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## GAS DETECTION IN HUMID ATMOSPHERE USING $\text{In}_2\text{O}_3$ - AND $\text{SnO}_2$ -BASED SENSORS

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*Interaction of  $\text{SnO}_2$ - and  $\text{In}_2\text{O}_3$ -based sensors with the reducing  $\text{CO}$  and  $\text{CH}_4$  gases in a humid atmosphere has been studied. The atmospheric moisture is shown to have a significant influence on the sensor conductivity, as well as on the correlation between the sensor sensitivity and catalytic activity. The results obtained are analogous for various oxides and reducing gases. The mechanism of interaction of a reducing gas with the oxide surface in the humid environment is proposed. Using the calculations carried out in the framework of the density functional theory, two different types of hydroxyl radicals on the oxide surface are identified. They differently affect the conductivity and sensitivity of the sensor at its interaction with reducing gases. The proposed model is experimentally confirmed by joint measurements of the sensitivity and catalytic activity of studied oxides.*

*Keywords:* gas sensors, tin dioxide, indium oxide, methane, carbonic oxide, moisture, catalytic activity, density functional theory.

### 1. Introduction

Semiconductor-based gas sensors possess a lot of advantages over other methods of gas detection. In particular, these are their cheapness, compactness, high selectivity, and sensitivity [1]. Wide-gap semiconducting oxides  $\text{SnO}_2$  and  $\text{In}_2\text{O}_3$  are actively used as materials for gas sensors, owing to their rapid response and high thermal stability [2]. Sensors that are based on those materials and whose operation principle consists in a variation of the conductivity in the presence of various gases demonstrate a high sensitivity to such widespread harmful substances as  $\text{CO}$  and  $\text{CH}_4$  [3,4]. Since the procedure of gas registration directly depends on the processes that run at the sensor surface, the investigation of the surface properties of metal-oxide structures and the mechanisms of in-

teraction between molecules of the detected gas and adsorption centers under various external conditions is a challenging task.

Under operating conditions, sensitive elements, as a rule, are in an environment with moisture (water vapor). The parameters of  $\text{SnO}_2$ - and  $\text{In}_2\text{O}_3$ -based sensors reveal a considerable dependence on the moisture. In the majority of works, the presence of moisture gave rise to a reduction of the sensor sensitivity [5–7]. However, in some works [8,9], on the contrary, the moisture caused an enhancement of the sensor sensitivity under certain conditions. From whence, a conclusion can be drawn that, till now, there is no unambiguous understanding of the influence of water vapor on the parameters of gas sensors fabricated on the basis of metal oxides.

In this work, on the basis of the simulation of the surfaces of tin and indium oxides, as well as the results of joint measurements of the catalytic activity and the sensitivity of gas sensors on the basis of  $\text{SnO}_2$  and

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$\text{In}_2\text{O}_3$ , an explanation for the influence of moisture on the operating parameters of metal-oxide-based sensors is proposed. A new mechanism describing the interaction of oxides with reducing gases is suggested, which allowed to explain the obtained set of experimental data.

## 2. Materials and Methods

Thin tin dioxide films were pyrolytically deposited from an aqueous solution of tin sulfate [10]. The synthesis was carried out at temperatures of 620–700 K. The thickness of the obtained  $\text{SnO}_2$  films was 20–30 nm, and the average size of crystallites amounted to 8–15 nm. The chosen technological regime corresponded to the maximum gas sensitivity of sensors [11]. Films on the basis of polycrystalline indium oxide were also synthesized pyrolytically from an aqueous solution of  $\text{InCl}_3$  at temperatures of 620–820 K. The size of indium oxide crystallites varied from 10 to 80 nm. The thickness of indium oxide films amounted to 40 nm.

