UDC 546.814-31, 544.723, 621.315.592

S.V. Nagirnyak, T.A. Dontsova, I. M. Astrelin
National Technical University of Ukraine "KPI", Kyiv, Ukraine

ONE-DIMENSIONAL TIN (IV) OXIDE NANOSTRUCTURES AS GAS-SENSING MATERIALS

Background. Gas sensors based on SnO_2 are characterized by small size and low cost. However, its significant disadvantages are insufficient sensitivity, small selectivity and low stability. Therefore, the determination of basic parameters, a change that will create effective, highly sensitive and selective semiconductor sensors based on SnO_2 nanostructures, is extremely important.
Objective. The purpose of this paper is to establish the main parameters affecting the sensitivity, selectivity and stability of semiconductor sensors.
Methods. A critical review of recent scientific literature is done. Found that the usage of 1D tin (IV) oxide nanostructures (as pure and doped) will increase the sensitivity and selectivity of the metal oxide sensors due to high values of surface to volume ratio and the creation of active centers in relation to the detected gases.
Results. It was determined that the creation of efficient and sensitive semiconductor sensors requires the use of 1D SnO_2 nanostructures and their directed modification by various additives.
Conclusions. In terms of data presented in contemporary scientific literature, to create effective semiconductor tin (IV) oxide based sensors 3S parameters of these sensors need to be improved. From this point of view, 1D SnO_2 nanostructures deserve special attention due to the totality of their physical and chemical properties. Vapor transport method (method CVD) is enough effective for the synthesis of 1D nanostructures. It secures superior performance in conjunction with relative simplicity and availability. And this method allows us to obtain single-crystal nanostructures of controlled morphology. However, as of day there is no almost information on the impact of operational parameters of CVD synthesis on physico-chemical characteristics of obtained nanosized SnO_2. Therefore, the advanced study of scientific bases of purposeful synthesis and systematization of approach in the selection a dopant to increase selectivity of metal oxide gas sensors is the main task.
Keywords: semiconductor sensor; tin (IV) oxide; one-dimensional nanostructures; vapor transport method; additive.

Introduction

The present-day gas sensor devices can be categorized into three general groups depending on the technology of their use: spectroscopic, optical and solid-state. Spectroscopic and optical systems are quite expensive for everyday use and sometimes it is difficult to apply them in situ, for example as detectors of car engine exhaust. From this point of view, solid-state or so-called chemical gas sensors are the most attractive due to their fast response time, ease of implementation and low cost [1].

According to the operating principle and manufacturing technology distinguish electrochemical [2], catalytic (calorimeter) [3], semiconductor [4] and microelectronic sensors [5]. In recent literature, there is growing interest to semiconductor gas sensors due to their compact size and easy production.

Semiconductor sensors are usually manufactured on the basis of metal oxides, which conductivity varies depending on the type and concentration of gas. Strict requirements that apply to chemical gas sensors – high sensitivity and selectivity of the response, low power consumption and stable performance – cause constant search of ways to improve characteristics of semiconductor metal oxide based sensors.

It is found [6] that all semiconductor materials have sensory effect, but exactly group of semiconductor metal oxides, such as SnO_2, ZnO, In_2O_3, WO_3, differs record sensitivity and capable to detect of O_3, NO_x, Cl_2, ClO_2, CO_x, HCl microconcentrations in gas mixtures. To improve the sensory and performance characteristics of the sensitive layers based on these oxides the latest are doped by various additives (dopants) [7].

In order to characterize sensor performance a set of parameters is used. The most important of them are sensitivity, selectivity, response time, detection limit, stability and recovery time.

Despite the obvious advantages of gas sensors based on semiconducting metal oxides (small size, low power consumption, high sensitivity and low cost), these devices have small life time and low selectivity to target components in gas mixtures [8]. And recent studies [9] for enhancement the work of gas devices devoted improving these parameters and also sensitivity that is called "3S": Selectivity, Sensitivity, and Stability in the modern world-wide literature [10].

The sensitivity is highly dependent on film porosity, film thickness, operating temperature, presence of additives and crystallite size. The increasing of selectivity of semiconductor layers of

gas sensors is possible due to doping by various catalytic additives or modifying the surface of the sensitive layers for better absorption of target component from gas mixture [11]. Previous heat treatment at temperatures above the working temperature of sensor for 1–8 hours promotes the increase in stability of sensitive layers [12]. To create tiny sensors with minimal power consumption and high "3S" characteristics it is necessary to ensure implementation of several conditions, among which the main ones are the following:

1) sensitive layer must have high adsorption properties with respect to oxygen and target components of the gas mixture at low temperatures;

2) electrical circuit for monitoring sensor parameters must be perfect.

Functional properties of metal oxides depend on many chemical and structural characteristics such as chemical composition, various kinds of deficiencies, morphology, particle size, surface to volume ratio, etc. By varying either of these characteristics, the electrical, optical, magnetic, and chemical properties can be regulated, giving the possibility of fabricating smart devices.

It is known that the reversible chemisorption of reactive gases on the surface of the oxide semiconductor is accompanied by reversible changes in conductivity. Depending on type of determinate impurity (electron acceptor or electron donor) and conduction type (*n*- or *p*-type), the resistance of the sensitive layer of the sensor is increased or decreased. Oxidizing gases or electron acceptors such as NO_2 produce a decrease in the conductance of *n*-type semiconducting materials (i.e., electrons are the major carriers, such as ZnO, SnO_2, In_2O_3) and an increase in the conductance of *p*-type semiconducting materials (i.e., holes are the major carriers, such as CuO); reducing gases or electron donors such as H_2S, CO, H_2 and water vapor act in a reverse manner [13, 14].

Metal oxides SnO_2, ZnO, In_2O_3, WO_3, CdO and TiO_2 are wide-bandgap *n*-type semiconductors and the most frequently used as a sensitive material for the gas sensors. Tin (IV) oxide is the most studied and popular in literature. SnO_2 belongs to a class of materials that combine high electrical conductivity (*n*-type semiconductor with a band gap 3.6 eV at 300 K) with a number of unique functional properties – a low electrical resistance, high transparence in the visible region, high chemical stability, mechanical strength, heat resistance, high adhesion to glass and other substrates [15, 16].

