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Modification of Surface of ZnO:Mn Nanocrystals Synthesized by the Cryochemical Method

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The paper presents the results of studies of the effect of surface modification of ZnO:Mn nanocrystals obtained by cryochemical (freeze-drying) method on their physical characteristics. The modification was carried out by annealing the samples in the thermal decomposition products of polyvinyl alcohol, as well as in the hydrogen atmosphere. The concentration of Mn in the samples is 2, 4 and 8 at. %, respectively. It is found that modification of the surface of nanocrystals leads to an increase in their agglomeration properties. X-ray phase diffraction analysis and EPR (electron paramagnetic resonance) method showed that the solubility limit of Mn in ZnO nanocrystals does not exceed 4 at. %. Annealing of samples in the thermal decomposition products of polyvinyl alcohol increases the solubility limit of Mn. Thermal treatment of samples in a hydrogen atmosphere results in ferromagnetic properties at room temperature.

Keywords: Diluted magnetic semiconductor, ZnO, Cryochemical (freeze-drying) method, Hydrogenation, Ferromagnetism.

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1. INTRODUCTION

The method of cryochemical (freeze-drying) synthesis (CCS) is based on the thermal decomposition of salts of the initial components, the solutions of which were previously frozen in the form of small drops and dried by sublimation [1, 2]. The use of this method in the synthesis of diluted magnetic semiconductors, including zinc oxide doped with manganese, allows achieving high homogeneity of distribution of the initial components, as well as to ensure high purity of the technological process. This method does not require expensive equipment, allows getting a sufficiently large amount of the final product and is characterized by low cost. The nanocrystals (NC) obtained by the CCS method have an inactive surface. They are resistant to the environment, are not hygroscopic, and are not agglomerated during storage. Such low reaction properties of NC surfaces are used to stabilize nanopowders from the action of physical and chemical factors in the production of medical preparations [3], as well as in the synthesis of fine, low agglomerated powders – precursors in the production of nanoceramics dioxide zirconium [4]. But this hinders the possibility of practical use of these nanopowders in functional electronic devices as chemical catalysts, gas sensors, etc.

It is known that for improving the reactivity of ZnO NC they are doped with additional admixtures, or their surface is modified by heat treatment of samples in various gaseous media [5, 6]. Studies have shown that modification of the NC surface of semiconductors leads to a change in their defective state and energy levels of the band structure, which affects the appearance of new physical properties. Therefore, the development of methods for modifying the surface of these materials is an urgent problem.

The effect of modifying the surface of ZnO:Mn NC by annealing the samples at the products of the thermal decomposition of polyvinyl alcohol (PVA) and in hydrogen atmosphere on their physical properties is investigated in the study.

2. SYNTHESIS TECHNIQUE AND NANOCRYSTAL RESEARCH METHODS

ZnO:Mn NC with manganese concentrations of 2, 4, and 8 at. % were synthesized according to the technique given in [7]. In this case, sulfates of zinc and manganese with a value of acidity $pH = 2.5$ were used. The solutions were sprayed into droplets of size $d = 20$-100 μm, which were then frozen in liquid nitrogen. The obtained cryogranules were dried in a sublimation unit for 16 hours. To obtain the final product it was necessary to fulfill the heat treatment of dry granules, as a result of which the initial chemical compounds disintegrated. Annealing of the cryogranules was carried out at a temperature of $T = 850$ °C.

To reduce the size of NC, heat treatment was short-term: within 20 min. It was carried out both in air and in the thermal decomposition products of PVA. In this case, a mixture of dry granules and PVA in a ratio of 1:1 was prepared for annealing. Also, the obtained samples were subjected to heat treatment at $T = 550$ °C for 15 min in a stream of a gas mixture of nitrogen and hydrogen in a ratio of 3:1. To preserve the modified state of nanocrystals obtained during the synthesis, the samples were cooled in a stream of gaseous nitrogen, this process was also short-term: within 15 min.

