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DEVELOPMENT AND CREATION OF GAS-SENSOR SYSTEM BASED ON LOW DIMENSIONAL METAL OXIDES

Peculiarities of photoluminescent properties of metal oxide nanopowders (ZnO, TiO_2, SnO_2, WO_3) including laser-modified and surface doped by impurities (Au, Ag, Pt, Ni, Cu, Sn), in gases (O_2, N_2, H_2, CO, CO_2) have been studied. The sensor properties of the metal oxide nanopowders (adsorption capacity, speed, sensitivity, selectivity) have been established; the best structure and materials for the development of a multicomponent recording matrix have been selected. The efficiency of the sensor system for detection and analysis of gases and their mixtures has been found. The developed gas sensor system enables detecting not only separate gas components, but their mixture with high sensitivity and selectivity, which makes it possible to reach the advanced level of the formation of gas sensor systems with improved performance.

Keywords: metal oxide nanopowders, luminescence, and gas sensor.

The detection of active gases and air monitoring are key priorities of the advanced economies in the environment protection sphere. This requires improving means for measurement of chemical composition of gaseous environments and creating new, more effective, and cheap metering devices. This problem is especially important under conditions of aggravating environment pollution, increasing plant emissions, and raising threat of terroristic attacks with the use of explosive and poisonous gaseous mixes. However, the existing sensor systems enable recording only limited number of gas components at relatively low sensitivity, selectivity, and speed of response. As of today, Ukraine urgently needs the creation of low dimensional effective poly-sensors having a selective sensitivity to wide range of gases and mixes, signal processing circuit, and low energy consumption. This research is aimed at raising the selectivity of gas sensor materials, and gas sensors as a whole. This research is notable for integrated approach to the problem solution as it uses the method for obtaining nanopowder materials and structures based on them designed by the authors hereof [1—4] and the luminescent method for detecting gas particles adsorbed on nanopowder metallic oxides [5].

The operation of semiconductor chemical sensor is based on transformation of adsorption level into electronic signal corresponding to the number and type of gas particles adsorbed from the environment [6]. The electronic signal reflects the properties of semiconductor adsorbent when detected gas particles arrive in its surface. The adsorbed gas particles are able to exchange charge with extensional areas of adsorbent or interact directly with electrically active defects and impurities of semiconductor metallic oxides thereby changing their electronic properties [7, 8]. High sensitivity of electronic properties of metallic oxides to gas adsorption and its controllability enable production of gas sensors based on them [9, 10]. These sensors are cheap, low dimensional, highly sensitive, and highly selective. The selected, synthesized, and used semiconductor materials ZnO, TiO_2 SnO_2, In_2O_3, WO_3 have a good

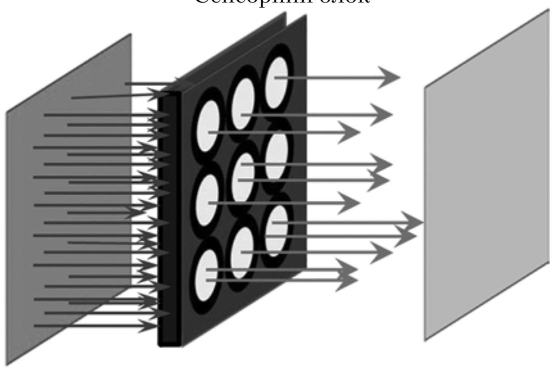

Fig. 1. Functional diagram of gas sensor system laboratory model

adsorption ability and a sufficient chemical stability not to form stable chemical compounds with adsorbed particles. The chosen oxides having a high sensitivity to adsorption because of a low concentration of their own free charge carriers meet the mentioned requirements.

RESULTS OF EXPERIMENTS AND THEIR ANALYSIS

The main specific feature of the designed sensor system (Fig. 1) is registration of photoluminescence of nanopowder metallic oxide with gas particles adsorbed on it (Figs. 2, 3) [5], instead of record of electric signal as in the conventional gas sensors [6, 9]. The electronic energy levels generated by adsorbed particles in the adsorbent make it possible to observe individual spectral electronic levels of adsorbed atoms, which enables their selective identification.

