all samples are monophase ZnO. Dopants of 0.1 and 0.3 at.% Ga have no effect on the unit cell parameters of the samples (see Table 1). All samples are semiconductors of the *n*-type.⁵

It is known that for doping of ZnO, III Group elements are the main substitution admixtures, which act as donors, occupying cationic sites of the oxide lattice.^{3,6} The results obtained show that under conditions of the experiment, doping of ZnO with gallium results not only in an increase in the electroconductivity

of the samples, but also in a change in their chemisorption properties and reactivity.

In the 19–350 °C temperature region, the kinetics of chemisorption of SO₂ on the samples both doped with gallium and without a gallium dopant is described by the Zel'dovich–Roginskii equation:⁷

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

where Γ is the amount of the sorbed gas, and τ is time.

The amount of chemisorbed SO₂ depends on the dopant concentration and temperature (Fig. 1). In the 19–100 °C temperature region, the coverage of the surface is virtually the same. The amount of sorbed SO₂ decreases as the temperature increases to 350 °C.

An increase in the concentration of Ga₂O₃ also results in a decrease in the amount of sorbed SO₂ (Table 2). The results obtained show that in the presence of Ga₂O₃ the coverage of the surface is lower than that for the sample containing no dopant.

The chemisorption isotherms are described by the Freundlich equation:

$$\Gamma = Cp^n,$$

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

For both samples, we observed two forms of chemisorption, reversible and irreversible (Fig. 2). At the concentration of 0.1% Ga for temperatures higher than 19 °C, the amounts of reversibly and irreversibly sorbed SO₂ are approximately equal. As the temperature increases, the content of both forms on the surface decreases.

For the sample with a concentration of 0.3% Ga, as the temperature increases, the contribution of the irre-

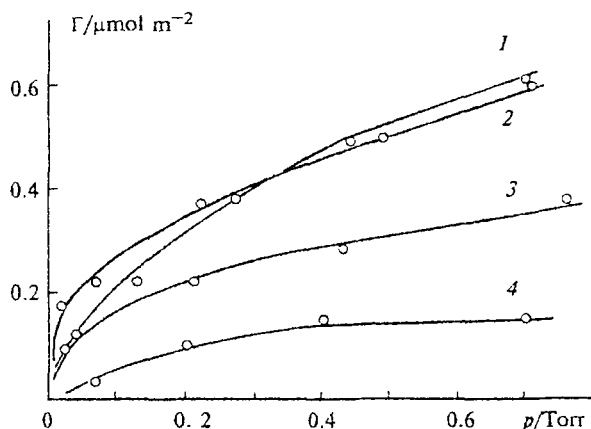


Fig. 1. Chemisorption isotherms of SO₂ on the ZnO+0.1% Ga surface at T/°C = 19 (1), 100 (2), 250 (3), and 350 (4).

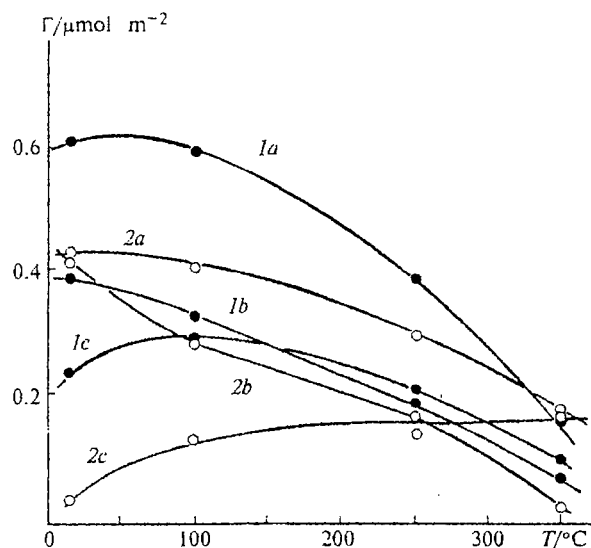


Fig. 2. Chemisorption of SO_2 upon isothermic saturation of the $\text{ZnO}+0.1\% \text{ Ga}$ (1) and $\text{ZnO}+0.3\% \text{ Ga}$ (2) surfaces: a, total amount; b, reversible sorption; and c, irreversible sorption.

versible form increases from 4% at 19 °C to 93% at 350 °C, while the fraction of the reversible form decreases sharply.