The catalytic activity of sensors was measured on a thermal analysis system “Mettler TA-3000,” using the method of differential scanning calorimetry (DSC). When measuring the sensitivity, the sensors were put into a flow-type reactor with a volume smaller than  $2 \text{ cm}^3$  and a constant gas flow rate of  $500 \text{ cm}^3/\text{min}$ . The measurements were performed in the steady regime in the gas–air mixtures: CO (1000 ppm) + air for  $\text{SnO}_2$  and  $\text{CH}_4$  (10000 ppm) + air for  $\text{In}_2\text{O}_3$ . The required humidity level was provided with the help of a commercial moisture generator Bronkhorst LFC-CEM V202A by admixing humid air to a flow of dry one. The film conductivity was measured, by using the two-probe method in the dc mode. The sensor sensitivity was measured on the basis of the relative conductivity variation  $G/G_0$ , where  $G_0$  and  $G$  are the sensor conductivity in the air atmosphere and in the environment containing the detected gas, respectively.

To analyze the surface properties of materials, the plane-wave pseudopotential method [12], which is included into the software package CASTEP [13], in the framework of the electron density functional theory (DFT) was applied. The electron–electron interaction was described with the help of the generalized gradient approximation using the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional [14]. The cut-off energy amounted to 340 eV. The integration

over the Brillouin zone was carried out for the  $\Gamma$ -point only.

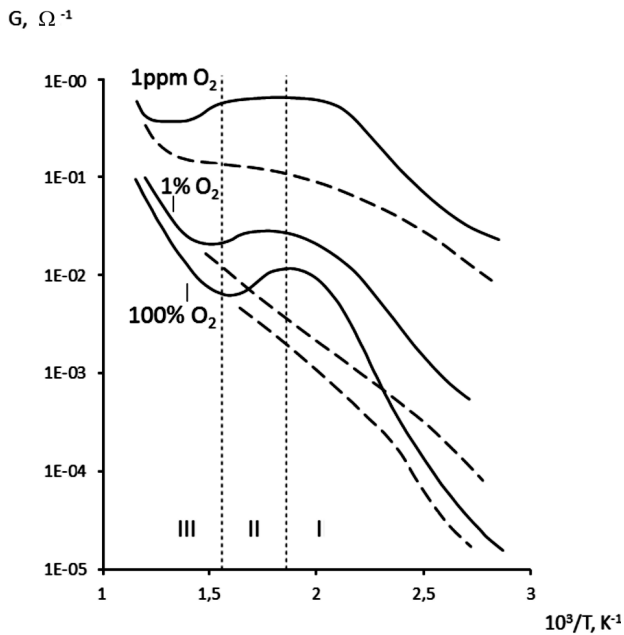
For the modeling of the corresponding surfaces of tin and indium oxides, a supercell in the form of a slab, which was periodic in two directions, was used. The thickness of the vacuum gap in the non-periodic direction amounted to 15 Å. In the case of tin oxide, a spatially periodic  $\text{Sn}_{30}\text{O}_{60}$  cell containing 90 atoms was used in calculations. The lattice parameters were carefully optimized and amounted to  $a = 4.927 \text{ Å}$  and  $c = 3.283 \text{ Å}$ . In the case of indium oxide, an  $\text{In}_{24}\text{O}_{40}$  cell with 64 atoms was chosen for the calculations. Its surface was relaxed, following the procedure used in work [15]. After the relaxation, the lattice constant for indium oxide was equal to 10.30 Å.

## 3. Results and Discussion

The temperature dependence of the conductivity (TDC) for the examined sensors had an S-like shape, which is typical many oxides used in the fabrication of gas sensors. The TDC for tin dioxide is shown in Fig. 1. Similar curves were observed for indium oxide [16].

A specific feature of the measured TDC consists in the presence of three temperature intervals. When a specimen is heated up, its conductivity grows in temperature interval I ( $T < 450 \text{ K}$ ); then a drastic decrease is observed (interval II,  $450 \text{ K} < T < 600 \text{ K}$ ); and, finally, the conductivity monotonically increases again (interval III,  $T > 600 \text{ K}$ ). The anomalous recession of the conductivity in interval II is typical. It was observed both when the partial pressure of oxygen grew (Fig. 1) and when the atmosphere humidity increased (Fig. 2). Such a behavior is associated with the growth of the surface concentration of adsorbed oxygen [9], as well as with the presence of hydroxyl groups on the surface, which appear in the humid atmosphere as a result of the dissociation of a water molecule [17].