Gas sensors based on tin (IV) oxide are widely used as unique threshold sensors that react to the presence of harmful for human health or hazardous gases (such as CO, NO, NO_2, H_2, etc.) [7]. However, SnO_2 based sensory materials have certain drawbacks, which include deficient sensitivity, small selectivity and low stability. Decreasing the SnO_2 crystallite size and/or adding dopants (usually precious metals or other metal oxides) helps to overcome these deficiencies [17].

Formulation of the problem

The purpose of this paper is to establish the main parameters affecting the sensitivity, selectivity and stability of semiconductor sensors.

SnO_2 nanostructures as gas-sensing materials

Nanocrystalline materials are characterized by the highest values of the sensor signal due to the high surface to volume ratio, and thus a higher adsorption capacity [14, 17]. Tin (IV) oxide particles diameters of 10–30 nm are capable to adsorb much more molecules of various gases compared with solid materials through more extensive structure of their surface [18]. It is well known that the sensitivity of sensor based on tin (IV) oxide is directly related to the SnO_2 particle and crystallite size and particle connections.

Figures 1 and 2 show the dependence of resistance and sensitivity of sensor as a function of the SnO_2 crystallite size on the results of work [19]. As seen in Fig. 1, there dramatic increase in the sensor resistance for crystallite sizes less than ~6 nm.

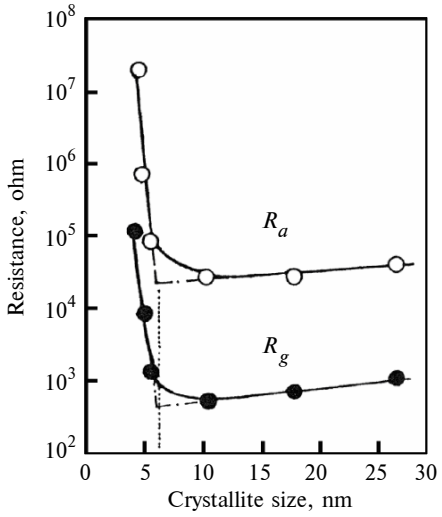

Fig. 1. Experimental data showing the effect of SnO_2 crystallite size on sensor resistance for undoped SnO_2 generated using sol-gel synthesis processing: R_a – the resistance of the sensor in air, ohm; R_g – the resistance of the sensor in the test gas, ohm [19]

A similar dependences obtained for the measurement of sensitivity as a function of the SnO_2 crystallite size of tin (IV) oxide based sensor to 800 ppm of CO and H_2 in the air (Fig. 2).

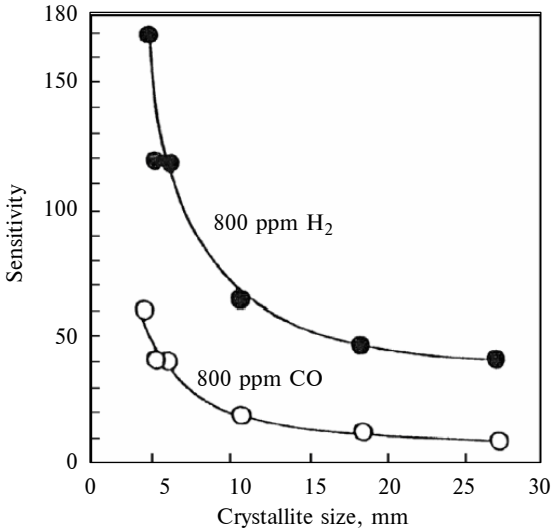

Fig. 2. Experimental data showing the effect of SnO_2 crystallite size on sensor sensitivity for undoped SnO_2 generated using sol-gel synthesis processing. Data are shown for sensor response to 800 ppm of H_2 in air, and 800 ppm of CO in air at a sensor operating temperature of 300 °C [19]

Besides the crystallite size and particle connection, surface to volume ratio also has a major impact on sensor sensitivity [20], thus one-dimensional (1D) nanostructures deserve special attention [17].

One-dimensional (1D) metal-oxide nanostructures are ideal systems for exploring a large number of novel phenomena at the nanoscale and investigating size and dimensionality dependence of nanostructure properties for potential applications. 1D nanomaterials are also expected to play an important role as both interconnects and functional units in fabricating electronic, optoelectronic, electrochemical, and electromechanical devices with nanoscale dimensions [21].

Low-dimensional nanoscale materials, with their large surface areas and possible quantum confinement effects, exhibit superior mechanical, thermal, chemical, electrical, and optical properties distinct from their bulk counterparts. The manipulation of well-controlled precise dimensions, crystallinity, and composition of 1D nanostructures gives rise to unique properties, thus enabling a variety of applications that would not be possible with materials with bulk dimensionality [21]. Among the variety of 1D nanostructures, tin (IV) oxide semiconductor nanostructures is particularly interesting because of their promising application in optoelectronic and electronic devices due to good conductivity and transparency in the visible light region.

1D nanostructures of SnO_2 have the following advantages as sensitive elements of gas sensors: a morphology of one-dimensional nanostructured SnO_2 materials provides high value of surface to volume ratio while maintaining enough of their chemical and thermal stability with minimum power consumption and low weight. High values of surface to volume ratio indicate that much of atoms (or molecules) concentrated on the surface. Thus, the reaction between the target gas and reactive chemisorbed molecules (O^-, O^{2-}, H^+ and OH^-) are possible already at low temperatures.

Typical 1D nanostructures are nanowires, nonotubes, nanorods, nanoribbons and others. Synthesis and assembly of SnO_2 1D nanostructures with special morphologies, shapes, and compositions have attracted great interests very recently because they process unique properties and functionalities that are not accessible in the single-component materials, due to the combination of material classes such as metals, metal oxides, semiconductors, and polymers [21].

1D SnO_2 nanostructures synthesis methods. Development of synthesis techniques of 1D nanostructures is one of the main directions in the field of nanoscience and nanotechnology [22]. The method of synthesis influences the properties of obtained powder, particularly the shape, size, crystal morphology and the degree of crystallinity. The most common methods to obtain 1D metal oxide nanostructures are hydrothermal synthesis, sol-gel method, template synthesis and vapor transport method (called method CVD).