The adsorption of gas particles of various kind can cause similar changes in electronic properties of adsorbent. This complicates detecting certain component of gaseous mixture and constitutes the problem of selectivity. In order to partially avoid this problem, both adsorbents of various metallic oxides and their different defect structures, including the laser modified ones are proposed [11]. Certain impurities of catalytically active metals at given concentration ~(1—5)% enable shifting sensitivity maximum towards the selected gas. In particular, metallic atoms adsorbed on the surface of ZnO stimulate weakening sensitivity to hydrogen atoms, as a result of isolation of main adsorption sites. However, as doping level increases the influence of hydrogen atoms on adsorption sites of excessive metallic atoms changes. In their turn, excessive atoms of Au, Ag, Pt, Pd, Zn, Al, Ni, Cu,Ga, In, and Sn on the surface of ZnO activate detectors with respect to various gases. The creation of localized boundary between the materials with different electronic properties (for example, Zn—ZnO nanosystems of *core — shell* type created by the authors team [1, 2]) looks very promising for enhancing the sensor sensitivity. In these heterogeneous systems, chemisorption of gas components defines the height of energy barrier for charge carriers on the heteroboundary of nanocrystalline system, which stimulates increased (up to ten times and more) gas sensitivity as compared with ordinary ZnO. At the same time, doping of nanopowder material or its laser anneal can change the Debye screening length and, consequently, leads to an increase in the number of adsorbed particles on low-dispersive structures of ZnO. In its turn, the proper choice of structure and type of adsorbent and its size enables selective adsorption of active gas particles.

Sensitivity of sensor proposed by the team of authors increases in the case of ZnO nanopowder material doped with various metallic impurities, insofar as in the course of doping, both impurity adsorption sites and additional impurity levels in semiconductor forbidden band, near the conductivity band, occur and, respectively, the probability of occupation of this zone by electrons increases. An essential decrease in gas sensitivity of nanopowders is reported at an air humidity ≥70%, with sensitivity varying in the case of doping.

One of the important characteristics of the sensor is speed of response defined by response time and recovery time where the response time is time interval for which given value varies by up to 0.9 of the peak magnitude. The recovery time is time

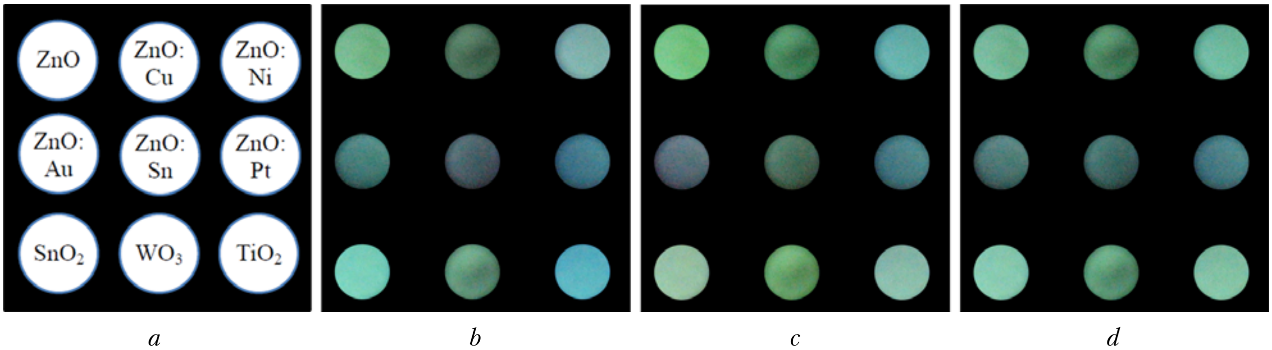

Fig. 2. Photoluminescence of sensor matrix cells (*a*) in gaseous environment (*b* – air, *c* – CO, *d* – vacuum, T = 23 °C, ψ = 60%)

