УДК 544.723,621.315.592

WAYS FOR IMPROVEMENT SELECTIVITY OF SEMICONDUCTOR GAS SENSORS

Nagirnyak S.V., Dontsova T.A.
National Technical University of Ukraine «Kyiv Polytechnic Institute»

A review of the literature on the main approaches for increasing the selectivity of semiconductor gas sensors done. Found that, in addition to regulation of working temperature and usage of dopants, a promising way to improve the selectivity of metal-oxide gas sensors is to create a multisensor systems containing arrays of sensing elements. The basic directions for further development of multisensors to design highly selective sensor system formulated.
Keywords: solid-state sensor, semiconductor sensor, selectivity, dopant, «electronic nose».

Introduction. The presence of hazardous contaminants in the air and the necessity for rapid detection of leakage of toxic volatile chemical components promotes intensive development of gas sensors. Solid-state gas sensors present a high potential for this application due to their fast response time, ease of implementation and low cost [1-3].

Among the solid-state sensors distinguish the following three main types: electrochemical [4, 5], catalytic (calorimeter) [6-8], semiconductor [9, 10].

Electrochemical sensors measure the change in potential or conductivity of sensing element based on solid electrolytes depending on the concentration of the active gas component.

Catalytic sensors fix the temperature change by the exothermic oxidation reaction of combustible gas or vapor on the surface of the catalyst.

Principle of semiconductor gas sensors based on the change in conductivity sensing surface layer depending on presence gas in the environmental. This conductivity change can be easily detected and is often used as the gas response signal.

For use in practice, the gas sensor must satisfy certain requirements. In order to characterize sensor performance a set of parameters is used. An ideal chemical sensor would possess high sensitivity, selectivity and stability, low detection limit, good response time and long life cycle. However, real sensor does not need to have all the ideal characteristics at once. Generally value of characteristics substantially depends on the intended use, and accordingly, requirements for the sensor.

The comparison the main indicators of solid-state gas sensors are presented in Table 1 [11].

Table 1

Comparison of various types of gas sensors

Parameter	Type of gas sensor		
	Semiconductor	Catalytic	Electrochemical
Sensitivity	e	g	g
Accuracy	g	g	g
Selectivity	p	b	g
Response time	e	g	p
Stability	g	g	b
Durability	g	g	p
Maintenance	e	e	g
Cost	e	e	g
Suitable to portable instruments	e	g	p

e: excellent; g: good; p: poor; b: bad

As can be seen in Table 1 among the presented three types electrochemical sensors are characterized by the worst indicators of stability, durability, response time and possible use in portable devices. Catalytic sensors have good parameters, but are inferior in selectivity. Gas sensors based on semiconducting metal oxides deserve special attention due to the obvious advantages: high sensitivity, low cost, fast response time, good suitability to portable instruments. But these devices have low selectivity to target components in gas mixtures which limits their use [12, 13].

Ways to improve selectivity of metal-oxide gas sensors. Selectivity relates to the specificity of the gas sensor response to a target gas in the presence of a mixture of gases. Selectivity plays a major role in gas identification. And high selectivity is the main task to the developers of metal-oxide gas sensors.

For improving the selectivity of gas sensor use several approaches include controlling the sensor operating temperature, using additives and using sensor arrays.

Temperature dependence of a metal-oxide sensor signal to the presence of a given analyte has a maximum at a certain temperature for each gas [14]. This dependence arises due to several reasons: the charge of oxygen species adsorbed at the oxide's surface depends on temperature [15], rate of the oxidation reaction increases with temperature and all adsorption, desorption, and diffusion processes are temperature dependent [16]. Heilig and co-workers in their work [17] showed that when the target gas interacts with the SnO_2 sensor, the reaction can be either endo- or exothermic, leading to a measurable change in the sensor operating temperature and the sensor resistance (i.e. the sensor sensitivity).

The reason of low selectivity of sensor materials is the presence of oxygen vacancies on the surface [18] which are active centers and allows to simultaneously interact with different molecules from gas phase. Using additives 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. As the dopants most commonly used metals of platinum group – Pt, Pd, Ru, Rh, or oxide catalysts – Fe_2O_3, La_2O_3, Cr_2O_3, V_2O_5, NiO, CuO. Important step – choice modifier for the gas and the change the reactivity of the material by changing the modifier concentration. Usually, the additive loadings required for improved sensor performance are low (typically less than 10% mass or mole basis) [19]. The choice of dopant is carried out depending on the nature of the gas, clusters of noble metals used for doping sensor elements aimed at determining gas-oxidants (O_2, NO_2) and gases not have defined acid-base properties (CO, H_2, CH_4). For detection of basic and acidic gases using clusters of oxide catalysts – oxides of molybdenum and vanadium to identify the basic gases; oxides of copper, nickel, iron, lanthanum for detection of acid gases.

