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The Influence of Surface Doping on Adsorption Ability of Nanopowder Metal Oxides for Gas Sensors

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In this paper the features of photoluminescent properties in gases of ZnO nanopowders including laser-modified and surface-doped with impurities of noble metals (Au, Ag, Pt) have been studied. The influence of laser modified and surface doping of ZnO nanopowders with impurities of noble metals on the adsorption ability have been studied and it was found that there is a growth in sensory sensitivity to gases. Established the tendency to reduce the adsorption ability ZnO nanopowders with decreasing size nanogranules to 40-60 nm. Physicochemical regularities of formation of adsorption surface electronic states in initial and doped nanopowders during adsorption of gases have been studied.

Keywords: Gas sensor, Nanopowder, Metal oxide, Photoluminescence.

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1. INTRODUCTION

Zinc oxide is a valuable material for micro and optoelectronics, which still attracts researchers for its extensive study [1]. It has a large band gap (3.4 eV), a high binding energy of the exciton (60 meV), transparent in the visible region of the spectrum, high radiation resistance, and so on. ZnO nanopowders exhibit efficient photoluminescence in the visible range [2]. The photoluminescence spectra of metal oxide nanopowders is sensitive to the presence of oxidizing and reducing gases in the ambient air [3, 4]. The adsorption of oxidative and reductive gases on the surface of nanopowders leads to a change in the charge density on the surface and a shift of the Fermi level. This induces a change in the electron distribution in the nanomaterial [5-7]. The ZnO surface has a high adsorption ability and reactivity [8] due to its developed intrinsic defect structure. However, a wide range of adsorption centers determines the low selectivity of the material, which causes the need to find ways to increase it. The difficulty of selective detection caused, in particular, similar mechanism of interaction of reducing gases with ZnO surface. The sensitivity of metal oxides to type and concentration of adsorbed molecules are significantly depended by the microstructure of their surface, which can be modified by the laser annealing or the formation of complex heterogeneous systems, in particular, metal-semiconductor type "core-shell". To prevent the chemical interaction of the components, it may lead to the formation of solid solutions or chemical compounds, the modification of the ZnO surface may be carried out by platinum group metals, which substantially affect the electronic and catalytic properties of metal oxides in the almost complete absence of oxidation of metals themselves.

Laser reactive technology is a promising method for synthesizing structures based on ZnO. This method allows you to adjust the stoichiometric composition of the material to conduct doping impurities and to form quantum structures, in particular, nanopowders, thin films including complex metal oxides by evaporation of metallic targets in an oxygen environment, which is the result of the high reactivity of the laser erosion plasma.

Aims of the works at solving the problem of increasing the selectivity of the gas sensitive materials and accordingly gas sensors in general. Its feature is an integrated approach to solving problems that is to use the methods to fabrication of nanopowders and structures on their based developed by us [9] and application the photoluminescent method for the detection of adsorbed gas particles on the surface of metal oxides nanopowders [3, 9]. This approach is promising due to its inherently very high sensitivity and miniaturization capability.

2. EXPERIMENTAL DETAILS

All samples were obtained by the method of pulsed laser ablation in a chemically active environment [9]. The research of phase and structural analyses of nanopowders were carried out using an X-ray diffractometer DRON-4. The sizes of particles were determined according to electron microscopy images received by means of electron microscope PEM-125K.

Doping of nanopowders was carried out by pulsed laser deposition of a metallic thin film on nanopowders surface with further activation by laser annealing [10, 11]. The process of pulsed evaporation of the target material was carried out using a YAG:Nd^{3+} – laser ($\lambda = 1.06$ μm, $\tau = 10^{-3}$-10^{-8} s, $q = 10^5 \div 10^8$ W/cm², $n = 14$-56 Hz, $d = 5$ mm, $E_i = 0.005$-0.350 J/cm²). Laser radiation

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focused on the target's lenses which is in the vacuum chamber ($P = 10^{-3}$ Pa), which allows to obtain chemically pure condensates of the activator. Under the influence of a pulsed laser target material is evaporated and forming plasma plume. The plume was located strictly perpendicular to the surface of the nanopowder layer and did not depend on the radiation-incident angle. The atoms condensed on the surface of nanopowders forming a thin film of dopant. To uniformly condense the film over the entire surface of the nanopowder, the cell was placed on a specially designed vibration device with a frequency of 10-60 Hz. Due to such vibrational oscillations, the nanopowder was well stirred, allowing a uniformly deposited film to be obtained on its surface. In order to activate the impurities diffuse and its uniform distribution in the volume of nanogranule, held laser annealing nanopowders. Under the influence of a pulsed laser doping metallic impurities from the surface diffuses into the granules and electrically activated. Laser annealing and implantation were mostly in nanopowder transparency and thus has intense absorption by metallic impurity without significant heating of the matrix.