Hydrothermal synthesis involves use of water as a solvent at elevated temperatures (usually to 300 °C) and pressures in a closed system. Sol-gel method implemented by hydrolysis and subsequent polycondensation of SnO_2 precursors in water and aqueous-alcoholic environments [23]. Template synthesis is the technique for the controlled synthesis of nanostructured materials under the influence of various factors spatial constraints due to a kind of pattern – template. In case of 1D nanostructures template provides channels for guiding the growth or deposition of materials in 1D form [24].

Vapor transport method (method CVD) is a simple process in which condensed or powder source material is vaporized at an elevated temperatures (1300 °C) and the resultant vapor phase condenses under certain conditions (temperature,

pressure, atmosphere, substrate, etc.) to form the desire product [25]. This method deserves special attention because it secures superior performance in conjunction with relative simplicity and availability. In addition, this method allows to obtain single crystals of SnO_2 controlled and varied morphology with a high degree of crystallinity [25].

Fabrication of 1D SnO_2 nanostructures using vapor transport method. The formation of tin (IV) oxide particles by CVD method can occur by two mechanisms: "vapor–liquid–solid" (VLS) and "vapor–solid" (VS). Often in the literature, these mechanisms take one for the other. Consider their differences and peculiarities.

According to the VLS growth mechanism, a droplet of liquid metal guides the wire-like crystal growth. The droplet surface has a higher sticking coefficient and is therefore a preferred absorption site for incoming vapor reactants. As the liquid droplet becomes supersaturated with the vapor reactants, whisker growth will occur by means of a precipitation process of reactants. The role of droplet in the crystal growth process is analogous to a catalyst in a chemical reaction. That's why VLS mechanism also called catalysis growth [25]. Droplet size of catalyst can be controlled by varying the film thickness of the catalyst on the substrate. In general, the thinner the film, the smaller drops are formed during heating, leading to growth of nanowires with smaller diameter.

SnO_2 crystal formation on the VS mechanism occurs due to the reaction of disproportionation:

$$2SnO = Sn + SnO_2,$$

that implemented without addition a catalyst in the reaction zone. This reaction attracts attention due to the greater simplicity of the process compared to the catalytic growth and the possibility of obtaining tin (IV) oxide structures with diverse morphology. The morphology of the obtained particles can significantly change by changing the synthesis conditions of SnO_2. However, the influence of synthesis parameters of SnO_2 by this method on the morphology of the particles almost not investigated and barely illuminated in literature. But, undoubtedly, in this case the growth of 1D SnO_2 nanostructures can take place after the formation of metallic tin, which serves as a center of crystallization of one-dimensional tin (IV) oxide from gas phase. Thereby the VS mechanism transforms into the VLS mechanism. Thus, for the synthesis of 1D SnO_2 nanostructures is necessary to identify the conditions under which the VS mechanism converts into VLS mechanism and define parameters that will allow to control the morphology and size of the obtained particles. There are several processing parameters, such as evaporation and crystallization temperature, pressure, type of carrier gas and its flow rate, duration of the process, that impact the morphology of the particles. The choice of temperature mainly depends on volatility of the source material. Usually, it is lower than the melting point of the source material. The pressure is determined according to the evaporation rate or vapor pressure of source material. Duration of evaporation process affects not only the amount but also the size and the morphology of the product (especially in the case of the VS mechanism). Oxygen in the vapor phase also influences the formation of SnO_2 particles with a specific morphology.

Mechanism for gas sensing in metal oxide gas sensors

Sensitivity mechanism of semiconducting metal oxide gas sensors is due to interaction between the sensor surface and surrounding gases. Oxygen from the air is adsorbed onto the surface of sensor. Electrons from the surface region are transferred to the adsorbed oxygen, leading to the formation of an electron-depleted region, also called space-charge layer, is an area of high resistance and the core region of the particle, where electron densities are high, is an area of relatively low resistance. So, on the surface of semiconductor sensor there are both chemical and electrical processes [17].

In general there are following stages in the mechanism for detecting an analyte in air by sensitive semiconductor material: 1) oxygen adsorption on the surface; 2) transfer of the electron; 3) adsorption of analyte; 4) chemical reaction; 5) electron transfer to metal oxide material; 6) desorption of reaction products [26].

The form of the adsorbed oxygen (either molecular o atomic) depends on the temperature of the sensor. Depending on the operating temperature may occur following reaction [9]:

$$O_{2\,gas} + e^- \rightarrow O^-_{2\,ads} \quad (80–150\ ^\circ C),$$

$$O^-_{2\,ads} + e^- \rightarrow 2\,O^-_{ads} \quad (150–260\ ^\circ C),$$

$$O^-_{ads} + e^- \rightarrow O^{2-}_{ads} \quad (300–500\ ^\circ C).$$

Detectable gas adsorbed on the SnO_2 surface and reacted with chemisorbed oxygen anions. A

chemical reaction with the release of electrons occurs as a result:

$$Z_{O^-_{ads}}(\ ) + O^-_{ads} \rightarrow Z(O_{ads}) + e^- .$$

As a result, the concentration of electrons increases, the thickness of the space charge reduces, and therefore the electrical conductivity of semiconductors rises [17].

The general steps involved in sensor response upon exposure to air and to a gas, are shown in Fig. 3.

The conductivity of sensing layer (σ) in the presence of the investigated gas depends on the concentration of the latest according to the relation [27]:

$$\sigma \sim \sqrt{P_i} \sim \sqrt{C} ,$$

where is P_i – partial pressure of the investigated gas, C – its concentration.

Since tin (IV) oxide is an *n*-type semiconductor, the sensor conductivity increases in the presence of a reducing gases (such as CO, H_2 and others), and decreases in the presence of an oxidizing gases (such as O_2) [17].