The synthesized samples were studied by electron scanning microscopy using a REMMA-102-02 microscope, X-ray diffraction analysis (XRD) on a DRON-2.0 diffractometer, and electron paramagnetic resonance (EPR) on a Radiopan SE/X-2543 spectrometer. Magnetic properties were studied by vibration magnetometry.

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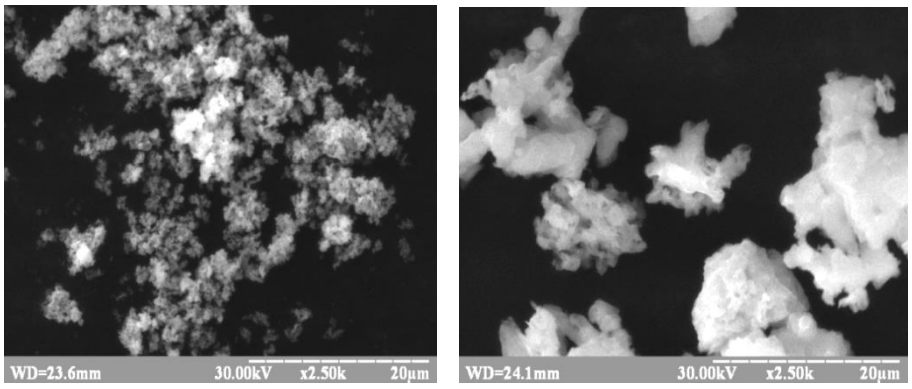
3. STUDY RESULTS AND DISCUSSION

It is known that particle sizes of the synthesized powders are determined by the activity of the NC surface, which causes their tendency to agglomerate. Therefore, according to the effects of various external factors during the synthesis on the size of the powder particles, it can be concluded about their ability to modify the surface of the NC. In the CCS method, the solvent (water molecules) is removed from the frozen granule without destroying its crystal structure formed by freezing the droplet in liquid nitrogen [7]. Therefore, the synthesized NC have a defect-free, inactive surface, and their powders consist of particles of small size. This conclusion is confirmed by the results of studies of samples by electron scanning microscopy (Fig. 1).

Analysis of the results shown in Fig. 1 indicates that the ZnO:Mn NC samples obtained during heat treatment in air have a little ability to agglomerate; therefore, they form small nanopowder particles with $D \sim 1\text{-}2$ μm. During the heat treatment of dry granules in the thermal decomposition products of PVA, the surface of the synthesized NC is modified, increasing their ability to agglomerate. This, in turn, results in an increase in the particle size up to $D \sim 10\text{-}20$ μm. The effect of this thermal annealing is explained by the fact that the active product of the thermal decomposition of PVA is hydrogen. It forms OH^- hydroxyl groups, which are separated from the surface during annealing. Thus, numerous surface defects are formed on the surface of the NC, the presence of which increases the reactivity of the NC and determines the intensity of the agglomeration process.

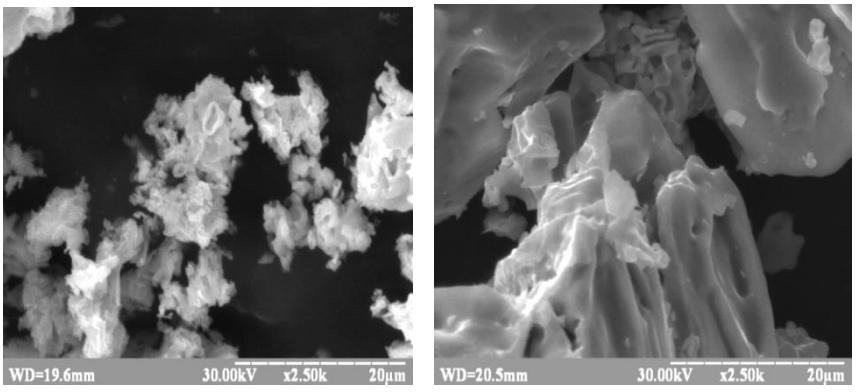
After additional heat treatment of the ZnO nanopowder in a hydrogen atmosphere, the size of its particles also increases several times and reaches a value of $D \sim 15\text{-}50$ μm (Fig. 2). Physical processes during such heat treatment are similar to those that we observed when modifying the surface with an admixture of PVA. During annealing, hydrogen interacts with oxygen on the surface of ZnO NC, forming many defects and hydrogen complexes [8]. This results in an increase in the agglomeration properties of NC and helps to combine them into large particles of ZnO nanopowder. Modification by hydrogen entails not only an increase in the particle size, but also leads to a change in the morphology of their surface (Fig. 2b). Hydrogenation of the NC near-surface layer occurs, and many intrinsic defects appear. This leads to recrystallization of the near-surface layer of powder particles with the formation of a vitreous, amorphous state [9]. At the end of the thermal treatment, the vitreous state of the surface is preserved due to the special cooling conditions of the samples – rapid cooling in an inert gas medium.