Photoluminescent studies of nanopowder oxides in gas environment were carried out on a mounted computerized installation using a dual monochromatograph DMR-4 (Fig. 1) (8). Excited photoluminescence was carried out using UV-LED with $\lambda_{max} = 355$ or $\lambda_{max} = 375$ nm (1). Registration of photoluminescence spectra of nanopowders was carried out at room temperature. Investigated samples (5) were placed in a quartz cell (4) connected to the vacuum installation VUP-5M (15) and multichannel gas inlet system SNA-2, which made it possible to conduct photoluminescent researches in various gas environments at the set of pressures. Registration of signal was carried using photomultiplier FEU-27 (9). Recording and normalization of spectra was conducted automatically using PC (11) with specially developed software.

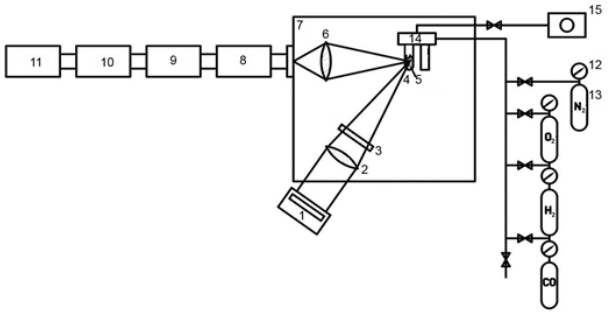

Fig. 1 – Scheme of the installation for studying the photoluminescence properties of nanopowders in gases: 1–UV source; 2, 6 – lens; 3 – optical filter UFS-2; 4 – quartz cell; 5 – sample; 7 – light-defensive camera; 8 – monochromator DMR-4; 9 – photomultiplier FEU-27; 10 – amplifier; 11 – PC; 12 – vacuum gauge IV-2; 13 – gas bottle; 14 – active volume; 15 – vacuum assembly VUP-5M

3. RESULTS AND DISCUSSION

The photoluminescence spectra of ZnO:Pt at room temperature consist of two major emission bands the intensive ultraviolet ($\lambda = 382$ nm) and visible band at around 525 nm. The intense peak of ultraviolet radiation ($\lambda = 382$ nm) corresponds to the exciton luminescence ZnO at room temperature. The intensity of edge luminescence is stronger than the intensity of visible luminescence from the intrinsic defect structure, indicating the excellent crystal quality of nanoparticles and underdevelopment of the intrinsic defect structure, which can be modified by means of pulsed laser annealing. X-ray diffraction (Fig. 2) studies show wurtzite crystal structure of ZnO samples. The character of visible photoluminescence determined by the intrinsic defect structure of the material and depends on the technological parameters obtaining of nanopowders. The adsorption of oxidative and reductive gases on the surface of nanopowders leads to change in visible photoluminescence spectra (Fig. 3).

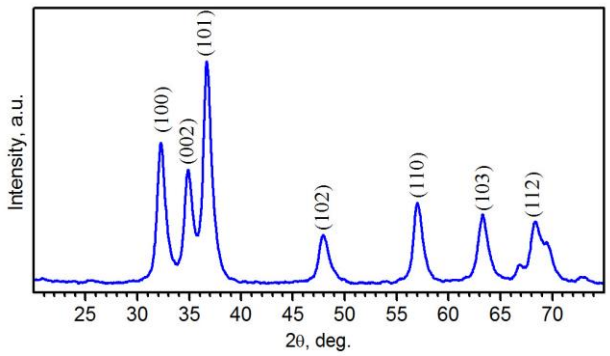

Fig. 2 – XRD pattern ZnO nanopowders

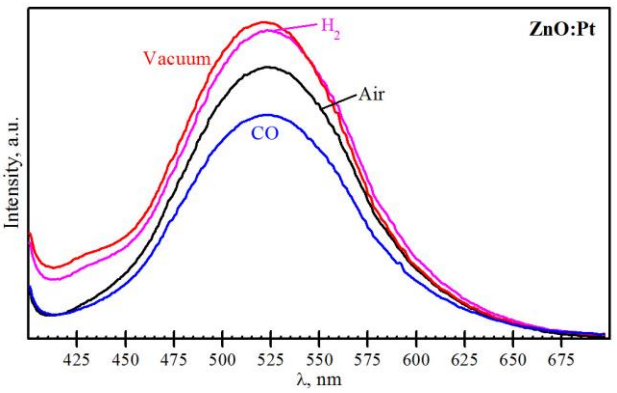

Fig. 3 – Photoluminescence spectra of ZnO:Pt in various gas environments

Surface doping with noble metals (Au, Ag, Pt) of semiconducting ZnO promotes the breakdown of its covalent bonds and exhibits a catalytic effect on the process of following oxidation. As shown in the work [12], low-temperature mixing of metal and semiconductor atoms and screening by free electrons of metal of valence bonds of semiconductor atoms is taking place. As a result, the bonds weaken and break, at the same time, the semiconductor atoms form connections with the metal and the condensed gas atoms. In the process of such doping, donor-acceptor pairs can be formed, the transition of carriers which causes the corresponding luminescence.

