THE INFLUENCE OF STRUCTURAL FACTORS ON SENSITIVITY OF SnO_2-BASED GAS SENSORS TO CO IN HUMID ATMOSPHERE

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The influence of a crystallographic orientation of SnO_2 grain surfaces on the gas-sensing characteristics is considered by the example of the interaction of CO with different tin oxide surfaces in the presence of water. The charge state of a chemisorbed hydroxyl group varies depending on the predomination of different atomic faces of SnO_2 nanocrystallites prepared in different technologies. Involving the differently charged OH groups in the catalytic reaction with CO affects the sensor sensitivity.

1. Introduction

Tin dioxide, SnO_2, has found an important technical application in the field of chemical sensing due to its ability to transduce different gas-surface interactions to conductivity changes. However, despite that the structure and electronic properties of the SnO_2-based sensor surface have been experimentally studied in great details [1—4], highly specific and sensitive SnO_2 sensors are not yet available and peculiarities of their operation are not fully understood. Thus, a strategic trend in the chemical sensor development is the transition from the empirical approach in the gas sensor design and manufacturing to a basic-understanding approach with the aim to obtain a complete description of the sensing mechanism for SnO_2-based sensors [3, 5].

The morphology and grain structure of nanocrystalline materials play a key role in the determining of their main physical and chemical properties. Usually, it is displayed through the so-called "dimension effect", e.g. the comparability of a grain size with the Debye length. Its influence on the gas sensitivity is now considered as well-known and may be attributed to the fundamentals of the gas sensor operation [3, 6]. On the other hand, such important factor as the influence of a crystallographic orientation of grain surfaces on the sensing mechanism is not well understood [7, 8]. In the present paper we analyze the role of the grain habit and the faceting of SnO_2 grains deposited by spray pyrolysis [9] on the sensitivity to carbon monoxide in the presence of water.

2. Experiment

SnO_2 films with thickness of 30—400 nm were deposited from a $SnCl_4$-water solution, using the apparatus and technological modes described in [9]. Films were deposited onto Si and alumina ceramic substrates heated at 350—450°C. Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), High Resolution TEM (HRTEM), and X-ray Diffraction (XRD, $\theta/2\theta$ mode), were used in the analysis of the SnO_2 film surface morphology and crystallographic structure. XRD analysis has been performed with a diffractometer Siemens D5000 working on the K_α of Cu. The TEM characterization has been carried out using a Philips CM30 SuperTwin electron microscope operating at 300 keV. Computer image simulations have been performed using the EMS software package.

The gas-sensing characteristics and electrophysical properties of SnO_2 films were controlled using a flow-type reactor. CO (1000 ppm) was a testing gas. The relative humidity (RH) of the detected gas was varied from 1—2 to 35—40%. The lowest level of air humidity was reached using the method of freezing in a nitrogen