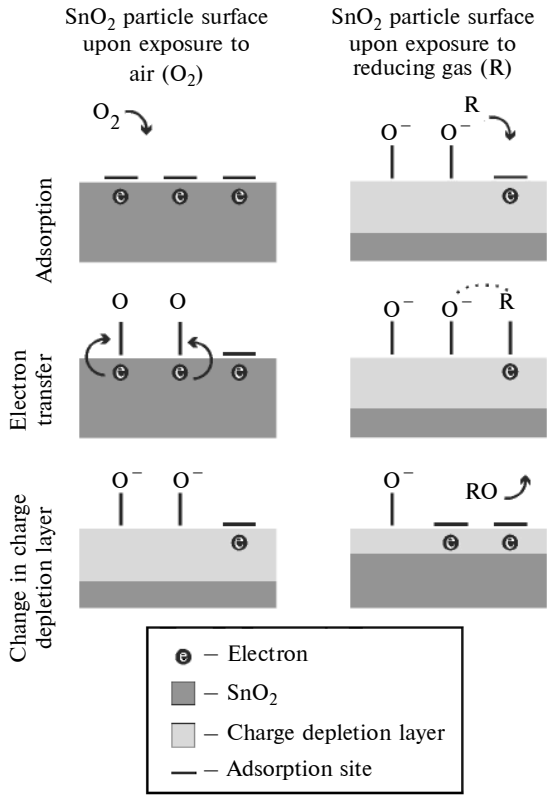

Fig. 3. Schematics indicating the mechanisms leading to SnO_2 sensor response to analyte [17]

An extremely important characteristic of the gas sensor, which determines its stability and lifetime, is reversibility of its condition at cyclic changes of environment. Based on this, the chemical interaction of the semiconductor oxide surface with gas phase can be schematically represented as a cyclical process, as shown in Fig. 4 [9].

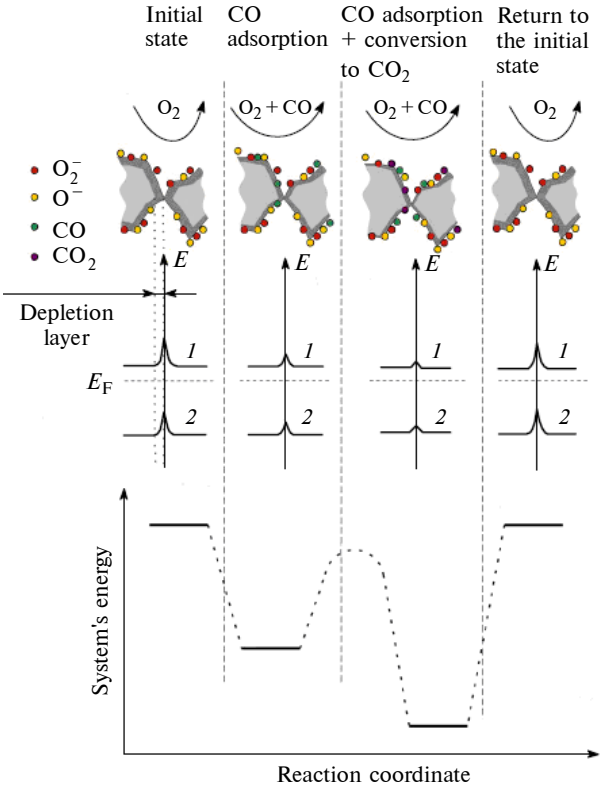

Fig. 4. Scheme of interaction of the analyte (CO) with the SnO_2 surface and energy change of the system: *1* – degree of curvature of the conduction band of the semiconductor, *2* – degree of curvature of its valence band [9]

Mechanism for gas sensing in doped SnO_2 sensors

Commercial gas sensors based on SnO_2 do not have sufficient sensitivity and selectivity of response that restricts the use of SnO_2 in warning systems. Low sensitivity of SnO_2 is caused by relatively small amount of available locations for oxygen adsorption due to potential barriers on the particle surface [28]. The reason of the low selectivity of sensor materials based on SnO_2 is the inability to distinguish the contribution of a particular type of molecules in integral conductivity change of sensitive material. The source of the nonselectivity of sensor materials based on nanocrystalline SnO_2 is the presence of oxygen vacancies on the surface [9] which are active centers and allows to

simultaneously interact with different molecules from gas phase.

Different physical and chemical approaches use to improve the selectivity of gas sensitive semiconductor materials: application of semipermeable membranes [29], catalytic membranes on the surface of sensitive layers [30], dynamic temperature conditions of the sensors [31] and chemical modification of the surface of sensor material [9]. Chemical modification of the surface of sensor material is the most promising method of increasing of selectivity. It provides for the creation of new active centers on the surface (so-called "receptor sensitivity") in relation to certain gases by applying catalytic clusters or modifying the microstructure of the material. Usually, the additive loadings required for improved sensor performance are low (typically less than 10 % mass or mole basis) [17]. As modifiers can use clusters of Au, PdO_x, PtO_x, RuO_x, and oxides of d-elements: CuO, NiO, Fe_2O_3, MoO_3, V_2O_3, etc. [9].

Additives can have several effects on the SnO_2 properties important to gas sensing applications, including inhibiting SnO_2 grain growth, modifying the electron Debye length and modifying the gas-surface interactions. Thus, each dopant affects the particle size of SnO_2 in varying degrees and possibly through different mechanisms.

To describe the chemical and physical processes of the interaction of gas with a surface of SnO_2 with additives we use two mechanisms: electronic and catalytic. In the case of the electronic mechanism (so-called Fermi energy control mechanism), reducing gas reacts with the surface of the metal additive. As a result electron released and transported to SnO_2. Changes in the electron density near the surface of SnO_2 lead to a decrease in resistance. For catalytic mechanism, also known as chemical, metal dopant acts as catalyst from which compressed gas is transported to the surface of SnO_2, where reacts with absorbed oxygen. And released electron leads to a decrease in resistance. The main difference between the electronic and catalytic mechanism is to transport particles between the additive and SnO_2. In the electronic model takes place the transfer of electrons; in the chemical model – transportation of atoms. Fig. 5 schematically shows both the detection mechanisms on metal oxide doped semiconductor.

As seen in Fig. 5, in chemical scheme reaction takes place on the surface of oxide. In electronic mechanism reaction occurs on the surface of dopant and metal oxide used as material for measuring of changes in electric signal.

