DEPENDENCE OF Gd-DOPED ZnO SURFACES FLUORESCENT PROPERTIES ON DOPANT CONCENTRATION

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Abstract

Substrates containing zinc oxide and different amounts of gadolinium on the surface of the zinc oxide nano particles for biosensorics were obtained for the first time by the standard sol-gel technique. This is a new material has not yet been extensively studied.

In this paper, we present the results of the photoluminescent response of the zinc oxide surface when it is modified by various amounts of gadolinium during the classical sol-gel method of the surface obtaining. Aspects of creating a modified surface of zinc oxide are highlighted. The used concentrations of gadolinium vary from 1 to 33% caused both quenching and ignition of photoluminescence at the wavelength of 356 nm upon excitation into the absorption band of protein 280 nm. The photoluminescence intensity of zinc oxide without doping is 40 relative value units, the addition of 8% Gd increases the photoluminescence by 7 times (280 r.u.), the addition of 31% Gd decreases the photoluminescence by 40 times compared to undoped zinc oxide. The resulting possibility of increased luminescence when the doping of the films with gadolinium willing, apparently, to increase the ratio "signal/background", and therefore increase the sensitivity of the biosensor with fluorescent registration.

Keywords: Optical biosensors, new materials, zinc oxide substrates, gadolinium, immobilization, photoluminescence, photoluminescence quenching, photoluminescence ignition

1. INTRODUCTION

Recently, scientists have attracted special attention to nanoparticles, which have multifunctionality. Especially nanoparticles that combine several properties, for example semiconducting and luminescent [1]. Such materials contribute to a significant expansion of their application and zinc oxide is one of them.

Zinc oxide is a thermally and chemically stable material, while it is biocompatible. On the basis these properties zinc oxide is in use at biological systems and biosensors.

Due to its unique optical, acoustic and electrical properties, zinc oxide has found application in gas sensors, varistors, and devices for generating surface acoustic waves. Being transparent in a wide spectral range, ZnO has a high resistance to irradiation, it is chemically etched and relatively cheap, which makes it attractive for use in microelectronics [2,3]. Doping of ZnO films with some elements leads to an increase in the width of the forbidden band, an increase in the activation energy of the donor centers and their stability [4]. The authors [5-7] studied the effect of doping with cadmium, magnesium and sulfur on the structural characteristics of ZnO films by an x-ray diffraction method and observed an increase in the lattice parameter c with increasing impurity concentration. Doping elements of the III group - aluminum, gallium, and indium - allows to obtain n-ZnO films with high conductivity. Doping elements of the V group made it possible to obtain ZnO films of p-type conductivity. To successfully create light-emitting devices based on ZnO in the form of p-n junctions or

optoelectronic devices on heterostructures using ZnO, careful studies of the properties of doped ZnO films are necessary.

The preparation of materials based on zinc oxide is currently carried out using various techniques having both advantages and disadvantages. In the present work was used the sol-gel method, one of the most effective methods for the formation of films whose surface is structured at the nanolevel. With its help, materials of ZnO-Gd (III), which have not been studied before, have been obtained. The change in their spectral characteristics has been studied with varying concentrations of dopant-gadolinium ion - from 1 to 35 stoichiometrically percentage. These films are the basis of an optical biosensor device with fluorescent detection, designed to detect biomacromolecules in concentrations of 10-15M and lower by fluorescence spectroscopy method.

1.1. Basic physical and chemical properties of zinc oxide

There are three types of crystals of zinc oxide occurring in nature: hexagonal wurtzite, cubic modification (with NaCl type structure) and cubic sphalerite (zinc blende) [8-11]. The form of sphalerite can be stable when growing zinc oxide on substrates with a cubic lattice. The cubic modification is stable only at relatively high pressures [8-12] among them a phase transition between the hexagonal wurtzite and a NaCl-type structure under certain conditions (pressure and temperature) was studied in detail in [12,13]. The most common form is wurtzite [8,10,11].

Well known that wurtzite-like zinc oxide is a unique semiconductor material with a band gap of 3.37 eV and a significant binding energy of excitons (60 meV), in comparison with the thermal energy of electrons at room temperature (26 meV) [8,10, 11,14-16]. The binding energy of excitons (60 meV) contributes to the attainment of effective laser generation at room temperature. That is why zinc oxide can be effective as laser and light-emitting diodes. Due to the width of the forbidden band 3.37 eV, ZnO can be used for registration of ultraviolet radiation (320 - 400 nm). Besides,

wurtzite zinc oxide is used in the field of photocatalysis [17-19] , biomedical sciences [20-23], in the manufacture of sensory devices [24,25], as an additive to rubber [26,27], is also a catalyst in the production of methanol [28,29].