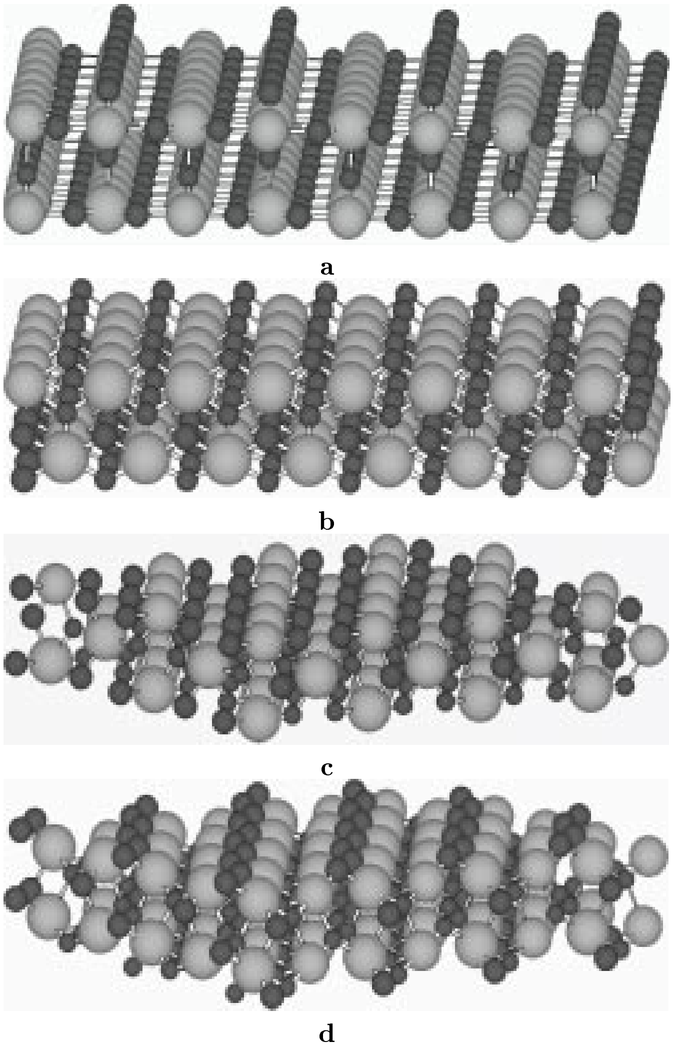

Fig. 1. Models of unrelaxed rutile *a* — (110), *b* — (100), *c* — (001), *d* — (101) surfaces. The lighter balls represent tin atoms and the darker balls do oxygen atoms

trap. The testing structures had Au contacts. The distance between contacts was equal to 6—10 mm. In this case we could ignore the influence of contacts on the measured characteristics. Before measurements, samples were annealed in air at $T_{an} = 500$ °C during 30 min.

3. Characterization of SnO_2 Nanocrystalline Faces

The models of unrelaxed rutile (110), (100), (001) and (111) surfaces are shown in Fig. 1. The [110] direction of the rutile structure of SnO_2 consists of neutral groups of three parallel planes O—Sn_2O_2—O, and the cleavage cut between these groups of planes breaks the least number of cation-anion bonds. Therefore, the (110) face, shown in Fig. 1,*a*, is the most stable and dominant of low-index faces of rutile. Both of the opposing faces formed by this cleave are identical. The (110) surface is not atomically flat. The symmetric rows of 'bridging' O ions lie at equal distances above and below the surface plane, resulting in a non-polar surface which contains the equal numbers of five- and six-fold coordinated cations. The bridging O ions can be easily removed and replaced, depending upon surface treatment [10]. In the case of stoichiometric surface, the 5-fold coordinated surface tin atoms are of particular interest in providing active sites for adsorbates. The (110) faces exhibited (4×1), (2×2), (1×2), and (1×1) LEED patterns for various annealing temperatures [1,11,12].

A model of the (100) rutile surface is shown in Fig. 1,*b*; the opposing cleaved faces both have this structure. This is a rather rough surface, with O rows lying above the surface plane. All of the cations on this surface are five-fold coordinated with O ligands and therefore may serve as surface sites for adsorbates. The formation of a bridging oxygen vacancy results in the arising of 4-fold coordinated tin ions. The deep reducing of the surface may lead to the appearance of 3-fold coordinated cations.

The (001) surface of rutile, in spite of the high symmetry of the lattice in that direction, is the least stable of the low-index faces. Cleaving between adjacent charge-neutral planes would produce two identical surfaces, whose ideal structure is shown in Fig. 1,*c*. The nearest-neighbor ligand coordination of the surface cations has been reduced from six to four. Although this surface is non-polar, the low ligand coordination of the surface cations favors a reconstruction to increase that coordination. A possible mechanism of the reconstruction is the cation rehybridization into some inactive form, for example, into distorted sp^3. Usually [13, 14], the surface reconstruction resulted in such a rehybridization displaces the superficial cations down and causes the oxygen raise above the surface plane.

The ideal cleavage of the (101) atomic face of rutile is shown in Fig. 1,*d*. This is also a non-polar, microscopically rough surface with non-symmetrically coordinated O rows lying above the surface plane and forming a rectangular pattern. The surface concentration of such two-fold 'bridging' oxygen is higher, and they are located closer to the atomic plane than to the (110) face. All of the cations on this surface are five-fold coordinated with O ligands and therefore may serve as surface sites for adsorbates. The involving of weakly bound bridging oxygen in surface reactions results in the arising of 4-fold coordinated tin ions.