The analysis of the paramagnetic properties of  $\text{SnO}_2$ , which was carried out in work [18], showed that, at low temperatures ( $T < 450 \text{ K}$ ), the main form of adsorbed oxygen is  $\text{O}_2^-$ . At temperatures above 450 K, the signal given by  $\text{O}_2^-$  decreases, whereas the signal given by atomic oxygen  $\text{O}^-$  increases. At temperatures exceeding 600 K, the latter signal also decreases. The modification in the forms of adsorbed oxygen within the corresponding temperature inter-

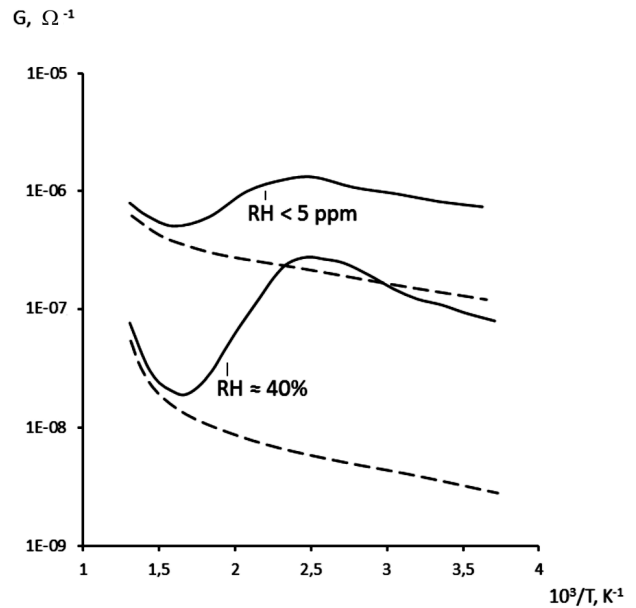


**Fig. 1.** Temperature-induced conductivity of SnO<sub>2</sub>-based sensors in the dry environment (at a humidity lower than 5 ppm) at various partial oxygen pressures: 10<sup>6</sup>, 10<sup>4</sup>, and 1 ppm (O<sub>2</sub> in N<sub>2</sub>). The backward TDCs are shown by dashed curves

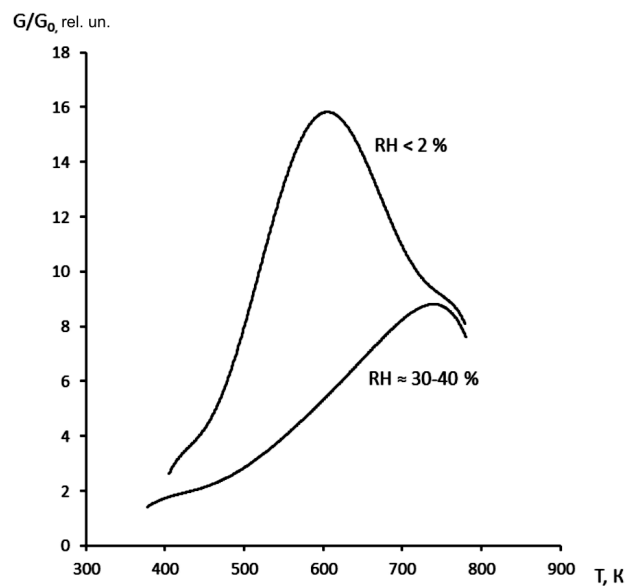
vals is also confirmed by experimental data obtained with the use of the IR spectroscopy and temperature-programmed desorption methods [18]. The temperature intervals of existence for two forms of surface oxygen, which were described in the cited works, coincide well with the sections in the TDC measured for tin dioxide. This fact allowed us to propose the following model.