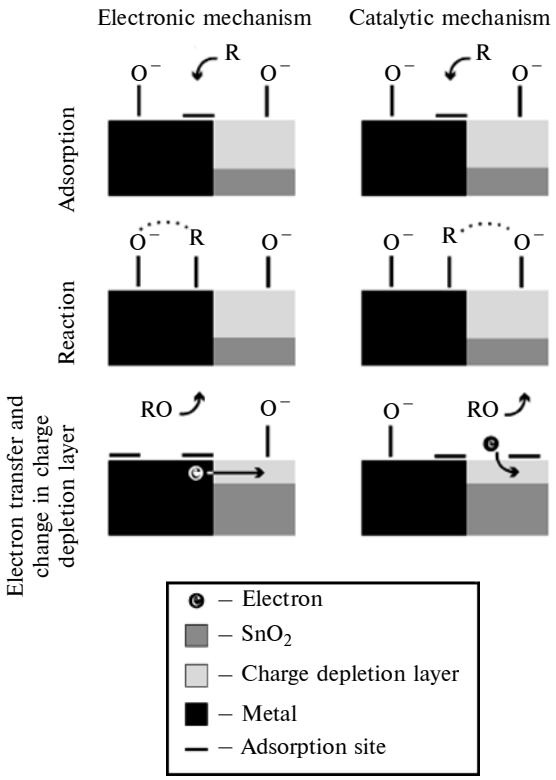

Fig. 5. Schematic indicating the general steps involved in the electronic and catalytic mechanisms active in SnO_2 sensors with additives [17]

The temperature influence on the sensor response of sensitive layers based on SnO_2

Since all stages of the interaction of oxygen (so-called sensitizing gas) with a surface of sensitive layer of tin (IV) oxide based sensor occurring with certain thermal effects, its sensitivity to different gases depends on the temperature [31]. Consider the effect of temperature on sensitivity of metal oxide sensors.

At first oxygen interacts with the active centers of tin (IV) oxide surface:

$$Z_{O^-_{ads}}(\,) + O^-_{ads} \rightarrow Z(O_{ads}) + \Delta H_1,$$

where ΔH_1 – adsorption heat of neutral form of adsorbed oxygen.

Then physically sorbed oxygen interacts with the electron:

$$Z(O_{ads}) + e^- \rightarrow Z(O^-_{ads}) + \Delta H_2,$$

where ΔH_2 – formation heat of a charged form of adsorbed oxygen.

The condition of the formation of $Z(O_{ads})$ is $\Delta H_1 \geq kT_0$, where T_0 – detection temperature.

Then, the reducing gas G is adsorbed on the surface and reacts with chemisorbed oxygen $Z(O^-_{ads})$:

$$Z_G(\ ) + G \rightarrow Z_G(G) + \Delta H_3,$$

$$Z(O^-_{ads}) + Z_G(G) \rightarrow Z(B^-) + Z_G(\ ) + \Delta H_4,$$

where $Z_G(\ )$ – the G adsorption center.

The condition of the formation of $Z_G(G)$ is $\Delta H_3 > kT_0$.

Chemisorbed reaction product $B(g)$ may be characterized by a lower placement of energy level relative to the bottom of the conduction band compared to $Z(O^-_{ads})$. This leads to the emission of an electron to the conduction band and according to the reaction:

$$Z(B^-) + \Delta H_5 \rightarrow Z(B) + e^-, \qquad (1)$$

the prerequisite course of which is $|\Delta H_5| < |\Delta H_2|$. The final stage of the whole process is the desorption of a product:

$$Z(B) + \Delta H_6 \rightarrow Z(\ ) + B(g),$$

that cause regeneration of free adsorption centers of sensitizing gas.

The overall reaction of detection:

$$G + Z(O^-_{ads}) + \Delta H_5 + \Delta H_6 \rightarrow$$

$$e^- + Z(\ ) + B(g) + \Delta H_3 + \Delta H_4. \qquad (2)$$

As seen from the equation (1), one electron returns to the conduction band at every act of formation of vacancy for sensitizer adsorption. Since adsorption centers $Z_G(\ )$ is not included in (2), the energy does not depend on the mechanism of interaction of gas with chemisorbed oxygen.

However, this model explains the influence of gas on the electrical conductivity only in the presence of oxygen in the environment. The narrow temperature range, in which there is a sensitivity of adsorbent to determined gas, may be due to the fact that the desorption of reaction products will not occur at low operating temperature T_0, therefore regeneration of oxygen adsorption centers will be impossible. If T_0 is large enough oxygen adsorption as well as adsorption of reducing gas becomes impossible.

Conclusions

In terms of data presented in contemporary scientific literature, to create effective semiconductor tin (IV) oxide based sensors 3S parameters of these sensors need to be improved. From this point of view, 1D SnO_2 nanostructures deserve special attention due to the totality of their physical and chemical properties. Vapor transport method (method CVD) is enough effective for the synthesis of 1D nanostructures. It secures superior performance in conjunction with relative simplicity and availability. And this method allows us to obtain single-crystal nanostructures of controlled morphology. However, as of day there is no almost information on the impact of operational parameters of CVD synthesis on physico-chemical characteristics of obtained nanosized SnO_2. Therefore, the advanced study of scientific bases of purposeful synthesis and systematization of approach in the selection a dopant to increase selectivity of metal oxide gas sensors is the main task.

List of literature

1. *Review* of chemical sensors for in-situ monitoring of volatile contaminants / C.K. Ho, M.T. Itamura, M. Kelley, R.C. Hughes: Report SAND2001-0642. – Albuquerque NM: Sandia National Laboratories, 2001. – 34 p. doi: 10.2172/780299.
2. *Xu Y., Zhou X., Surensen O.T.* Oxygen sensors based on semiconducting metal oxides: an overview // Sensors and Actuators B. – 2000. – **65**. – P. 2–4. doi: 10.1016/S0925-4005(99)00421-9.
3. *Menil F., Coillard V., Lucat C.* Critical review of nitrogen monoxide sensors for exhaust gases of lean burn engines // Sensors and Actuators B. – 2000. – **67**. – P. 1–23. doi: 10.1016/S0925-4005(00)00401-9.
4. *Surface* chemistry prototypical bulk II–VI and III–V semiconductors and implications for chemical sensing / F. Seker, K. Meeker, T Kuech., A.B. Ellis // Chem. Rev. – 2000. – **100**, № 7. – P. 2505–2536. doi**:** 10.1021/cr980093r.
5. *High* temperature catalytic metal field effect transistors for industrial applications / A. Lloyd Spetz, P. Tobias, L. Uneus et al. // Sensors and Actuators B. – 2000. – **70**. – P. 67–76. doi: 10.1016/S0925-4005(00)00559-1.
6. *Choopun S., Hongsith N., Wongrat E.* Metal-oxide nanowires for gas sensors // Recent Advances. – 2012. – **21**, № 5. – P. 3–24. doi: 10.5772/54385.
7. *Abdullah M.M., Suhail M.H., Abbas S.I.* Fabrication and testing of SnO_2 thin films as a gas sensor // Archives Appl. Sci. Res. – 2012 – **4**, № 3. – P. 1279–1288.