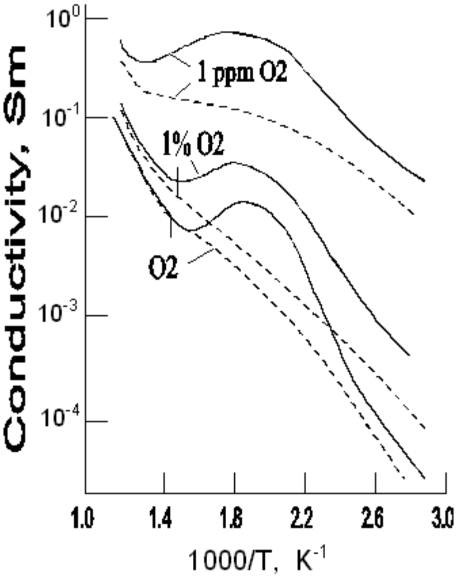

Fig. 2. Temperature-stimulated conductance measurements of a SnO_2-based thick-film sensor measured in a dry (humidity less than 5 ppm) atmosphere at different oxygen partial pressures (10^6, 10^4, and 1 ppm of O_2). The conductance value indicates an irreversible behavior of the activation energy of conductance during a heating-cooling cycle

The catalytic activity of atomic faces is determined to a large extent by the surface concentration of non-saturated cations and weakly bound bridging oxygen. Taking into account such an assumption, the following rank can demonstrate the catalytic activity (CA) of ideal SnO_2 atomic planes:

$$\mathrm{CA}_{(110)} < \mathrm{CA}_{(001)}, \quad \mathrm{CA}_{(100)} < \mathrm{CA}_{(101)}. \tag{1}$$

On the other hand, simple estimations show that dissociative chemisorption is facilitated with distance decreasing between the cation atoms. According to this parameter, the SnO_2 ideal atomic planes form the following rank:

$$d_{(110)} \sim d_{(100)} < d_{(101)} < d_{(001)} \tag{2}$$

(for the indicated planes, the distance between the tin atoms is equal to ~ 3.18, 3.7, and 4.7 Å, respectively).

Apparently, the situation is even more complicated for a semiconductor gas sensor, where the response signal is based on conductivity changes. In this case, priority should be given to the surface, where gas-surface interactions are the most effectively transduced to conductivity changes. The role of orientation effects can be clearly seen by the example of the interaction of CO with different tin oxide surfaces in the presence of water.

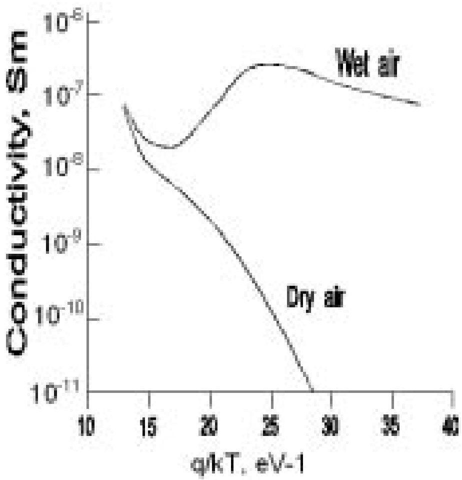

Fig. 3. Influence of air humidity on the temperature dependences of SnO_2 thin film conductivity: dry air – humidity H< 5 ppm; wet air — RH≈40%

4. Effect of Ambient Humidity on the SnO_2 Gas Response to CO

The typical sigmoid behavior of temperature-stimulated conductance measured in air has been observed on the major groups of metal oxide materials found the application as semiconductor gas sensors (Figs. 2 and 3). Such a behavior was associated either with the dissociative adsorption of molecular oxygen or with the desorption of hydroxyl groups at elevated temperatures. Both mechanisms found reliable supporting evidences in the literature [15, 16].

It was reported also that SnO_2 films deposited in different technological modes behave in different ways while exposed to reducing gases in the presence of water. In the number of publications dealing with the sensors on the base of SnO_2 powders prepared under equilibrium conditions (the sol-gel method), increasing the sensitivity to CO in a humid atmosphere was reported [17, 18]. On the other hand, the SnO_2 films deposited by spray pyrolysis exhibit dumping of the sensitivity to CO with increase in RH, as is shown in Fig. 4.