At temperatures of 450–500 K, molecular oxygen O<sub>2</sub> starts to dissociate into ionically sorbed atomic oxygen O<sup>-</sup>. This process is accompanied by the intensive capture of electrons from the tin dioxide bulk. The reduction of the free charge carrier concentration in the material can be associated with the anomalous recession of the conductivity in the S-like TDC for tin dioxide. Analogously, the anomalous behavior of the conductivity can be associated with the presence of water molecules in the environment. When H<sub>2</sub>O molecules dissociate, the negatively charged hydroxyl groups that arise on the surface can also give rise to a reduction of the conductivity of a material.

The measurements of the SnO<sub>2</sub>-based sensor sensitivity to carbon oxide at various relative humidities

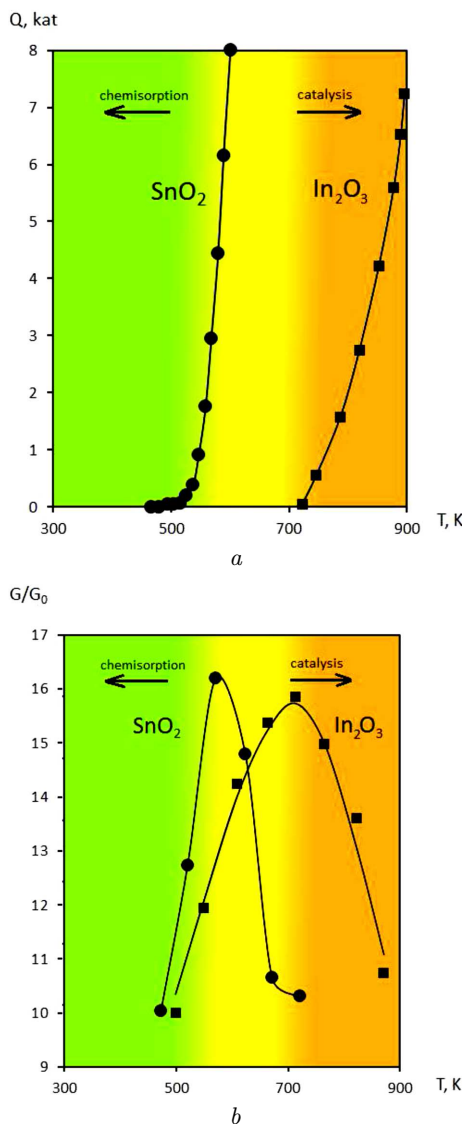


**Fig. 2.** Temperature dependences of the SnO<sub>2</sub>-based sensor conductivity in air with the relative humidities RH < 5 ppm and 40%. The backward TDCs are shown by dashed curves



**Fig. 3.** Sensitivity of SnO<sub>2</sub>-based sensors to CO (0.1 vol%) in the environment with the relative humidities RH = 30÷40% (1) and 1÷2% (2)

(see Fig. 3) testify that the presence of moisture in the atmosphere diminishes the response of a gas sensor. This phenomenon was observed for a lot of other substances, including In<sub>2</sub>O<sub>3</sub>. However, as was marked



**Fig. 4.** Catalytic activity curves for SnO<sub>2</sub>- and In<sub>2</sub>O<sub>3</sub>-based sensors measured with the use of the DSC method at a CO concentration of 1000 ppm and a CH<sub>4</sub> concentration of 1 vol%, respectively (a). Temperature dependences of SnO<sub>2</sub>- and In<sub>2</sub>O<sub>3</sub>-based sensor sensitivities (b)

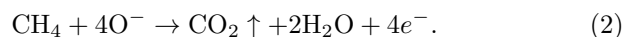
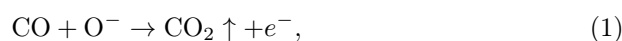
above, the analysis of literature data showed that a change of the environment humidity leads to an ambiguous behavior of a sensor: its sensitivity can either decrease or increase, when the humidity grows [8, 9]. Owing to that, the elucidation of the origin of such a contradictory behavior of the sensor in the humid environment is a challenging task at present.