8. *Warren B.E.* X-ray Diffraction. – New York: Dover Publications, Inc., 1990. – 400 p.
9. *Кривецкий В.В., Румнцева М.Н., Гаськов А.М.* Химическая модификация нанокристаллического диоксида олова для селективных газовых сенсоров // Успехи химии. – 2013. – **82**, № 10. – С. 917–941. doi: 10.1070/RC2013v082n10ABEH004366.
10. *Prudenziati M., Hormadaly J.* Printed Films: Materials Science and Applications in Sensors, Electronics and Photonics. – Elsevier, 2012. – 608 p.
11. *Influence* of the catalytic introduction procedure on the nano-SnO_2 gas sensor performances. Where and how stay the catalytic atoms? / A. Cabot, A. Diéguez, A. Romano-Rodríguez et al. // Sensors and Actuators B. – 2001. – **79**. – P. 98–106. doi: 10.1016/S0925-4005(01)00854-1.
12. *Electroless* addition of catalytic Pd to SnO_2 nanopowders / R. Díaz, J. Arbiol, A. Cirera et al. // Chem. Mater. – 2011. – **13**, № 11. – P. 4362–4366. doi**:** 10.1021/cm011131h.
13. *Huang J., Wan Q.* Gas sensors based on semiconducting metal oxide one-dimensional nanostructures // Sensors. – 2009. – **9**. – P. 9903–9924. doi: 10.3390/s91209903.
14. *Synthesis* and properties of tin (IV) oxide obtained by chemical vapor deposition method / S.V. Nagirnyak, V.A. Lutz, T.A. Dontsova et al. // NanoScale Res. Lett. – 2015. – **10**. – P. 1–14.
15. *Астафьева Л.В., Скорняков Г.П.* Установка для получения пленки двуокиси олова // ПТЭ. – 1980. – № 5. – С. 235–237.
16. *Синтез* і характеристика нанодисперсних порошків оксиду стануму (IV) з оксалату стануму (II) / С.В. Нагірняк, Т.А. Донцова, І.М. Астрелін та ін. // Наукові вісті НТУУ "КПІ". – 2012. – № 2. – С. 151–155.
17. *Nanosturctured* tin dioxide materials for gas sensor applications / T.A. Miller, S.D. Bakrania, C. Perez, M.S. Wooldridge // Functional Nanomaterials. – 2006. – **30**. – P. 453–476.
18. *Петрук В.Г., Кравец А.Г.* Сенсоры угарного газа CO на основе наночастиц SnO_x // Журнал технической физики. – 2007. – **77**, вып. 2. – С. 86–90.
19. *Yamazoe N.* New approaches for improving semiconductor gas sensors // Sensors and actuators, B. Chemical. – 1991. – **5**. – P. 7–19. doi: 10.1016/0925-4005(91)80213-4.
20. *Structural* study of ultrathin metal films on TiO_2 using LEED, ARXPS and MEED / J.-M. Pan, B.L. Maschhoff, U. Diebold, T.E. Madey // Surface Sci. – 1993. – **291**, is. 3. – P. 381–394. doi: 10.1016/0039-6028(93)90455-S.
21. *Pan J., Hao S., Sanjay M.* One-dimensional SnO_2 nanostructures: synthesis and application // J. Nanotechnol. – 2012. – **2012**. – 12 p. doi: 10.1155/2012/917320
22. *One-chip* fabrication of SnO_2-nanowire gas sensor: the effect of growth time on sensor performance / L.V. Thong, N.D. Hoa, D.T.T. Le et al. // Sensors and actuators, B. Chemical. – 2010. – **146**, is. 1. – P. 361–367. doi: 10.1016/j.snb.2010.02.054.
23. *Stabilization* of nanoscale tin (IV) oxide on the surface of carbon nanotubes / T. Dontsova, I. Ivanenko, I. Astrelin, S. Nagirnyak // J. Electric. Eng. – 2014. – **2**, no. 1. – P. 34–38.
24. *Cao G., Wang Y.* Nanostructures and Nanomaterials: Synthesis, Properties and Applications. – Singapore: World Scientific Publisher Co., 2011. – 581 p.
25. *Zu Rong Dai, Pan Zheng Wei, Wang Zhong L.* Novel nanosturctures of functional oxides synthesized by thermal evaporation // Adv. Functional Mater. – 2003. – **13**. – P. 9–24. doi: 10.1002/adfm.200390013.
26. *Механизмы* сенсорного эффекта в кондуктометрических датчиках на основе диоксида олова для детектирования газов-восстановителей / В.Ф. Громов, Г.Н. Герасимов, Т.В. Белышева, Л.И. Трахтенберг // Ж. Рос. хим. об-ва им. Д.И. Менделеева. – 2008. – Вып. 5 – С. 80–87.
27. *Петров В.В., Королев А.Н.* Наноразмерные оксидные материалы для сенсоров газов. – Таганрог: Изд-во ТТИ ЮФУ. – 2008. – 153 с.
28. *Morrison S.R.* Selectivity in semiconductor gas sensors // Sensors and Actuators B. – 1987. – **12**. – P. 425–440. doi: 10.1016/0250-6874(87)80061-6.
29. *Low* temperature deposition of glassmembranes for gas sensors / A. Althainza, A. Dahlke, J. Goschnick, H.J. Ache // Thin Sol Films. – 1994. – **241**. – P. 344–347. doi: 10.1016/0040-6090(94)90454-5.
30. *Ryzhikov A., Labeau M., Gaskov A.* Al_2O_3 (M = Pt, Ru) catalytic membranes for selective semiconductor gas sensors // Sensors and Actuators B. – 2005. – **109**. – P. 91–96. doi: 10.1016/j.snb.2005.03.004.
31. *Давыдов С.Ю., Мошников В.А., Томаев В.В.* Адсорбционные явления в поликристаллических полупроводниковых сенсорах. – СПб: [б. и.], 1998. – 56 с.