On the whole, doped and real surfaces characterized by the presence of a developed structure of surface electronic states, which giving reasons for considering them as disordered systems [13]. In bandgap of such systems there are a number of continuously placed electronic levels and localized electronic states (so-called fluctuation levels). Such levels occur, in particular, on the sur-

face when forming bonds between a metal and a semiconductor in the process of nucleation and formation of metal islands when deposition a film on the surface of a nanopowders. Laser deposition of metallic film, which is characterized by a large number of centers of island nucleation's, contributes to the formation of a number of localized electronic states, which can function, in particular, as recombination centers.

Using catalysts, deposited on the surface as a fine-dispersed phase, leads not only to increase the given selectivity but also to increase sensitivity of the sensor in relation to the selected gas [14]. Mechanism of the influence of deposited catalysts on the magnitude and characteristics of the adsorption response of a sensor and its selectivity associated with the spillover effect, which is related to the change in the Fermi level of the adsorbent [15]. The influence of catalysts on the sensitivity and selectivity of a semiconductor sensor can also be showed through adsorption changes in the characteristics of the space charge region, which is located directly below the contact of catalytic metallic impurities with semiconductor. The processes existent when adsorbed on metal impurities cause changes in the electron subsystem and changes in the characteristics of the Schottky barrier, which is manifested in the change in the concentration of free carriers in the spatial charge region involved in the luminescent processes.

Implantation into the surface structure of the noble metals accompanied by formation of partially oxidized metal clusters of these metals on the surface of ZnO nanopowders. The metal components are located on the surface of the granules in the form of metallic or oxide segregation and can enter the structure of ZnO with the formation of a solid solution.

Study of surface modification processes ZnO nanopowder by Pt clusters due to the possibility of increasing their sensitivity and selectivity, in particular, to hydrogen. Detection of hydrogen is of particular interest, because hydrogen is the primary gas released during pyrolysis of materials at the initial stage of combustion, and therefore can be effectively used for early detection of fires. The selectivity of detecting hydrogen here manifests itself mainly due to oxidation on platinum clusters of other gases - reducing agents, in particular, carbon monoxide. The structure of the molecular orbitals of the oxide is such that the transfer of the electron density is possible both from the CO molecule to the free orbitals Zn, and on the contrary from d-orbitals Zn on free CO orbitals. On the ZnO surface, CO reacts with adsorbed or lattice oxygen, which leads to the formation of CO_2.

The sensory sensitivity of ZnO nanoparticles before and after deposition of noble impurities is shown in Fig. 4. To understand the effect of the metal decoration on the sensitivity ZnO nanoparticles, consider first the mechanism of sensitivity of ZnO nanoparticles without coating. Depleted layer plays a key role in the sensitivity mechanism [16]. The formation of a depleted layer occurs in accordance with available oxygen vacancies in ZnO, which act as traps to capture oxygen molecules. An increase in the thickness of the depleted layer leads to the change in the photoluminescent spectra of the ZnO. One way to increase the sensitivity of ZnO nanoparticles to reducing gases such as CO, is increasing the number of trapped electrons from adsorbed oxygen,

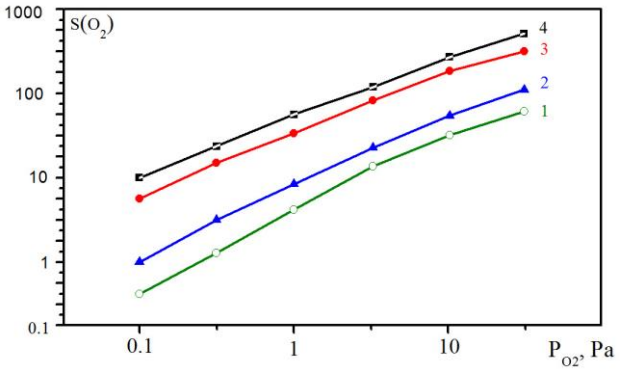

Fig. 4 – Dependence of the sensory signal value $S(O_2)$ of ZnO nanopowders (1 – ZnO, 2 – ZnO:Ag, 3 – ZnO:Au, 4 – ZnO:Pt) from the additional partial pressure of oxygen in the air

and thus obtaining a larger depleted layer a and, consequently, a maximum change in luminescence.