It was found with X-ray diffraction examination of the samples (Fig. 3) that ZnO:Mn NC have a hexagonal lattice of wurzite type.



a b

Fig. 1 – The image of ZnO:Mn nanopowder particles (8 at. %) obtained after thermal treatment in air (a) and in the thermal decomposition products of PVA (b)



a b

Fig. 2 – The images of the surface of ZnO NC particles synthesized by heat treatment of dry granules in air (a) and after additional heat treatment in hydrogen atmosphere (b)

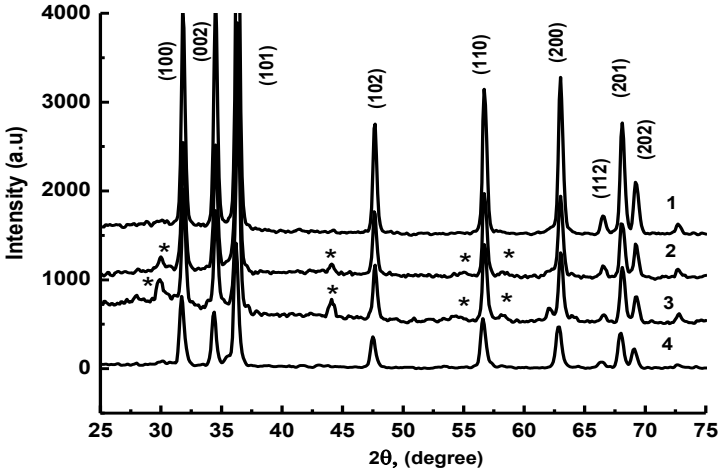


Fig. 3 – X-ray diffraction radiographs of ZnO:Mn NC obtained after thermal treatment in air with concentration of Mn 2 at. % (1), 4 at. % (2), 8 at. % (3) and 8 at. %, (4), after annealing in the thermal decomposition products of PVA. The * symbol is the secondary phase of Mn_2O_3

Table 1 – The crystal lattice parameters, the average size of the NC, the volume of the unit cell ZnO and ZnO: Mn NC

Concentration Mn, at. %	**The crystal lattice parameters, *a* and *c*, the average NC size, *D* and the volume of the unit cell, V**			
	***a*, Å**	***c*, Å**	***D*, nm**	***V*, Å³**
0	3.2465	5.2010	69.5	47.46
2	3.2457	5.2003	68.4	47.44
4	3.2457	5.2023	66.5	47.46
8	3.2436	5.1985	65.0	47.36

There are no additional lines of reflection of the synthesis products at the above presented radiographs. This indicates that the duration of heat treatment (20 min) is sufficient for complete decomposition of the initial components. For the obtained samples, the lattice parameters (a and c), the average NC size (D) and the unit cell volume (V) were calculated (Table 1). The size of the synthesized ZnO:Mn NC was $D \sim 69$-65 nm. As well known, the monocrystalline ZnO obtained under equilibrium conditions crystallizes in the wurzite structure with the unit cell parameters: $a = 3.249$ Å, $c = 5.205$ Å [10], for which the volume value is $V = 47.58$ Å³. A much smaller value of the unit cell volume (V) in the synthesized NC indicates the presence of an internal deformation state in them, which may be due to the short-term duration of heat treatment.