Earlier [20], it was suggested that hydrogen atoms released upon the dissociation of water interact with ionosorbed oxygen species conversing them into hydroxyl groups:

$$\mathrm{H_2O} + \mathrm{O_{ad}} \longrightarrow (\mathrm{Sn{-}OH}) + (\mathrm{O_{ad}H}). \tag{3}$$

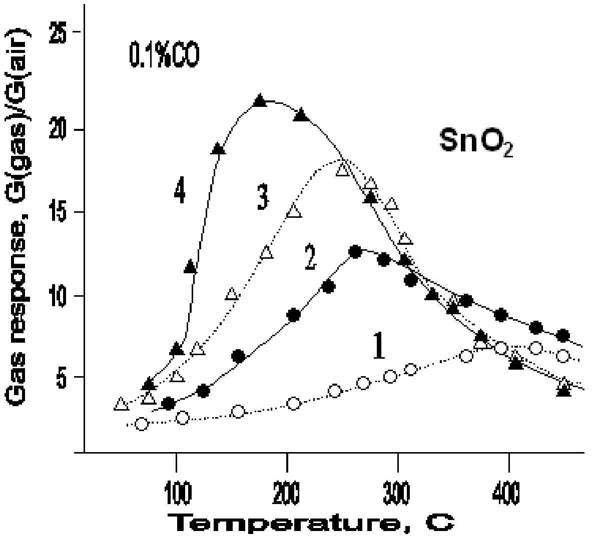

Fig. 4. Influence of air humidity on the temperature dependences of the SnO_2 film's gas response: *1, 2* — undoped SnO_2, *3, 4* — SnO_2 with Pd surface additives, *1, 3* — wet air (30—40%RH), *2, 4* — dry air (1—2%RH)

Therefore, during the CO exposure in addition to the reaction of CO with ionosorbed oxygen

$$CO^{gas} + O_{ads} \longrightarrow CO_2, \qquad (4)$$

a new reaction channel

$$CO^{gas} + (Sn-OH) + (O_{ad}H) \longrightarrow CO_2^{gas} + H_2O\uparrow \qquad (5)$$

opens, where the charge state of chemisorbed OH groups depends on the type of chemisorption involving localized or conduction electrons.

Thus, the charge state of hydroxyl groups involved in the reaction of catalytic oxidation plays a fundamental role in the mechanism of CO detection in the presence of water. It is supposed that, in the case where the chemisorption of OH groups is not accompanied by electron exchange with the bulk, the contribution of reaction (3) into the change in the surface potential is minor. At that, at a high level of surface hydroxylation, reaction (3) may predominate over reaction (2) that will obviously cause a decrease of the sensor sensitivity. On the other hand, the involving of charged OH^- groups in reaction (3) should lead to an increase in the sensor response to CO.

The results of simultaneous measurements of resistance and work function on tin dioxide sensors obtained by the high-temperature calcination of pre-washed nano-powder show that the detection of CO in humid air is associated with changes in the surface potential [18]. This indicates that the appearance of hydroxyl groups in such structures may be associated with the trapping of bulk electrons. On the other hand, the analysis of the measurements of temperature-stimulated conductance displays that, in the case of SnO_2 films deposited by spray pyrolysis, the formation of a great amount of OH groups is not accompanied by essential changes of the surface potential [21]. Indeed, the observed decrease of conductance at $T > 240$ °C cannot be connected with the influence of water. As follows from [14], the desorption of OH groups begins at these temperatures. This means that, under these conditions, the charge of the ensemble of OH-groups and accordingly both the surface potential and resistance must decrease. However, we don't observe this effect. Taking into account a great concentration of OH groups on the SnO_2 surface, this means that the concentration of the charged form of OH groups is very small. Thus, the interaction of CO with hydroxyl groups shouldn't cause essential changes in the surface potential.

Such a diversity in the experimental results can be understood in terms of differences in the morphology and chemical composition of differently prepared SnO_2 films.

A detailed analysis of SnO_2 nanocrystallites formed using different technologies [4, 19] has been made with HRTEM. It was found that SnO_2 nanocrystals grown under equilibrium conditions usually are faceted by (110) planes. It is known that this plane is the most thermodynamically stable plane of the SnO_2 lattice. The detailed analysis of the digital diffraction patterns of SnO_2 films deposited by spray pyrolysis has shown another structure of SnO_2 nanocrystals. It was determined that, in dependence on deposition parameters, the crystallographic planes different from the (110) atomic plane appear in SnO_2 nanocrystals. The crystallographic models of SnO_2 nanocrystals for the most common crystal orientation experimentally found are shown in Fig. 5. These models have been obtained on the basis of both the analysis of HRTEM images, and the results of computer simulations carried out using the software packages EMS and Rhodius [23].