Comparison of the coverages of the sample surfaces by irreversibly sorbed SO_2 shows that at 100 °C on the sample doped with 0.1% Ga, the amount of the irreversible form of SO_2 is twice as large as that for the sample with 0.3% Ga. This ratio decreases with a temperature increase, and at 350 °C the amount of irreversibly sorbed SO_2 is twice as large as that on the sample with 0.3% Ga (see Table 2).

The time and temperature dependences of the change in the conductivity of ZnO are complex. Isothermic sorption of SO_2 on the sample doped with 0.1% Ga in the 19–200 °C temperature region is accompanied by a decrease in the conductivity of the oxide. At 250–350 °C, the sorption occurs with a decrease in the conductivity only in the moment of admission of the first two portions of the gas (the initial pressure is 0.10 Torr). The further adsorption of SO_2 results in a stable increase in the conductivity (Fig. 3).

Chemisorption of SO_2 on the samples doped with 0.3% Ga is accompanied by a decrease in the oxide conductivity in the 19–350 °C temperature region.

The change in the electroconductivity of the samples at different amounts of sorbed SO_2 is shown in Fig. 4. At the concentrations of 0.1% Ga and temperatures below 100 °C, an insignificant decrease in the conductivity, which slightly depends on the content of SO_2 , is observed. In the region of higher temperatures, chemisorption of SO_2 results in an increase in the conductivity, which increases proportionally to the amount of the sorbing gas. When the concentration of the Ga dopant increases to 0.3%, the sorption of SO_2 decreases the conductivity in the whole temperature region studied.

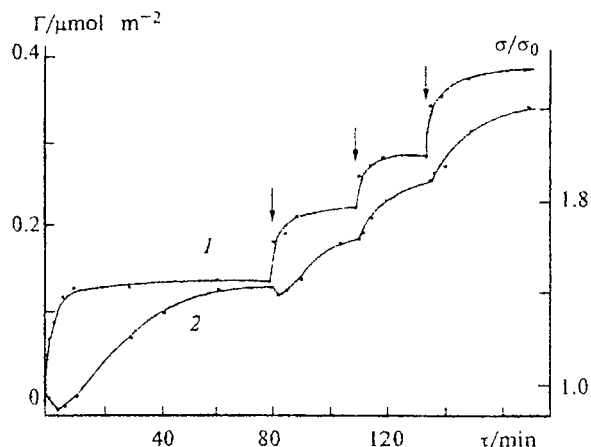


Fig. 3. Kinetics of chemisorption of SO_2 Γ (1) and a change in the electroconductivity σ/σ_0 (2) of the $\text{ZnO}+0.1\% \text{ Ga}$ sample at 250 °C.

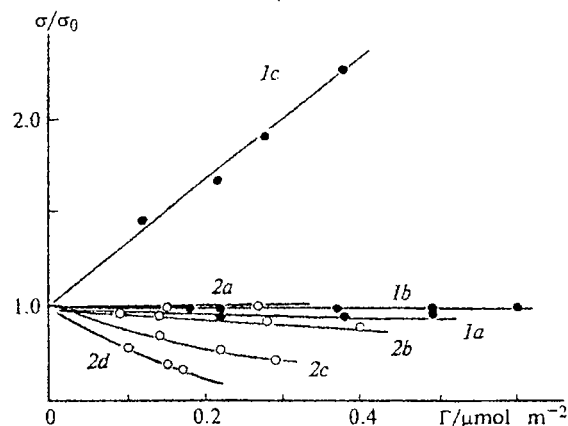


Fig. 4. Dependences of the change in the electroconductivity σ/σ_0 of the $\text{ZnO}+0.1\% \text{ Ga}$ (1) and $\text{ZnO}+0.3\% \text{ Ga}$ (2) samples on the amount of SO_2 chemisorbed at $T/^\circ\text{C} = 19$ (a), 100 (b), 250 (c), and 350 (d).