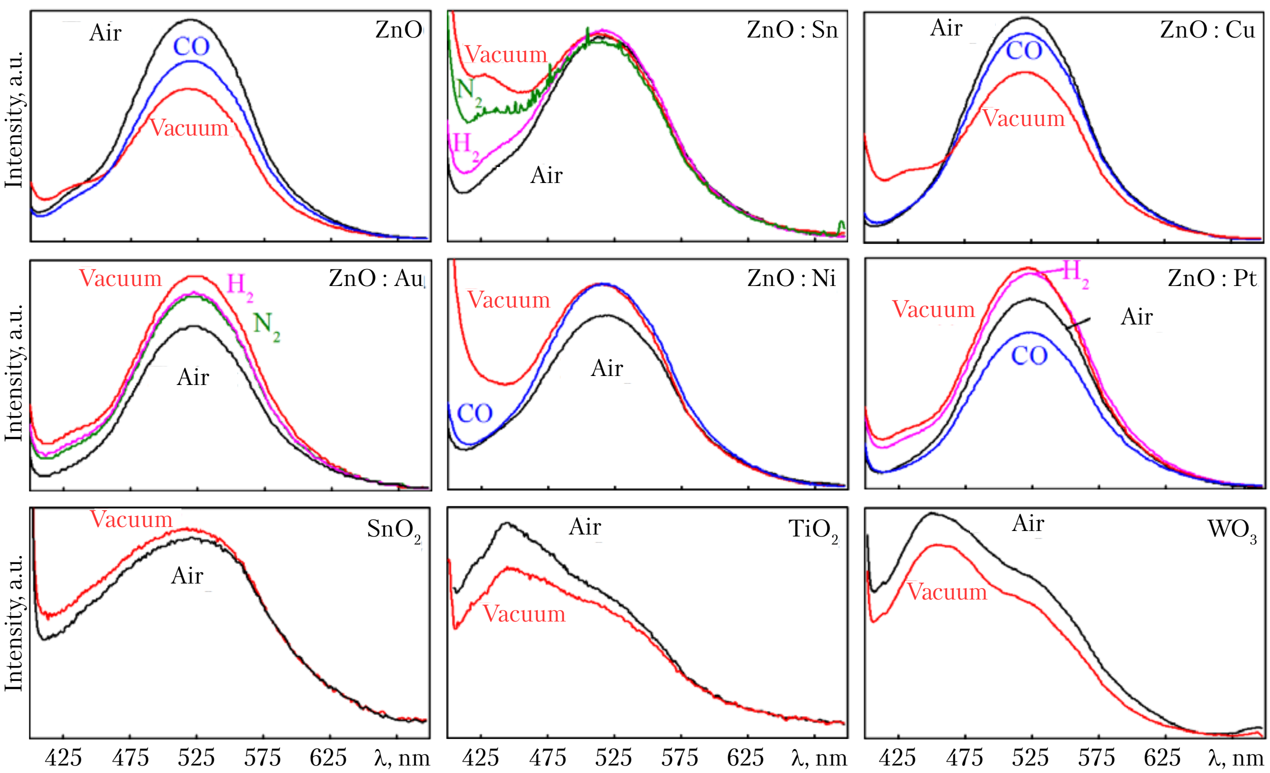

Fig. 3. Photoluminescence spectra of nanopowder sensor cells (Fig. 2, *a*) in various gaseous environments

interval for which the measured parameter is resumed to 0.1 of the peak magnitude. Gas sensitivity of nanopowder materials has been established to have high speed of response, as for ZnO it amounts to ~100 ms for reaching signal ≥90% (Fig. 4). the observed increase in luminescence intensity after its rapid drop on the kinetic curve can be explained by adsorption and diffusion processes on the surface of nanopowder ZnO as its electronic properties change. Change in concentration of free charge carriers in ZnO can influence kinetics of afterglow. Increasing concentration of free electrons when a donor gas (for instance, hydrogen) is adsorbed leads to appearance of maxi-