The perspective is to use a multisensory system (sensor arrays) for identification components of gas mixtures. Such arrays of gas sensors usually call «electronic nose». The term «electronic nose» is understood to describe an array of chemical gas sensors with a broad and partly overlapping selectivity for measurement of volatile compounds combined with computerised multivariate statistical data processing tools [20]. Based on the wellknown definition, an «electronic nose» is an instrument, which comprises an array of electronic chemical sensors with partial specificity and an appropriate pattern-recognition system, capable of recognising simple or complex odors [20].

Background of creation of the multisensory systems. The «electronic nose» («e-nose») has derived its name because it in several aspects tries to resemble the human nose (Figure 1). In the case of «electronic nose» signals can be obtained simultaneously from several sensors, which differ in some way (e.g., doping element, doping ratio, grain size, or temperature) [15]. «Electronic noses» use various types of electronic gas sensors that have partial specificity. Unlike traditional sensor systems that require highly selective sensing elements, «e-nose» can contain a set of low selective sensors.

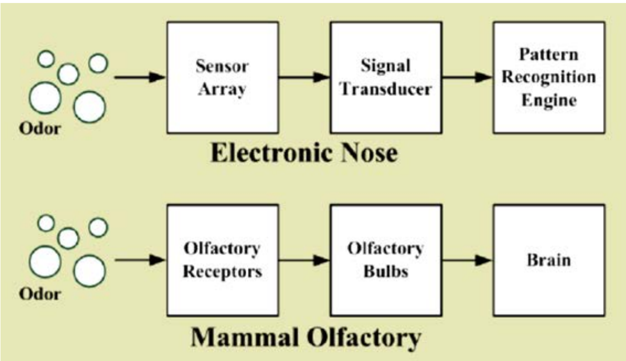

Fig. 1. The basic gas identification system blocks: an electronic nose and a mammal olfactory [21]

Figure 2 shows an example of the block diagram of multisensory system [22]. Generally «e-nose» includes the following components: matrix of sensitive semiconductor sensors; sampling system; analog adapter to maintain operating modes in a matrix of sensors and sensor output signal conversion into digital code; microprocessor for signal preprocessing of sensors and standard interface for connection to a computer; computer software for device management and authentication.

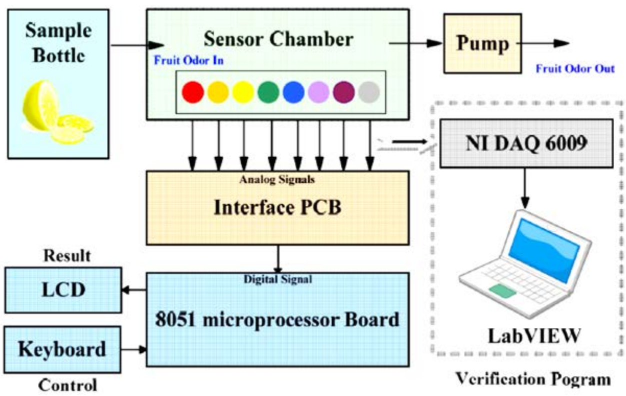

Fig. 2. Block diagram of e-nose system [22]

The main part of «electronic nose» is the sensing system and the others components chose depending the matrix. When using single sensor you can usually judge only about relative selectivity, since the sensor gives the response of a number of gases, and it is very difficult to understand what caused the change in conductivity of the layer – gas type or it's concentration. And in the case of electronic nose a particular gas interacts with a large array of different sensors. From each sensor comes a distinct response signal. By aggregating the set of signals from the sensor array, a distinct chemical «fingerprint» can be constructed for any particular chemical (Figure 3).