It is commonly accepted that the electroconductivity of the solid is determined by the concentration of charge carriers and their mobility. Under the experimental conditions, the change in the electroconductivity upon chemisorption is due to the change in the number of electrons in the surface layer of the sample.

Our data show that an increase in the content of the Ga dopant in the sample results in negative charging of its surface, and the effective negative charge of sorbed SO_2 particles increases with a temperature increase.

It is known⁸ that depending on the state of the oxide surface, SO_2 can be sorbed in both donor and acceptor forms. It has been shown previously that ZnO is characterized by the presence of both forms on the surface. Their ratio depends on the concentration of free electrons in the surface oxide layer. The acceptor form of sorption predominates on the ZnO surface without dopants. A decrease in the number of electrons of conductivity due to the modification of the surface (for

example, by Li_2O additives) results in a change in the ratio of sorption forms: in the presence of Li atoms, the donor form becomes predominant.^{2,4}

The results obtained by us show that the ratio of sorption forms is shifted toward the acceptor form in the presence of Ga resulting in an increase in the number of electrons in the surface layer. As the Ga concentration increases, the contribution of the acceptor form increases, and that of the donor form decreases. For example, on the surface of the sample with the 0.1% Ga dopant, the sorption of SO_2 in the acceptor form at 250–350 °C occurs only in the moment of gas admission. This is accompanied by a decrease in the concentration of electrons, which results in the fact that the further sorption occurs in the donor form and is accompanied by an increase in the surface conductivity (see Fig. 3). When the amount of the Ga dopant increases, the chemisorption of SO_2 gains the acceptor form in the whole temperature region studied.

Measurements of the electroconductivity upon removal of the reversibly sorbed form of SO_2 show that a weak increase in the conductivity is observed for the sample with 0.1% Ga at 19–250 °C. This indicates that the acceptor form is predominantly sorbed reversibly (see Table 2). The donor form becomes reversible with a temperature increase. Only the donor form is reversible for the chemisorption of SO_2 on the sample with 0.3% Ga in the 19–350 °C region. Thus, as the temperature increases, the contribution of the acceptor irreversible sorption of SO_2 increases. This tendency is more typical of the sample with 0.3% Ga.

The ratio of the amounts of SO_2 sorbed on the surface in the acceptor and donor forms depends on the parameters of the sample and experimental conditions. The possibility of transition of one sorption form to another during chemisorption cannot also be ruled out, which has been considered in detail for the sorption of SO_2 on the ZnO sample with an additive of Li_2O .² Nevertheless, the results obtained make it possible to estimate qualitatively the contribution of each of the sorption forms. The introduction of the Ga dopant, resulting in an increase in the concentration of electrons in the near-surface ZnO layer, leads to a change in the sorption ability of the oxide. The amount of the acceptor form of SO_2 on the surface increases, the strength of its bonding increases, and the content of the donor form decreases. It is most likely that the total amount of sorbed SO_2 in the presence of Ga is lower than that in the case of undoped ZnO precisely due to the suppression of the donor form.

The kinetics of chemisorption of Cl_2 occurs with high rates: 70% gas is sorbed within 1 min. In the whole temperature range, the sorption is completely irreversible and accompanied (at surface coverages <10%) by a decrease in the conductivity of the sample proportionally to the amount of the gas sorbed.

An increase in the sorption temperature results in a decrease in the change in the conductivity. For example,

the coverage of the surface of 9.5% monolayer (the estimate was obtained from the geometric sizes of the molecules under the assumption that the surface is covered uniformly) corresponds to a decrease in the conductivity by 76% at 19 °C and by 31% at 85 °C.