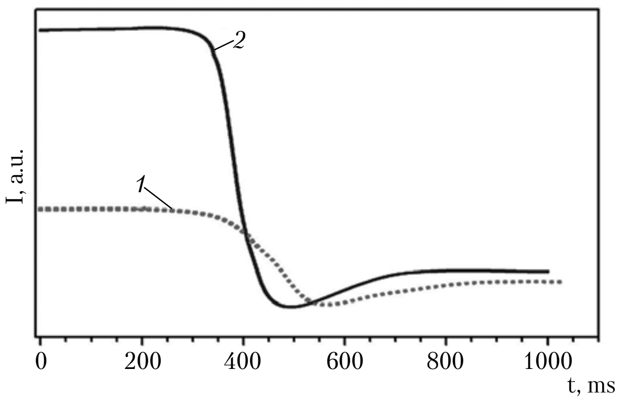

Fig. 4. Kinetics of changing photoluminescence intensity of ZnO in the case of oxygen addition (P_{O2} = 90 Pa): *1* — ZnO; *2* — ZnO:Al

mum on the afterglow kinetic curve, as a result of the fact that luminescence intensity is defined by concentration of both free electrons and ionized luminescence centers. In the case of acceptor gas (oxygen) chemisorption concentration of free electrons decreases and, consequently, luminescence intensity of material drops more sharply. However, increasing concentration of free holes can lead to an increase in the number of ionized luminescence centers and, respectively, to growing afterglow intensity observed. The studies of time dependence of photoluminescence intensity (Fig. 4) of initial (*1*) and doped (*2*) nanopowder ZnO have showed that the latter has a much higher speed of response because of much higher electron concentration in the doped material. Thus, in the case of acceptor gas chemisorption, changes in afterglow kinetics depend on which of two processes (decrease in concentration of free electrons or increase in concentration of ionized luminescence centers) has the larger effect on luminescence of nanopowder ZnO.

The use of catalytic impurities applied to the material surface as fine-dispersed phase has resulted not only in raising given selectivity, but also in increasing gas sensitivity to selected gas. The mechanism of catalyst influence on the value and properties of sensor's adsorption response and selectivity is associated with spillover effect, i.e. changing Fermi level of adsorbent semiconductor. The depleted layer is known to play key role in the sensitivity mechanism. The depleted layer is formed depending on available oxygen vacancies in ZnO acting as traps for catching the oxygen molecules. As a rule, as the depleted layer gets thicker, electric resistance of ZnO layer grows. One of ways to enhance the sensitivity of ZnO nanoparticles to reducing gases, such as CO, is to increase the number of electrons caught from adsorbed oxygen thereby getting larger depleted layer and, therefore, maximum luminescence variation. The observed raise in sensitivity of ZnO nanoparticles to oxygen is likely explained by combination of two effects, electronic sensibilization and action of catalytic impurities Pt on the surface of ZnO.

The specific features of nanopowder gas sensitivity that depends on the structure of defects and impurities under manifestation of Debye electrostatic radius when gas is adsorbed have been established. At the same time, the lesser is the size of nanogranules ($d \leq 40$ nm), the lower is adsorption ability of nanopowder. Therefore, nanopowders having particles ranging $d \geq 40 \div 60$ nm shall be used in gas sensors.