2. EXPERIMENTAL DETAILS

Synthesis of undoped and Gd doped ZnO was carried out using analytical grade zinc acetate [$(CH_3COO)_2Zn$], gadolinium nitrate [Gd $(NO_3)_3$] and monoethanolamine (C_2H_2NO) in as-received condition. The scheme of the experiment is presented on **Figure 1**. In the synthesis process, a required amount of zinc nitrate was completely dissolved in deionized water and a required amount of aqueous C_2H_2NO solution was added drop by drop to the aqueous zinc nitrate. The solution was stirred and maintained at room temperature for 40 min, and then kept at 60 °C for 2 h. until complete dissolution of the white precipitate For maturing the solution was kept at ambient temperature (22 ± 2)◦C for 2-7 days. After applying, the seed layer sol thickness of 70 nm on a substrate of glass placed in a muffle furnace for drying at a temperature of 140 ◦C for 10 min, then annealed at a temperature of 385◦C for 1 hour. The process of application and drying and annealing were repeated until the desired coating thickness. For the synthesis of Zn1xGdxO (from 0,01 to 0,33) NPs, a

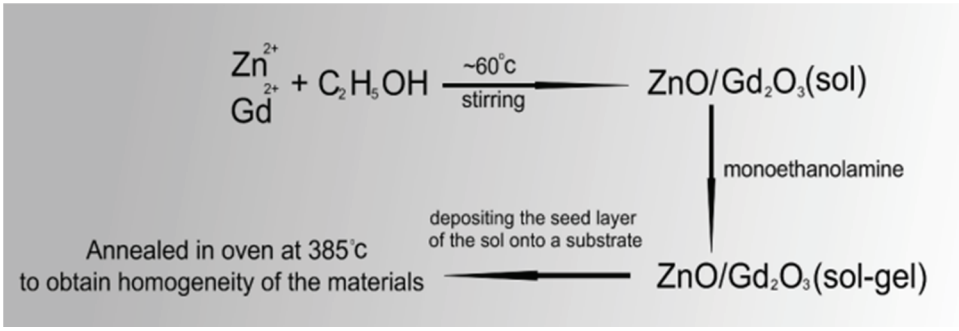

Figure 1 The flow diagram for the preparation of the thin films modified ZnO

calculated amount of gadolinium nitrate was mixed with zinc nitrate solution. The required amount of aqueous C_2H_2NO solution was added drop by drop to the homogenous mixture to get a white precipitate. Further, a similar procedure adopted for the preparation of undoped ZnO.

3. RESULTS AND DISCUSSION

The obtained samples were studied by fluorescence spectroscopy and Raman spectroscopy. **Figure 2** shows the kinetics of fluorescence of a zinc oxide film upon excitation of 280 nm. Within synthesis it intends temperature increased to 385 C until complete absence broadband fluorescence oxide and zinc hydroxide in a mixture of 350-400 nm.

Raman spectroscopy using a 473°nm laser showed the presence of two nodes, E2H and E1L, characteristic of the wurtzite structure and the presence of nanoscale zinc oxide particles with small displacements in cases of doping of film materials with gadolinium [30,31].

The range of doping of zinc oxide structures Gd from 1 to 33% in a weight ratio was chosen. Fluorescence of 20 different concentration values was measured.

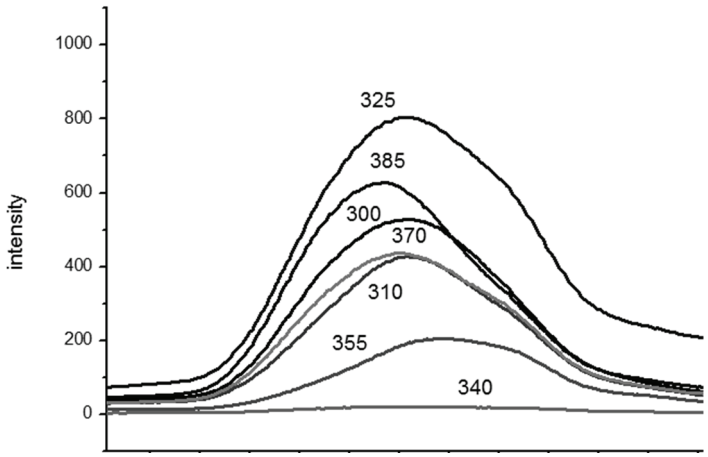

Figure 2 Dependence of the fluorescence intensity of ZnO films on the annealing temperature after depositing the sol on a quartz substrate