References

1. K. Ho Clifford *et al.*, "Review of chemical sensors for in-situ monitoring of volatile contaminants", Sandia National Laboratories, Albuquerque NM, Rep. SAND2001-0642, 2001. doi: 10.2172/780299.

2. Yulong Xu *et al.*, "Oxygen sensors based on semiconducting metal oxides: an overeview", *Sensors and Actuators B*, vol. 65, pp. 2–4, 2000. doi: 10.1016/S0925-4005(99)00421-9.
3. F. Menil *et al.*, "Critical review of nitrogen monoxide sensors for exhaust gases of lean burn engines", *Sensors and Actuators B*, vol. 67, pp. 1–23, 2000. doi: 10.1016/S0925-4005(00)00401-9.
4. F. Seker *et al.*, "Surface chemistry prototypical bulk II–VI and III–V semiconductors and implications for chemical sensing", *Chem. Rev*, vol. 100, no. 7, pp. 2505–2536, 2000. doi**:** 10.1021/cr980093r.
5. A. Lloyd Spetz *et al.*, "High temperature catalytic metal field effect transistors for industrial applications", *Sensors and Actuators B*, vol. 70, pp. 67–76, 2000. doi: 10.1016/S0925-4005(00)00559-1.
6. S. Choopun *et al.*, "Metal-oxide nanowires for gas sensors", *Recent Advances*, vol. 21, no. 5, pp. 3–24, 2012. doi: 10.5772/54385.
7. M.M. Abdullah *et al.*, "Fabrication and testing of SnO_2 thin films as a gas sensor", *Archives Appl. Sci. Res.*, vol. 4, no. 3, pp. 1279–1288, 2012.
8. B.E. Warren, *X-ray Diffraction*. New York: Dover Publications, Inc., 1990, 400 p.
9. V.V. Kryvetskiy *et al.*, "Chemical modification of nanocrystalline tin dioxide for selective gas sensors", *Uspehi Himii*, vol. 82, no. 10, pp. 917–941, 2013 (in Russian). doi: 10.1070/RC2013v082n10ABEH004366.
10. M. Prudenziati and J. Hormadaly, *Printed Films: Materials Science and Applications in Sensors, Electronics and Photonics*. Elsevier, 2012, 608 p.
11. A. Cabot *et al.*, "Influence of the catalytic introduction procedure on the nano-SnO_2 gas sensor performances. Where and how stay the catalytic atoms?", *Sensors and Actuators B*, vol. 79, pp. 98–106, 2001. doi: 10.1016/S0925-4005(01)00854-1.
12. R. Dнaz *et al.* "Electroless addition of catalytic Pd to SnO_2 nanopowders", *Chem. Mater*, vol. 13, no. 11, pp. 4362–4366, 2011. doi**:** 10.1021/cm011131h.
13. J. Huang *et al.*, "Gas sensors based on semiconducting metal oxide one-dimensional nanostructures", *Sensors*, vol. 9, pp. 9903–9924, 2009. doi: 10.3390/s91209903.
14. S.V. Nagirnyak *et al.*, "Synthesis and properties of tin (IV) oxide obtained by CVD method", *NanoScale Res. Lett.*, vol. 10, pp. 1–14, 2015.
15. L.V. Astafieva *et al.*, "An apparatus for manufacturing a film of tin dioxide", *Pribory i Tehnika Jeksperimenta*, no. 5, pp. 235–237, 1980 (in Russian).
16. S.V. Nagirnyak *et al.*, "Synthesis and Characterization of Nanodispersed Powders of Tin Oxide (IV) from Tin Oxalate (II)", *Naukovi Visti NTUU KPI*, no. 2, pp. 151–155, 2012 (in Ukrainian).
17. T.A. Miller *et al.*, "Nanosturctured tin dioxide materials for gas sensor applications", *Functional Nanomaterials*, vol. 30, pp. 453–476, 2006.
18. V.G. Petruk *et al.*, "Carbon monoxide CO sensors based on SnO_x nanoparticles", *Zhurnal Tehnicheskoj Fiziki*, vol. 77, is. 2, pp. 86–90, 2007 (in Russian).
19. N. Yamazoe, "New approaches for improving semiconductor gas sensors", *Sensors and Actuators, B. Chemical*, vol. 5, pp. 7–19, 1991. doi: 10.1016/0925-4005(91)80213-4.
20. J.-M. Pan *et al.*, "Structural study of ultrathin metal films on TiO_2 using LEED, ARXPS and MEED", *Surface Sci.*, vol. 291, is. 3, pp. 381–394, 1993. doi: 10.1016/0039-6028(93)90455-S.
21. J. Pan *et al.*, "One dimensional SnO_2 nanostructures: synthesis and application", *J. Nanotechnol.*, vol. 2012, 12 p., 2012. doi: 10.1155/2012/917320.
22. L.V. Thong *et al.*, "One-chip fabrication of SnO_2-nanowire gas sensor: the effect of growth time on sensor performance", *Sensors and Fctuators, B. Chemical*, vol. 146, is. 1, pp. 361–367, 2010. doi: 10.1016/j.snb.2010.02.054.
23. T. Dontsova *et al.*, "Stabilization of nanoscale tin (IV) oxide on the surface of carbon nanotubes", *J. Electric. Eng.*, vol. 2, no. 1, pp. 34–38, 2014.
24. G. Cao and Y. Wang, *Nanostructures and Nanomaterials: Synthesis, Properties and Applications*. Singapore: World Scientific Publisher Co., 2011, 581 p.
25. Dai Zu Rong *et al.*, "Novel nanosturctures of functional oxides synthesized by thermal evaporation", *Adv. Functional Mater.*, vol. 13, pp. 9–24, 2003. doi: 10.1002/adfm.200390013.
26. V.F. Gromov *et al.*, "Mechanisms for gas sensing in the tin dioxide based conductometric sensors to detect reducing gases", *Zhurnal Rossijskogo Himicheskogo Obshhestva im. D.I. Mendeleeva*, vol. 5, pp. 80–87, 2008 (in Russian).
27. V.V. Petrov and A.N. Koroljov, *Nanosized Oxide Materials for Gas Sensors*. Taganrog, Russia: Publishing house TTI SFU, 2008, 153 p. (in Russian).
28. S.R. Morrison, "Selectivity in semiconductor gas sensors", *Sensors and Actuators B*, vol. 12, pp. 425–440, 1987. doi: 10.1016/0250-6874(87)80061-6.