When coverages exceeding the monolayer have been achieved, the stage of slow increase in the conductivity begins after the chemisorption of Cl_2 has been completed. The change in the electroconductivity of the sample with a content of 0.3% Ga during the isothermic sorption of Cl_2 at 250 °C is shown in Fig. 5. The decrease in the conductivity is replaced by its increase at the surface coverages of ~2.0 monolayers. No stage of an increase in the conductivity was observed in the region of lower temperatures.

Thus, the chemisorption of Cl_2 is characterized by the following specific features: an increase in the uniformity of the surface during sorption, the absence of a proportional dependence between the change in the conductivity and temperature during chemisorption, and very high coverages of the surface. The amounts of chemisorbed Cl_2 is almost an order of magnitude higher than that on ZnO containing no Ga dopants (see Table 2).

A surface coverage exceeding the monolayer is impossible without the rearrangement of the surface reaction layer due to the interaction of chemisorbed Cl_2 with the adsorbent lattice, which results in the formation of metal chlorides and oxygen. This is confirmed by the data of the MS study of the surface.

The results obtained suggest that two processes occur on the surface during sorption of Cl_2 : chemisorption of Cl_2 in the acceptor form accompanied by a decrease in the conductivity of the sample and chlorination of the most active regions of the surface. The contributions of these processes depend on the temperature, the amount of sorbed gas, and duration of sorption. Chemisorption predominates at 19 °C, and the formation of chlorides is

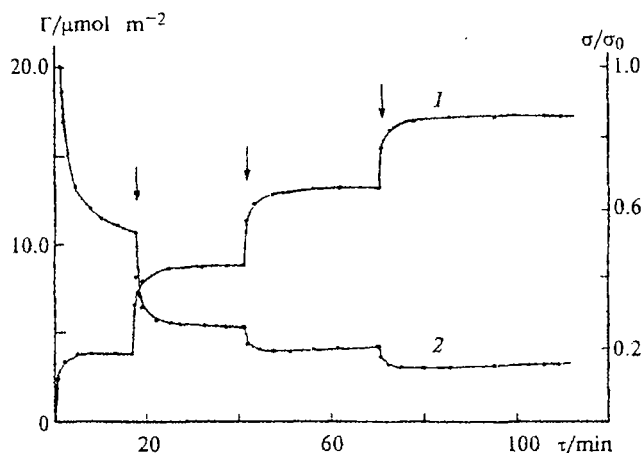


Fig. 5. Kinetics of chemisorption of Cl_2 Γ (1) and the change in the electroconductivity σ/σ_0 (2) of the ZnO+0.3% Ga sample at 250 °C.

the predominant process at 250 °C. In the absence of Ga, the formation of chlorides on the ZnO surface is observed only at temperatures >250 °C.

The regularities of sorption of Cl₂ on ZnO doped with Ga^{III} differ basically from the processes observed upon doping of ZnO with Fe³⁺ ions.¹ In this case, the introduction of a dopant results in a decrease in the electroconductivity of the sample, a decrease in the effective charge of chlorine particles sorbed, and weakening of their bonding with the surface, which provides a lower reactivity of the doped oxide during chlorination.

These results show that doping of ZnO with a dopant, increasing the concentration of electrons in the surface oxide layer, results in an increase in the electroconductivity and a change in the sorption properties and reactivity of the oxide as well. If the gas can be sorbed on the surface only in one form, acceptor (as, e.g., Cl₂), the amount of the gas sorbed increases sharply, and the temperature of formation of reaction products decreases. If the gas (for example, SO₂) possesses the capability of sorbing as both an acceptor and a donor, the donor form is suppressed. The sorption occurs predominantly in the acceptor form. The amount of the gas sorbed and the strength of its bonding with the surface increase proportionally to the concentration of the dopant.

These results indicate the possibility of purposefully controlling the properties of solids and changing their reactivity that through the introduction of microdopants affect the properties of the substance surface.

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