X-ray diffraction analysis (Fig. 3) shows that there are no secondary phases in samples of ZnO:Mn NC with a Mn concentration of 2 at. %. The secondary phase of Mn_2O_3 appears at admixtures concentrations of Mn 4 and 8 at. %. This fact indicates that the solubility limit of Mn in samples synthesized under normal conditions by annealing in air does not exceed 4 at. %. But in the ZnO:Mn NC sample (8 at. %), which was obtained by annealing in the thermal decomposition products of PVA, the secondary phase of Mn_2O_3 disappears (Fig. 3, curve 4). The result obtained indicates that the PVA admixtures activate the process of doping ZnO with manganese, and the solubility limit of Mn in the samples increases. This conclusion is confirmed by the results of the analysis of the EPR spectra of ZnO:Mn NC (Fig. 4).

In NC with admixture concentration of Mn 2 at. % (Fig. 4a), modification of the sample surface by annealing in the thermal decomposition products of PVA leads to an increase in the intensity of the hyperfine structure lines of the EPR spectrum of Mn^{2+} ions. This is explained by the fact that such annealing significantly affects the process of doping ZnO with manganese admixtures, increasing the number of Mn^{2+} ions that replace zinc vacancies in the sites of the ZnO crystal lattice. Further increase in the Mn concentration in the samples reduces the distance between the Mn^{2+} ions located at the ZnO crystal lattice sites, which is manifested in an increase in the intensity of the EPR line and further concentration broadening of the lines (Fig. 4b, c).

In the case if concentration of the admixture Mn is 8 at. %, the hyperfine structure of the EPR spectrum of Mn^{2+} ions is not recorded at all; instead, a single broad and intense absorption line is recorded (Fig. 4c).

The effect of surface modification of ZnO:Mn NC with a Mn concentration of 4 at. % after annealing of the samples in a hydrogen atmosphere on the structure of the EPR spectrum is shown in Fig. 4d. In this case, the intensity of the lines of the hyperfine structure of the EPR spectrum of Mn^{2+} ions also increases.

This result is due to the action of hydrogen, which changes the defective state of the NC surface, increases the number of oxygen vacancies. This increases the number of Mn^{2+} ions, which replace zinc ions at the ZnO crystal lattice sites. Comparing the EPR spectra of the ZnO:Mn NC samples with the admixture concentration of Mn 4 at. % to be heat treated by annealing in the thermal decomposition products of PVA (Fig. 4b) and in the hy-

drogen atmosphere (Fig. 4d), it can be concluded that NC surface modification using PVA is more effective. This is due to the fact that it has a volumetric nature in what happens during the synthesis of NC. The effect of hydrogen at additional heat treatment of samples at a temperature $T = 550$ °C for 15 min has a surface character; therefore the effect on the doping process of ZnO NC with manganese admixtures is much smaller.

Fig. 5 shows the results of studies of the effect of the modification of the surface of ZnO:Mn NC on their magnetic properties. Thermal annealing with PVA admixture leads to a significant increase in the paramagnetic properties of the samples (Fig. 5a). This is due to an increase in the amount of paramagnetic impurity Mn^{2+} in the sites of the ZnO crystal lattice, which, in turn, is confirmed by the results of studies of samples by the EPR. At the same time, a small ferromagnetic component with the value of the coercive force $H_c = 50$ Oe also appears (Fig. 5a, inset).