In order to clarify the influence of moisture on the sensor behavior, we studied the sensitivity of SnO<sub>2</sub>- and In<sub>2</sub>O<sub>3</sub>-based sensors and simultaneously measured their catalytic activity. The catalytic activity of the gas sensors on the basis of tin and indium oxides was measured, when they operated in an oxygen atmosphere containing carbon oxide and methane, respectively. The results of joint measurements obtained for the temperature dependence of the sensor catalytic activity and the sensor sensitivity are depicted in Fig. 4. One can see that, at temperatures above the critical one ( $T > 550$  K for indium oxide and  $T > 720$  K for tin dioxide), the sensor sensitivity decreases, whereas the catalytic activity starts to grow.

The behavior of the curves is identical in both cases: the oxidation of CO by tin dioxide, and CH<sub>4</sub> by indium oxide. This fact testifies that the mechanism of observed processes is the same: both for various oxides and for various reducing gases.

The catalytic activity of sensors is governed by the intensity of a chemical reaction of a gas with centers on the material surface and with the oxygen-containing radicals adsorbed on the surface, such as surface oxygen and hydroxyl groups. Chemical reactions on the surface can change the number of free charge carriers in the material bulk, so that the sensor sensitivity will change. If the reaction does not engage conduction electrons, it does not affect the sensor sensitivity.

One of the channels for the CO and CH<sub>4</sub> oxidations on the SnO<sub>2</sub> and In<sub>2</sub>O<sub>3</sub> surfaces, respectively, is the surface interaction with ion-sorbed oxygen (O<sup>-</sup>):



However, in temperature interval III, the concentration of ion-sorbed oxygen diminishes [18], and its contribution to the catalytic reaction substantially decreases. The involvement of bridging oxygen (O<sub>br</sub>) into the reaction in the tin dioxide case is not connected with the charge transfer into the conduction band, because, in accordance with work [19], the bridging oxygen vacancy creates a trapping center with a deep energy level in the energy gap. On the basis of those facts and taking into account that the concentration of bridging oxygen in interval III is much higher than the concentration of ion-sorbed oxygen,

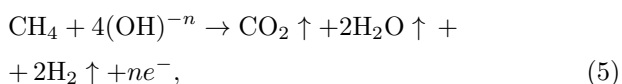
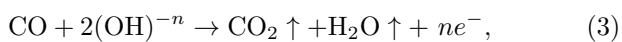
we can conclude that the involvement of bridging oxygen into the reaction with the detected gas promotes a substantial growth of catalytic activity and the simultaneous reduction of sensor sensitivity. The existence of a similar reaction channel is also possible, when gases interact with the indium oxide surface.

A comparison of the sensitivity of the SnO<sub>2</sub>- and In<sub>2</sub>O<sub>3</sub>-based sensors and the curves of their catalytic activity with the corresponding TDC curves shows that intense catalytic reactions emerge on the specimen surface when the sensor conductivity starts to diminish (interval II). The recession in the conductivity is associated with the dissociation of molecular oxygen and the formation of atomic one, with the latter being actively involved into catalytic reactions. At temperatures higher than 550 K for SnO<sub>2</sub> and 720 K for In<sub>2</sub>O<sub>3</sub>, the sensor sensitivity is mainly determined by catalytic processes on the sensor surface. At temperatures below the critical one, when the concentration of atomic oxygen on the surface is insignificant, the high sensitivity of the sensor is explained by adsorption-desorption processes, which take place, owing to the presence of unoccupied adsorption centers on the surface.

In the humid environment, in addition to adsorbed oxygen, hydroxyl groups coordinated with one another in various ways can exist on the oxide surface. Those radicals can differ by their charge states. Two types of hydroxyl groups can be distinguished: (i) OH groups coordinated at the metal atoms (Me-OH) and (ii) OH groups that are formed after the interaction with bridging oxygen (O<sub>br</sub>H).

The hydroxyl groups that were stabilized by capturing electrons from the semiconductor bulk make a contribution to a change of the sensor conductivity, when interacting with the reducing gas. At the same time, the participation of OH groups formed without the localization of conduction electrons in the catalytic reaction does not change the material conductivity.