One can see that the structure of SnO_2 crystals grown at a low pyrolysis temperature ($T_{pyr} < 400$ °C) is double pyramidal, with the lower pyramid truncated (Fig. 5,*a*). The upper pyramid is composed by the (111), $(11\bar{1})$, (200), and (020) planes, whereas the inferior one is formed by the $(\bar{1}\bar{1}1)$, $(\bar{1}\bar{1}2)$, $(1\bar{2}0)$, and $(\bar{2}10)$ planes. At the same time, the most of SnO_2nanocrystals deposited at $T_{pyr} \sim 400$—450 °C are columnar (Fig. 5,*b*), with a pyramidal upper side and a rhombic base. The upper pyramid is composed by the (101), $(10\bar{1})$, (110), and

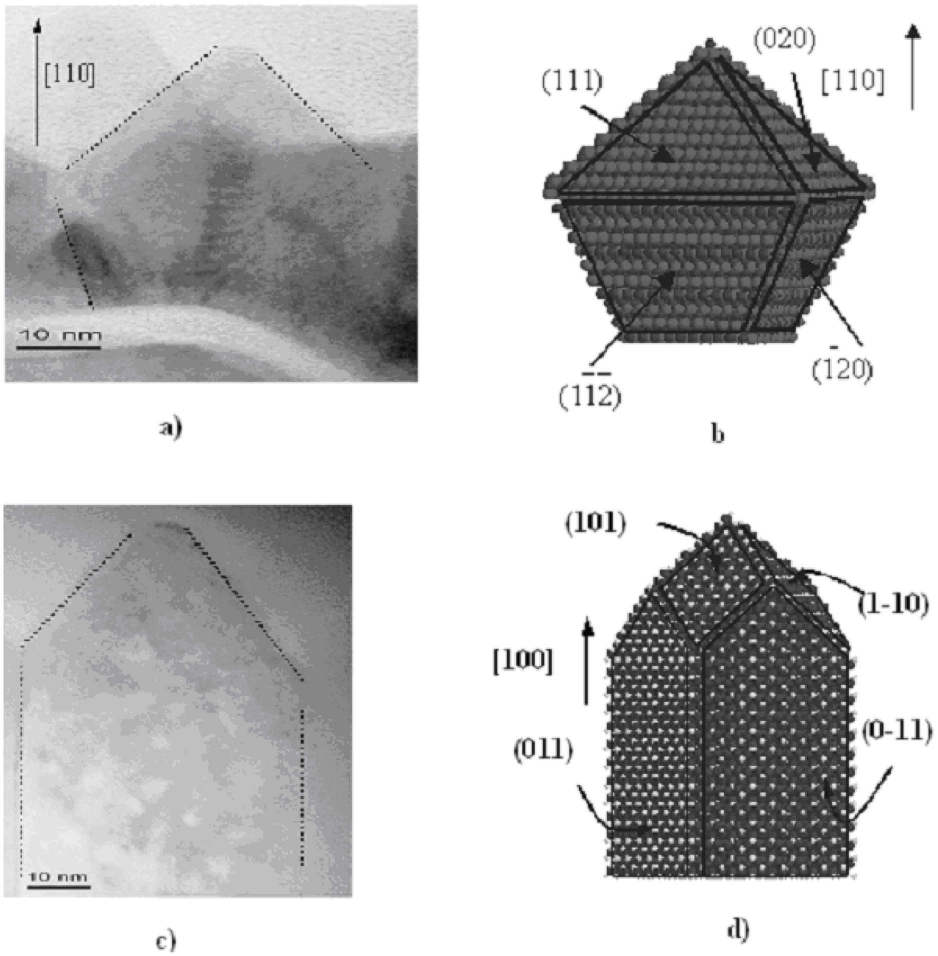

Fig. 5. Cross-section HRTEM micrographs (*a, c*) and a crystallographic model of SnO_2 nanocrystals (*b, d*) deposited by spray pyrolysis at a low temperature ($T_{\rm pyr} = 375$ °C) (*a, b*) and a medium temperature ($T_{\rm pyr} = 435$ °C) (*c, d*)

$(1\bar{1}0)$ planes, whereas the inferior facets are formed by the $(01\bar{1})$, $(0\bar{1}1)$, (011), and $(0\bar{1}\bar{1})$ planes.

So we have the direct confirmation that grains, which form the gas-sensing SnO_2-based matrix really can have different faceting. The observed differences in faceting may be associated with non-equilibrium conditions of the SnO_2 film deposition in the case of spray pyrolysis. The equilibrium morphology implies that the crystal face with the lowest surface energy will be the dominant face exposed. The growth morphology is based on the attachment energy, which assumes the kinetic control over the crystal growth. A crystal will grow in the direction of the face with the highest attachment energy, which will thereby create the adjacent faces. The slowest growing face, which has the lowest attachment energy, will dominate the morphology. Thus, besides the most stable (110) surface, the SnO_2 nanoparticles obtained in various technologies can be featured by the number of atomic faces with their peculiar electronic structures and the specific chemisorption and catalytic properties.