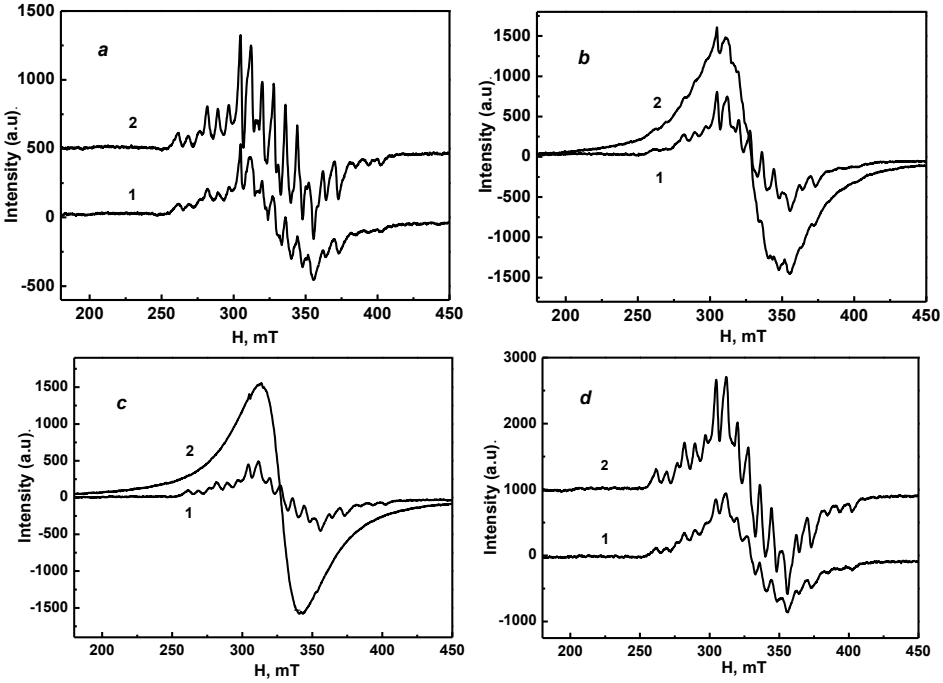


Fig. 4 – EPR spectra of ZnO:Mn NC: concentration of Mn 2 at. % (a), 4 at. % (b), 8 at. % (c), 1 – heat treatment in air, 2 – annealing in the thermal decomposition products of PVA; (d) a sample with concentration of Mn 4 at. % synthesized in air (1) and after additional annealing in a hydrogen atmosphere (2)