The observed increase in the sensitivity of ZnO nanoparticles to oxygen is probably due to the combination of two effects, namely, electronic sensitization and the effect of the action of Pt on the surface of metal oxide ZnO. The sensitization is due to the difference in work function between the areas decorated with platinum and the ZnO nanoparticles. Compared to ZnO, Pt has a higher value of work function. This means that the Fermi level of ZnO nanoparticles smaller than Pt, which results in the transfer of some free electrons of ZnO nanoparticles to particles Pt, since both systems reach thermodynamic equilibrium, a new Fermi level. There is a reduction of free electrons in ZnO nanoparticles leads to increasing the thickness of the depleted layer. Spillover effect due to increased dissociation of oxygen molecules to oxygen ions. With this mechanism a low binding is formed between the oxygen molecule and the platinum atom. This complex can easily be broken down into oxygen ions, by capturing free electrons, which diffuses to surface vacancies of ZnO nanoparticles. Thus, there are more captured electrons, which lead to increase the sensitivity of ZnO nanoparticles.

The nature of the sensory signal $S(O_2)$ of ZnO nanopowders is determined by the state of its self-defect and impurity structure under the conditions of the Debye electrostatic radius. It is shown the tendency to reduce the adsorption ability all ZnO nanopowders with decreasing size nanogranules to 40-60 nm (Fig 5).

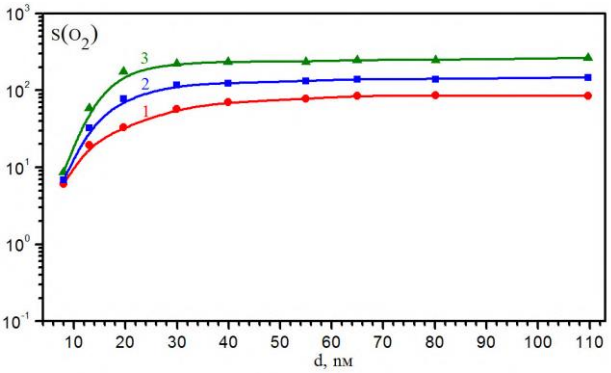

Fig. 5 – Dependence of the magnitude of the sensory signal $S(O_2)$ of nanopowder ZnO (initial (1), Al (3 at.%) doped (2) and laser annealed (3) (E_i = 0.22 J/cm², τ = 10 ns)) of the size of the nanoparticless (d)

The mechanism of the catalytic ability of gold on the surface of ZnO nanogranules beads can be double. On the surface of the gold clusters there is an active interaction of adsorbed oxygen with gold and additional activation of chemosorbed forms of oxygen at the boundary of the three-phase system Au-ZnO-O_2.

4. CONCLUSIONS

The features of photoluminescent properties of ZnO nanopowders doped by noble metals have been studied in various gas environments for use in gas sensing. The physicochemical regularities of the adsorption processes on the ZnO nanopowder surface are observed. The catalytic processes on the surface of ZnO nanogranules doped with noble metal impurities (Ag, Au, Pt) were studied and, the sensitivity of the nanopowder to gases was determined. The tendency to reduce the adsorption capacity ZnO nanopowders with decreasing size nanogranules to 40-60 nm are established. The nature of the sensor signal of ZnO nanopowder is determined by the state of native defects and impurity structure under the conditions of the Debye electrostatic radius.

Вплив поверхневого легування на адсорбційну здатність нанопорошкових металооксидів для сенсорів газів

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У роботі вивчені особливості фотолюмінісцентних властивостей нанопорошкового ZnO в т.ч. лазерномодифікованого та поверхнево легованого домішками благородних металів (Au, Ag, Pt). Досліджено вплив лазерної обробки та поверхневого легування благородними металами на адсорбційну здатність нанопорошкового ZnO та встановлено, що при цьому має місце ріст сенсорної чутливості до газів. Виявлено тенденцію до зниження адсорбційної здатності в міру зменшення розміру наногранул ZnO до 40-60 нм. Вивчено фізико-хімічні закономірності формування адсорбційних поверхневих електронних станів у вихідних і легованих нанопорошках при адсорбції газів.

Ключові слова: Газові Сенсори, Нанопорошки, Металооксиди, Фотолюмінесценція

Влияние поверхностного легирования на адсорбционную способность нанопорошковых металлооксидов для сенсоров газов

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В работе изучены особенности фотолюминесцентных свойств нанопорошкового ZnO в т.ч. лазерномодифицированного и поверхностно легированного примесями благородных металлов (Au, Ag, Pt). Исследовано влияние поверхностного легирования благородными металлами на адсорбционную способность нанопорошкового ZnO и установлено, что при этом имеет место рост сенсорной чувствительности к газам. Установлена тенденция к снижению адсорбционной способности по мере уменьшения размера наногранул ZnO к 40-60 нм. Изучены физико-химические закономерности формирования адсорбционных поверхностных электронных состояний в исходных и легированных нанопорошках при адсорбции газов.

Ключевые слова: Газовые сенсоры, Нанопорошки, Металооксиды, Фотолюминесценция.

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