In order to implement the proposed gas sensor the authors recommend to use multisensory multichannel system (Fig. 1) that has a set of adsorbents of various oxide modifications characterized by perfect sensitivity for various gas particles (Fig. 2, *a*) and simultaneous record of signals of all matrix cells (Fig. 2, *b*—*d*) using charge-coupled device (CCD) matrix with spectral characteristics given in Fig. 3. Their digital processing enables to significantly enhance the selectivity of analysis and to define simultaneously concentrations and type of many active gas particles adsorbed onto the surface of metallic oxide. An algorithm and program for identification of gas components by analyzing spectral luminescence of matrix cells have been developed and the gas sensor system built has been established to be effective with respect to detection and analysis of gases and gas mixes. The sensors are required to possess selective response to certain gas and high stabi-

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lity of signal reproducibility during a long period of sensor operation. This problem is addressed by periodical regeneration of surface by heat, vacuum and UV treatment, etc.

CONCLUSIONS

Peculiarities of photoluminescent nanopowder metal oxides ZnO, TiO_2, SnO_2, In_2O_3, WO_3, including those laser modified and doped with Au, Ag, Pt, Pd, Ni, Cu, and Sn in gases O_2, N_2, H_2, CO, CO_2 have been established. Gas sensor properties of nanopowder metallic oxides (adsorption capacity, speed of response, sensitivity, and selectivity) have been found, with configuration and optimal materials for recording multicomponent matrix (3×3) chosen. The luminescence record using CCD matrix with further digital analysis of the signal obtained enables to determine gas components in analyzed environment in terms of quality and quantity. An algorithm and program for identification of gas components by analyzing spectral luminescence of matrix cells have been developed and the gas sensor system built has been established to be effective with respect to detection and analysis of gases and gas mixes.

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РОЗРОБКА ТА СТВОРЕННЯ ГАЗОСЕНСОРНОЇ СИСТЕМИ НА ОСНОВІ НИЗЬКОВИМІРНИХ МЕТАЛООКСИДІВ

Вивчалися особливості фотолюмінісцентних властивостей нанопорошкових металооксидів (ZnO, TiO_2, SnO_2, WO_3), в т.ч. лазерномодифікованих та поверхнево-легованих домішками (Au, Ag, Pt, Ni, Cu, Sn), в газах (O_2, N_2, H_2, CO, CO_2). Встановлено характер газосенсорних властивостей нанопорошкових металооксидів (адсорбційна здатність, швидкодія, чутливість, селективність) та вибрано конструкцію і оптимальні матеріали для побудови реєструючої багатокомпонентної матриці. Встановлено дієздатність побудованої газосенсорної системи для розпізнавання та аналізу газів та їх сумішей. Розроблена газосенсорна система дає змогу детектувати не тільки окремі газові компоненти, але і їх суміші з високою чутливістю і селективністю, що забезпечує можливість вийти на сучасний рівень формування газосенсорних систем з покращеними експлуатаційними характеристиками.

Ключові слова: металооксидні нанопорошки, люмінесценція, газові сенсори.

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РАЗРАБОТКА И СОЗДАНИЕ ГАЗОСЕНСОРНОЙ СИСТЕМЫ НА ОСНОВЕ НИЗКОРАЗМЕРНЫХ МЕТАЛЛООКСИДОВ

Изучались особенности фотолюминесцентных свойств нанопорошковых металооксидов ZnO, TiO_2, SnO_2, WO_3, в т.ч. лазерномодифицированных и поверхностно легированных примесями Au, Ag, Pt, Ni, Cu, Sn, в газах O_2, N_2, H_2, CO, CO_2. Установлен характер газосенсорных свойств нанопорошковых металооксидов (адсорбционная способность, быстродействие, чувствительность, селективность) и выбраны конструкция и оптимальные материалы для построения регистрирующей многокомпонентной матрицы. Установлено дееспособность построенной газосенсорной системы для распознавания и анализа газов и их смесей. Разработанная газосенсорная система дает возможность детектировать не только отдельные газовые компоненты, но и их смеси с высокой чувствительностью и селективностью, что обеспечивает возможность выйти на современный уровень формирования газосенсорных систем с улучшенными эксплуатационными характеристиками.

Ключевые слова: металооксидные нанопорошки, люминесценция, газовые сенсоры.

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