Taking the aforesaid into account, new channels of carbon oxide and methane oxidations in the humid environment can be expressed in the following forms:



where  $n = 0$  or  $1$ . Hence, the charge state of a hydroxyl group can substantially affect the mechanism of gas detection in the humid atmosphere. In the case where the concentration of chemisorbed OH groups is insignificant, the contribution of reactions (3)–(5) is minimal. On the other hand, in the humid environment and at a high concentration of hydroxyl groups on the surface, reactions (3)–(5) will govern the behavior of the sensor.

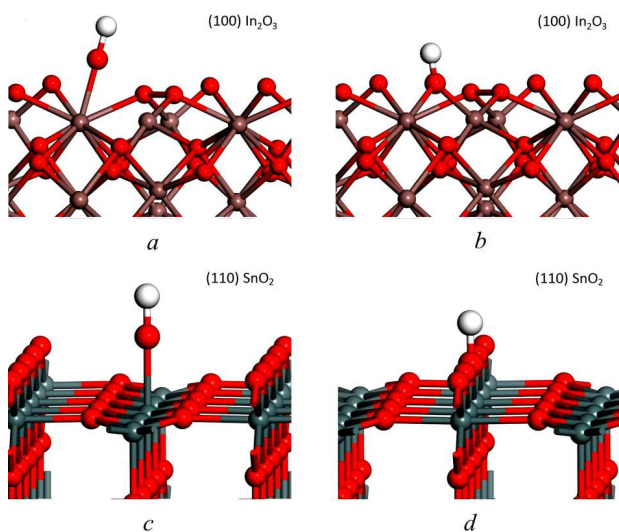
In order to verify the proposed model, DFT calculations were carried out for hydroxyl groups variously arranged on the SnO<sub>2</sub> and In<sub>2</sub>O<sub>3</sub> surfaces. For the simulation, the (110) surface was selected for SnO<sub>2</sub>, and the (100) surface for In<sub>2</sub>O<sub>3</sub>. According to literature data, those surfaces are the most thermally stable and, hence, the most abundant, which is confirmed by the result of X-ray diffraction analysis of our specimens [15, 20].

The reconstruction of the (100) surface of indium oxide was described in work [15]. The relaxed surface is a combination of several types of oxygen bridging atoms and peroxide oxygen radicals. It is non-stoichiometric and oxygen-depleted. The (100) surface of indium oxide is very disordered. It may contain undercoordinated indium atoms, as well as oxygen bridging atoms of several types. Typical hydroxyl groups, which can be formed on this surface, are illustrated in Fig. 5 (panels *a* and *b*). The (110) surface of tin dioxide with differently coordinated hydroxyl groups are also exhibited in Fig. 5 (panels *c* and *d*).

The charge states of hydroxyl groups on the surfaces of examined materials were studied using the Mulliken population analysis. The values of Mulliken charge for OH groups of various types and for surrounding metal atoms from the first coordination sphere on the tin dioxide and indium oxide surfaces are quoted in Table. The corresponding analysis shows that the chemisorption of Me-OH groups on the SnO<sub>2</sub> (110) and In<sub>2</sub>O<sub>3</sub> (100) surfaces is accompanied by the localization of negative charge on them. If those groups are desorbed, their charge becomes redistributed among the metal atoms on the surface, which form a conduction band. Therefore, we may assert that this type of hydroxyl groups will give rise to a variation in the sensor conductivity during the catalytic reaction with the reducing gas. The analysis of the charge distribution in the cases of O<sub>br</sub>H groups on the SnO<sub>2</sub> (110) and In<sub>2</sub>O<sub>3</sub> (100) surfaces testifies that, after the removal of those groups from the ox-

Mulliken population analysis for OH groups of two types on the SnO<sub>2</sub> and In<sub>2</sub>O<sub>3</sub> surface at various cell charge states ( $q = 0, -1$ ), projected on the hydrogen and oxygen atoms in the OH group and for atoms of a metal from the first coordination sphere

q	Me-OH						O <sub>br</sub> H					
	"0"			"-1"			"0"			"-1"		
	Atom	H	O	Me	H	O	Me	H	O	Me	H	O
SnO <sub>2</sub> (110)	0.42	-0.67	1.93	0.39	-0.78	1.93	0.43	-0.93	1.73	0.41	-0.94	1.68
In <sub>2</sub> O <sub>3</sub> (100)	0.43	-0.95	1.29	0.41	-0.98	1.28	0.45	-0.94	1.34	0.43	-0.94	1.29