29. A. Althainza *et al.*, "Low temperature deposition of glassmembranes for gas sensors", *Thin Sol Films*, vol. 241, pp. 344–347, 1994. doi: 10.1016/0040-6090(94)90454-5.
30. A. Ryzhikov *et al.*, "Al_2O_3 (M = Pt, Ru) catalytic membranes for selective semiconductor gas sensors", *Sensors and Actuators B*, vol. 109, pp. 91–96, 2005. doi: 10.1016/j.snb.2005.03.004.
31. S.Y. Davydov et al., *Adsorption Phenomena in Polycrystalline Semiconductor Sensors*. St. Petersburg, Russia, 1998, 56 p. (in Russian).

С.В. Нагірняк, Т.А. Донцова, І.М. Астрелін

ОДНОВИМІРНІ НАНОСТРУКТУРИ СТАНУМУ (IV) ОКСИДУ ЯК ЧУТЛИВИЙ МАТЕРІАЛ ДЛЯ ГАЗОВИХ СЕНСОРІВ

Проблематика. Сенсори, чутливим елементом яких є SnO_2, характеризуються малим розміром та низькою вартістю. Однак значними недоліками є їх недостатня чутливість, низька селективність та невисока стабільність. Тому визначення основних параметрів, зміна яких дасть змогу створити ефективні, високочутливі та селективні напівпровідникові сенсори на основі наноструктур SnO_2, є вкрай актуальним.

Мета дослідження. Метою роботи є встановлення основних параметрів, що впливають на чутливість, селективність і стабільність напівпровідникових сенсорів.

Методика реалізації. Здійснено критичний огляд сучасної наукової літератури, в результаті якого встановлено, що використання стануму (IV) оксиду у вигляді 1D наноструктур (як допованих, так і недопованих) дасть можливість збільшити чутливість та селективність металоксидних датчиків за рахунок високих значень питомої площі поверхні та створення додаткових активних центрів відносно газів, які детектуються.

Результати досліджень. Визначено, що для створення ефективних і чутливих напівпровідникових датчиків необхідними є використання 1D наноструктур SnO_2 та їх спрямована модифікація різноманітними домішками.

Висновки. Виходячи з даних, наведених у сучасній науковій літературі, для створення ефективних напівпровідникових датчиків на основі SnO_2 необхідно поліпшувати їх 3S характеристики. З цієї точки зору 1D наноструктури SnO_2 заслуговують на особливу увагу за рахунок сукупності їх фізико-хімічних властивостей. Досить ефективним для синтезу 1D наноструктур є метод парогазового транспорту (метод CVD), що має високу продуктивність при відносній простоті і доступності та дає змогу отримувати монокристалічні наноструктури контрольованої морфології. Проте на сьогодні майже відсутні відомості щодо впливу режимних параметрів синтезу CVD на фізико-хімічні характеристики отримуваного нанорозмірного SnO_2. Таким чином, головною задачею є поглиблене вивчення наукових засад цілеспрямованого синтезу та систематизація підходу при виборі допанту для підвищення селективності металоксидних газових сенсорів.

Ключові слова: напівпровідниковий сенсор; стануму (IV) оксид; одновимірні наноструктури; метод парогазового транспорту; допант.

С.В. Нагирняк, Т.А. Донцова, И.М. Астрелин

ОДНОМЕРНЫЕ НАНОСТРУКТУРЫ ОЛОВА (IV) ОКСИДА КАК ЧУВСТВИТЕЛЬНЫЙ ЭЛЕМЕНТ ДЛЯ ГАЗОВЫХ СЕНСОРОВ

Проблематика. Сенсоры, чувствительным элементом которых является SnO_2, характеризуются малым размером и низкой стоимостью. Однако значительными недостатками являются их недостаточная чувствительность, низкая селективность и невысокая стабильность. Поэтому определение основных параметров, изменение которых позволит создать эффективные, высокочувствительные и селективные полупроводниковые сенсоры на основе наноструктур SnO_2, является крайне актуальным.

Цель исследования. Целью работы является установление основных параметров, влияющих на чувствительность, селективность и стабильность полупроводниковых сенсоров.

Методика реализации. Проведен критический обзор современной научной литературы, в результате которого установлено, что использование олова (IV) оксида в виде 1D наноструктур (как допированных, так и недопированных) позволит увеличить чувствительность и селективность металлоксидних датчиков за счет высоких значений удельной площади поверхности и создания активных центров по отношению к детектируемым газам.

Результаты исследования. Определено, что для создания эффективных и чувствительных полупроводниковых датчиков необходимы использование 1D наноструктур SnO_2 и их направленная модификация различными добавками.

Выводы. Исходя из данных, представленных в современной научной литературе, для создания эффективных полупроводниковых датчиков на основе SnO_2 необходимо улучшать их 3S характеристики. С этой точки зрения 1D наноструктуры SnO_2 заслуживают особенного внимания в виду совокупности их физико-химических свойств. Достаточно эффективным для синтеза 1D наноструктур является метод парогазового транспорта (метод CVD), который владеет высокой производительностью при относительной простоте и доступности и позволяет получать монокристаллические наноструктуры контролируемой морфологии. Однако на сегодняшний день практически отсутствуют сведения относительно влияния режимных параметров синтеза CVD на физико-химические характеристики получаемого наноразмерного SnO_2. Таким образом, главной задачей являются углубленное изучение научных основ целеустремленного синтеза и систематизация подхода при выборе допанта для повышения селективности металлоксидных газовых сенсоров.

Ключевые слова: полупроводниковый сенсор; олова (IV) оксид; одномерные наноструктуры; метод парогазового транспорта; допант.

Рекомендована Радою
хіміко-технологічного факультету
НТУУ "КПІ"

Надійшла до редакції
22 червня 2015 року