It is known that the introduction [32] trivalent cations into the structure of zinc oxide leads to a change in the fluorescent properties of the material due to a change in such parameters as the band gap, the presence of exciton effects, the optical transmission, the exciton binding energy, and the luminescence. However, the change in fluorescent properties is usually linear in nature - ignition or quenching of fluorescence. The mean value of the position of the fluorescence maximum for most concentrations of the dopant was at position 356 ± 3 nm with the exception of the following concentrations of Gd in the film: 7%, 27%, 31%

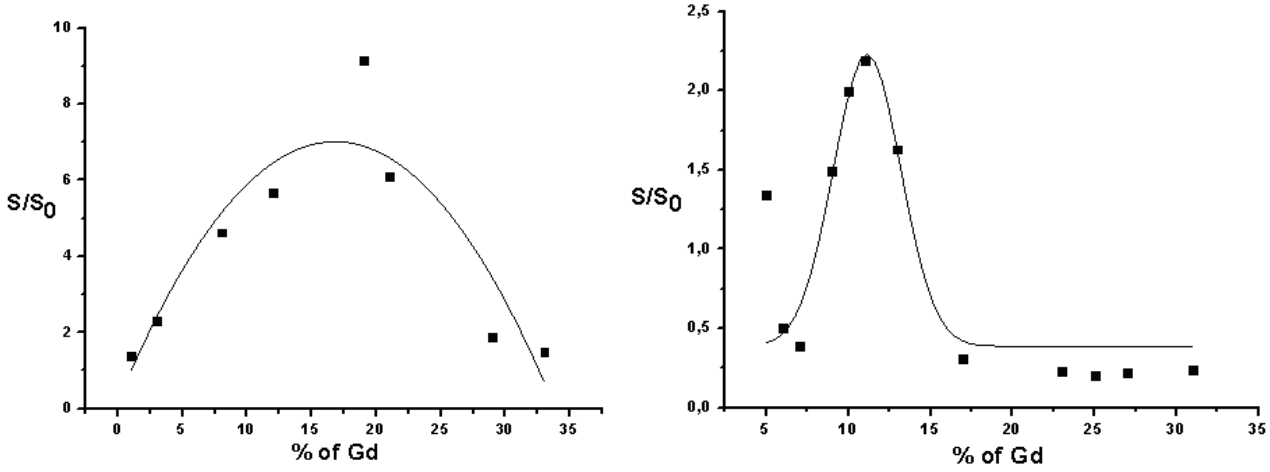

Figure 3 Integral fluorescence area of Gd dope zinc oxide films. Gd concentration 1,3,8,12,19,21,29,33% (a) and 6,7,9,10,11,13,17,23,25,27,31 (b)

In this study, we observed 2 types of changes in the fluorescent properties of the ZnO-Gd hybrid material (**Figure 3**) - ignition and quenching of fluorescence due to a change in one or more of the parameters listed above.

It is possible to isolate 2 fluorescence dependencies on the concentration of gadolinium according to the obtained data: for the range of concentrations 1,3,8,12,19,21,29,33%, and for concentrations, 6,7,9,10,11,13,17,23,25,27,31% which are shown in **Figure 3a** and **Figure 3b**, differing by approximately 2.5 times. We can assume that each dependence means different mechanisms of Gd ion interaction with ZnO structure. If so the concentration value Gd = 5% cannot be tied to any dependence and may mean the both iteration mechanisms work. The additional measurements as such methods as electron microscopy or X-ray structural analysis are needed for the full substantive availability of these mechanisms and their understanding, what is planned in future researches.

4. CONCLUSION

Studies of films of zinc oxide doped with gadolinium on a sol-gel method have been carried out. An extensive range of dopant concentrations revealed a difference in the fluorescent characteristics of the composite material. The explanation of the specificity and concretization of the influence of certain quantities of Gd has great prospects in biosensor technologies.

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