Note that SnO_2 films obtained by spray pyrolysis are featured by rather non-equilibrium conditions of their deposition and therefore their faceting differs from that of the films with the predomination of the most thermostable (110) surface. In the latter case of OH groups forming more deeply located acceptor-like energy levels in the band gap, their ensemble charge may be noticeable and reaction (3) may be accompanied by the release of electrons to the conduction band.

Taking into account the above-mentioned facts, we have performed a semi-empirical calculation of hydroxyl groups chemisorbed at the (110) and (011) faces of SnO_2.

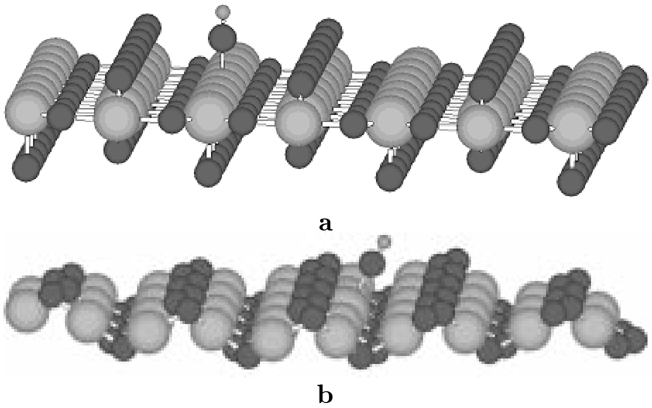

Fig. 6. Models of SnO_2, (*a*) — (110) and (*b*) — (101) surfaces with hydroxyl groups coordinated at 5-fold tin atoms. The lighter balls represent tin atoms and the darker balls do oxygen atoms

The corresponding clusters with OH groups attached to the Sn surface are shown in Fig. 6,*a* and 6,*b*. We have employed the semi-empirical PM3 method [22] which has proved to predict well enough the geometric structures and total energies in comparison with *ab initio* methods.

The results of the Mulliken population analysis demonstrate that the chemisorption of OH group on the (110) face is accompanied by the localization of a negative charge on it to a greater extent than that in the case of OH group chemisorbed on the (101) surface of SnO_2. This fact is in agreement with the above-made suggestion on the different reaction paths for the CO detection, which takes place in tin dioxide films deposited in various technological modes and therefore characterized by different grain habits and predominated atomic planes.

5. Conclusion

The role of orientation effects on the gas-sensing properties of nanocrystalline tin oxide sensors has been analyzed on the basis of microscopic studies of the grain habit. The wide possibilities of structural engineering in the optimization of tin oxide sensing properties have been demonstrated.

The proposed model considers the involving of hydroxyl groups in the reaction of CO catalytic oxidation in a humid atmosphere. The charge state of OH group depends essentially on its coordination at different surface sites. The different atomic faces, which predominate in SnO_2 crystallites formed in various technologies determine the charge of the ensemble of OH groups involved in the catalytic reaction and therefore affect the gas response to CO in the presence of water.

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ВПЛИВ СТРУКТУРНИХ ФАКТОРІВ НА ЧУТЛИВІСТЬ ДО CO ГАЗОВИХ СЕНСОРІВ НА ОСНОВІ SnO_2 У ВОЛОГІЙ АТМОСФЕРІ

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Резюме

Вплив орієнтаційних ефектів на газочутливі властивості двохокису олова досліджено на прикладі взаємодії CO з різноманітними поверхнями SnO_2 в присутності водяної пари. Полікристалічні шари SnO_2 з різною кристалографічною орієнтацією було одержано методом піролізу в різних технологічних режимах. Встановлено, що молекулярний кисень, гідроокисні групи та атомарний кисень визначають відповідно чутливість сенсорів на основі SnO_2 в температурних інтервалах 30—180 °C; 200—400 °C і вище за 450 °C. Зарядовий стан хемосорбованих гідроокисних груп визначається домінуючою кристалографічною поверхнею кристалітів. Введення різним чином заряджених OH-груп в реакцію каталітичного окислення CO визначає особливості газочутливих характеристик сенсорів, виготовлених в різних технологічних режимах.