**Fig. 5.** Schematic drawings illustrating the arrangement of Me-OH (panels *a* and *c*) and O<sub>br</sub>H (panels *b* and *d*) hydroxyl groups on the In<sub>2</sub>O<sub>3</sub> (100) (panels *a* and *b*) and SnO<sub>2</sub> (110) (panels *c* and *d*) surfaces, respectively

ide surface, the conductivity of the material does not change. The obtained theoretical results confirm our assumption that hydroxyl groups can exist in various charge states on various oxide surfaces and, accordingly, differently affect the conductivity of sensors fabricated on the basis of metal oxides.

#### 4. Conclusions

The presence of moisture in the atmosphere substantially affects the specific features of the conductivity in metal-oxide-based gas sensors and their sensitivity. The anomalous recession in the temperature-induced conductivity, which is typical of various oxides, in particular, SnO<sub>2</sub> and In<sub>2</sub>O<sub>3</sub>, can be a result of both the change of oxygen concentration adsorbed on the oxide surface and the formation of hydroxyl

groups of the Me-OH type on the oxide surface, owing to the dissociation of water molecules in the humid environment. The Me-OH hydroxyl groups are formed with the trapping of free charge carriers, and their desorption is accompanied by the sensor conductivity growth.

Another common feature for various oxides and detected gases is a recession of the sensor sensitivity at temperatures corresponding to the beginning of the sensor catalytic activity. At low temperatures (below 550 K for SnO<sub>2</sub> and 720 K for In<sub>2</sub>O<sub>3</sub>), the sensor sensitivity is governed by sorption processes running on its surface, whereas the main contribution at high temperatures is made by the catalytic processes. The catalytic activity associated with the participation of hydroxyl groups of the O<sub>br</sub>H type is not accompanied by the charge transfer into the conduction band of the material and, accordingly, does not affect the sensor sensitivity.

A mechanism of interaction of CO and CH<sub>4</sub> molecules with the SnO<sub>2</sub> and In<sub>2</sub>O<sub>3</sub> surfaces, respectively, is proposed. It takes into account the different charge states of adsorbed hydroxyl groups. The theoretical simulation of OH groups of various types that are formed on the oxide surface in the humid environment confirmed our assumption that OH groups can be formed both owing to the capture of free charge carriers from the conduction band and as a result of the local charge transfer between the adsorption center and the adsorbate. The proposed model is universal, describes well the experimental data, and explains a recession in the sensor sensitivity that correlates with the beginning of the sensor catalytic activity.

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ОСОБЛИВОСТІ ДЕТЕКТУВАННЯ  
ВІДНОВЛЮВАЛЬНИХ ГАЗІВ СЕНСОРАМИ  
НА ОСНОВІ In<sub>2</sub>O<sub>3</sub> І SnO<sub>2</sub> У ВОЛОГІЙ АТМОСФЕРІ

Резюме

В роботі досліджена взаємодія газових сенсорів на основі діоксиду олова (SnO<sub>2</sub>) та оксиду індію (In<sub>2</sub>O<sub>3</sub>) з чадним газом (CO) і метаном (CH<sub>4</sub>), у вологій атмосфері. Показано, що наявність вологи чинить сильний вплив на провідність сенсорів, а також на кореляцію між його чутливістю та каталітичною активністю, причому ці результати є спільними для різних оксидів та відновлювальних газів. В роботі запропоновано механізм взаємодії газів-відновників з поверхнями оксидів у вологій атмосфері. В результаті теоретичних розрахунків, що були виконані на основі теорії функціонала електронної густини (DFT), на поверхні оксидів виділені гідроксильні групи двох типів, які по-різному впливають на провідність та чутливість сенсора при його взаємодії з відновлювальними газами. Запропонована модель знаходить експериментальне підтвердження при сумісному вимірі каталітичної активності та чутливості, що проводились для розглянутих оксидів.