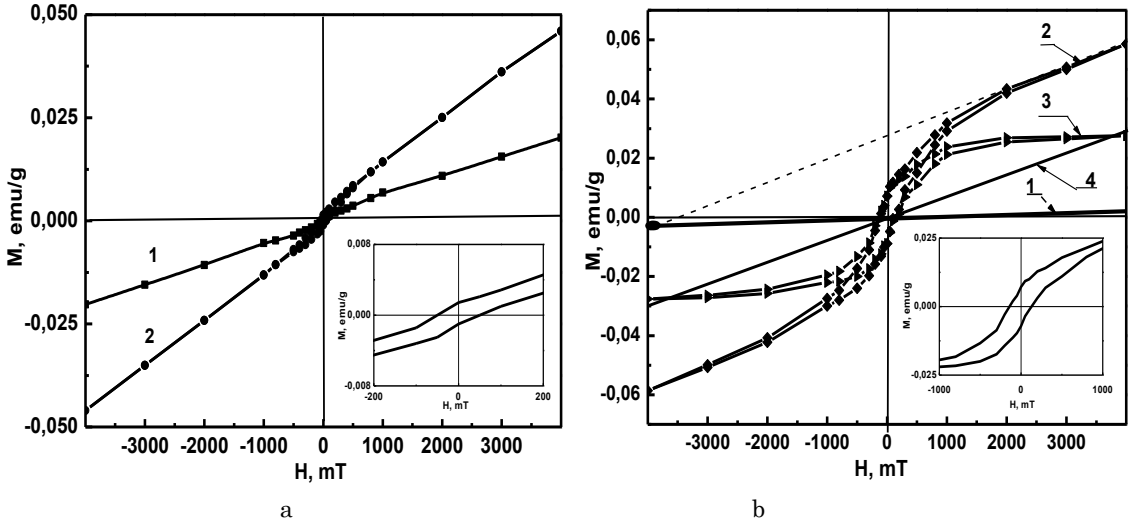


Fig. 5 – Magnetization of the ZnO:Mn NC sample with a concentration of Mn 4 at. %. a – the effect of annealing in the thermal decomposition products, of PVA: 1 – the sample is synthesized in air, 2 – the sample after annealing; b – the effect of annealing in a hydrogen atmosphere: 1 – the sample is synthesized in air and annealed at $T = 850$ °C for 1 hour, 2 – the sample after annealing, 3, 4 – the ferromagnetic and paramagnetic components of magnetization of the sample 2. The insets show magnetization curves of the samples after annealing (samples 2) at high resolution

From Fig. 5b (curve 1) it follows that the sample of ZnO:Mn NC with a concentration of Mn 4 at. % synthesized in air at $T = 850$ °C has no ferromagnetic properties. After heat treatment of this sample in a hydrogen atmosphere at a temperature $T = 550$ °C for 15 min, ferromagnetic properties appear at room temperature (Fig. 5b, curve 2). In this case, the magnetization curve of the sample has no saturation state, which indicates the presence of a paramagnetic phase in the ferromagnetic sample. The latter can be distinguished, given that the paramagnetic properties of the samples have a linear dependence on the magnetic field, as well as the fact that they disappear at zero magnetic field. This fact allows to build a magnetization curve of the ferromagnetic component (curve 3) and determine the maximum magnetization of the sample in the saturation state $M_s = 0.022$ emu/g. In this case, the value of the coercive force $H_c = 150$ Oe (Fig. 5b, inset). A similar magnetization value ($M_s = 0.016$ emu/g) was obtained in [11] after heat treatment in a hydrogen atmosphere at a temperature $T = 500$ °C of a paramagnetic ZnO powder doped with Mn concentration of 2 at. %.

4. CONCLUSIONS

The studies have shown that the modification of the surface of ZnO:Mn NC by annealing the samples in the thermal decomposition products of PVA and in the atmosphere of hydrogen significantly affects their physical properties. As a result of such treatment, the tendency of NC to agglomerate increases, which leads to an increase in the particle size of the synthesized nanopowder.

It is shown that the thermal treatment of samples in the thermal decomposition products of PVA activates the process of doping ZnO with manganese, increasing the solubility limit from 4 to more than 8 at. %. The thermal treatment of ZnO:Mn NC in a hydrogen atmosphere at a temperature of $T = 550$ °C leads to the appearance of ferromagnetic properties in samples at room temperature.

On the basis of the obtained results, ZnO:Mn NC can be synthesized with predictable physical characteristics for use in nanoelectronic devices.

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Модифікація поверхні нанокристалів ZnO:Mn, синтезованих кріохімічним методом

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В роботі представлені результати досліджень впливу модифікації поверхні нанокристалів ZnO:Mn шляхом відпалу зразків в продуктах термічного розкладу полівінілового спирту та в атмосфері водню на їх фізичні властивості. Нанокристали ZnO:Mn було отримано методом кріохімічного синтезу, концентрація домішок Mn в них складала 2, 4 та 8 ат. % відповідно. Модифікація зразків приводила до підвищення їх агломераційних властивостей та зміни морфології поверхні. Методом рентгенофазового аналізу встановлено, що межа розчинності Mn в нанокристалах ZnO не перевищує 4 ат. %. Методом ЕПР доведено, що відпал зразків у продуктах термічного розкладу полівінілового спирту збільшує межу розчинності Mn. Відпал зразків у продуктах термічного розкладу полівінілового спирту та в атмосфері водню приводить до появи в нанокристалах ZnO:Mn феромагнітних властивостей при кімнатній температурі.

Ключові слова: Розбавлений магнітний напівпровідник, ZnO, Кріохімічний (леофільний) метод, Гідрогенізація, Феромагнетизм.