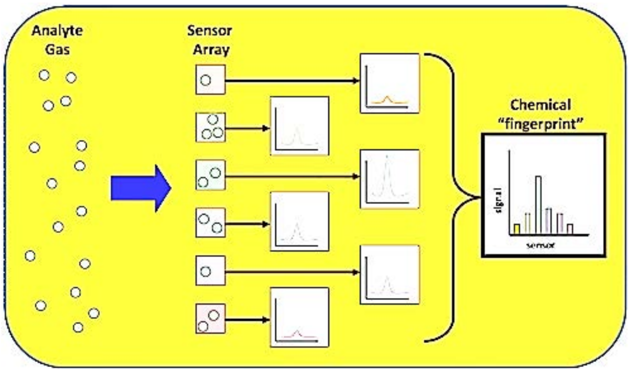

Fig. 3. Schematic of an electronic nose [23]

In the case of multisensory systems for easier presentation of the sensory response results of various sensing elements usually use two kinds of charts. Figure 3 shows column histogram chart for response results of multisensor which contains 6 different sensing elements. In Figure 4, the sensory response data of multisensory system based on 13 sensing elements are presented as a radar chart. Such charts are convenient for estimating selectivity of various sensing elements towards to the same gas.

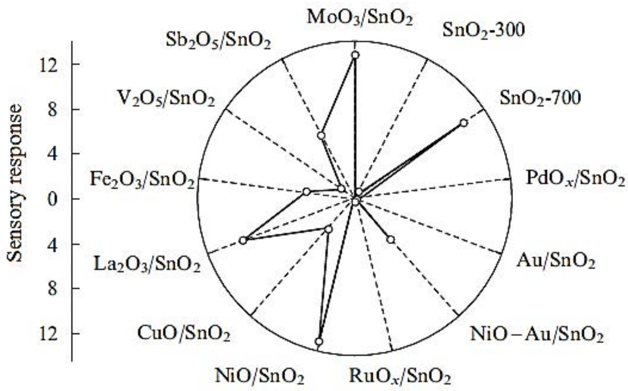

Fig. 4. Sensory response of SnO_2-based sensors on NO_2 at an operating temperature of 300°C [18]

Conclusions. In terms of data presented in contemporary scientific literature, to improve the selectivity of semiconducting gas sensors several approaches can be used, namely controlling of operating temperature, using additives and creation of multisensory system. The last approach deserves special attention due to the using low-selective sensing elements. The number of sensitive layers for such multisensory system can vary from 3 to 30. And, as of day there is no explanation of criteria for of selection of an array of gas sensors. This refers not only to the selection of layers with certain parameters, but also to the selection of number these layers. Therefore, the main task for researchers is the finding the optimal number of sensitive layers for development of highly selective sensory system.

References:

1. Cerrato G. Structural and morphological modifications of sintering microcrystalline TiO_2: an XRD, HRTEM and FTIR study / G. Cerrato, L. Marchese, C. Morterra // Applied Surface Science. – 1993. – 70/71. – P. 200-205.
2. Ueda A. Two conversion maxima at 373 and 573 K in the reduction of nitrogen monoxide with hydrogen over Pd/TiO_2 catalyst / A. Ueda, T. Nakao, M. Azuma, T. Kobayashi // Catalysis Today. – 1998. – 45. – P. 135-138.
3. Turkoviæ A. Comparative Raman, XRD, HREM and SAXS studies of grain sizes in nanophase TiO_2 / A. Turkoviæ, M. Ivanda, S. Popoviæ, A. Tonejc, M. Gotiæ, P. Dubèek, S. Musiæ // Journal of Molecular Structure. – 1997. – P. 271-273.
4. Jones A. The chemistry of solid state gas sensors / A. Jones, P. Moseley, B. Tofield // Chemistry in Britain. – 1987. – P. 749-754.
5. Yulong Xu Oxygen sensors based on semiconducting metal oxides: an overeview / Yulong Xu, Xiaohua Zhou, O. Toft Sorensen // Sensors and Actuators B. – 2000. – V. 65. – P. 2-4.
6. Jones T. A. Flammable gas detection / T. A. Jones, P. T. Walsh // Platinum Metals Rev. – 1988. – V. 32. – P. 50-60.
7. Gentry S. J. The role of catalysis in solid-state gas sensors / S. J. Gentry, T. A. Jones // Sensors and Actuators. – 1986. – V. 10. – P. 141-163.
8. Menil F. Critical review of nitrogen monoxide sensors for exhaust gases of lean burn engines / F. Menil, V. Coillard, C. Lucat // Sensors and Actuators B. – 2000. – V. 67. – P. 1-23.
9. Morrison S. R. Mechanism of semiconductor gas sensor operation / S. R. Morrison // Sensors and Actuators. – 1987. – V. 11. – P. 283-287.
10. Seker F. 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. – P. 2505-2536.
11. Korotcenkov G. Metal oxides for solid-state gas sensors: What determines our choice? / G. Korotcenkov // Materials Science and Engineering B. – 2007. – 139. – P. 1-23.
12. Klug H. P. X-ray diffraction procedures / H. P. Klug, L. E. Alexander, J. Wiley, Sons Inc. // New York. – 1954.
13. Warren B. E. X-ray diffraction / B. E. Warren // Dover publications, Inc. , New York. – 1990.
14. Ahlers S. A rate equation approach to the gas sensitivity of thin film metal oxide materials / S. Ahlers, G. Müller, T. Doll // Sensors and Actuators B. – 2005. – 107. – P. 587-599.
15. Bochenkov V. E. Sensitivity, selectivity, and stability of gas-sensitive metal-oxide nanostructures / V. E. Bochenkov, G. B. Sergeev // Metal oxide nanostructures and their application. – 2010. – Vol. 3. – P. 31-52.
16. Wlodek S. Signal-shape analysis of a thermally cycled tin-oxide gas sensor / S. Wlodek, K. Colbow, F. Consadori // Sensors and Actuators B: Chemistry 3. – 1991. – P. 63-68.
17. Heilig A. Selectivity enhancement of SnO_2 gas sensors: simultaneous monitoring of resistances and temperatures / A. Heilig, N. Bârsan, U. Weimar, W. Göpel // Sensors and Actuators B. – 1999. – 58. – 302-309.
18. Кривецкий В. В. Химическая модификация нанокристаллического диоксида олова для селективных газовых сенсоров / В. В. Кривецкий, М. Н. Румнцева, А. М. Гаськов // Успехи химии. – 2013. – 82 (10). – С. 917-941.
19. Miller T. A. Nanosturctured tin dioxide materials for gas sensor applications / T. A. Miller, S. D. Bakrania, C. Perez, M. S. Wooldridge // Functional Nanomaterials. – 2006. – 30. – P. 1-24.
20. Gardner J. W. A brief history of electronic noses / J. W. Gardner, P. N. Bartlett // Sensors and Actuators B. – 1994. – 46-47. – P. 211-220.
21. Chiu Shin-Wen Towards a chemiresistive sensor-integrated electronic nose: a review / Shin-Wen Chiu, Kea-Tiong Tang // Sensors. – 2013. – 13. – P. 14214-14247.
22. Tang Kea-Tiong Development of a portable electronic nose system for the detection and classification of fruity odors / Kea-Tiong Tang, Shin-Wen Chiu, Chin-Heng Pan, Hung-Yi Hsieh, Yao-Sheng Liang, Ssu-Chieh Liu // Sensors. – 2010. – 10. – P. 9179-9193.
23. http://nano.caltech.edu/research/nems-olfaction.html

Нагірняк С.В., Донцова Т.А.
Національний технічний університет України «Київський політехнічний інститут»

ШЛЯХИ ПОКРАЩЕННЯ СЕЛЕКТИВНОСТІ НАПІВПРОВІДНИКОВИХ ГАЗОВИХ СЕНСОРІВ

Анотація
Проведено огляд літератури стосовно основних підходів для підвищення селективності напівпровідникових газових сенсорів. Встановлено, що крім регулювання робочої температури та використання допантів, досить перспективним способом покращення селективності металоксидних газових сенсорів є створення мультисенсорних систем, що містять масиви чутливих елементів. Сформульовані основні напрямки для подальшого розвитку мультисенсорів з метою розробки високоселективної сенсорної системи.
Ключові слова: твердофазний сенсор, напівпровідниковий сенсор, селективність, допант, «електронний ніс».

Нагирняк С.В., Донцова Т.А.
Национальный технический университет Украины «Киевский политехнический институт»

ПУТИ УЛУЧШЕНИЯ СЕЛЕКТИВНОСТИ ПОЛУПРОВОДНИКОВЫХ ГАЗОВЫХ СЕНСОРОВ

Аннотация
Проведен обзор литературы относительно основных подходов для повышения селективности полупроводниковых газовых сенсоров. Установлено, что кроме регулирования рабочей температуры и использования допантов, перспективным способом улучшения селективности металоксидных газовых сенсоров является создание мультисенсорных систем, содержащих массивы чувствительных элементов. Сформулированы основные направления для дальнейшего развития мультисенсоров с целью разработки высокоселективной сенсорной системы.
Ключевые слова: твердофазный сенсор, полупроводниковый сенсор, селективность, допант, «электронный нос».