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Preparation of zinc oxide nanopowders doped with manganese, which have ferromagnetic properties at room temperature.

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The paper analyzes magnetic properties, crystal structure and EPR spectra of ZnO:Mn nanocrystals obtained by ultrasonic spray pyrolysis. It has been investigated influence of the type of carrier gas - air and nitrogen on the magnetic properties of the nanocrystals at room temperature. Also it has been investigated effect of heat treatment at T = 800°C and phase of Mn_2O_3 presented in the nanocrystals of ZnO:Mn, on the magnetic properties.
Keywords: magnetic properties, spray pyrolysis, EPR spectra, nanocrystals.

Исследованы магнитные свойства, кристаллическая структура и спектры ЭПР нанокристаллов ZnO:Mn, полученных методом ультразвукового пиролиза аэрозоля. Исследовано влияние типа газа-носителя (воздух, азот) на магнитные свойства нанокристаллов при комнатной температуре. Определено влияние термообработки при T = 800°C и фазы Mn_2O_3, присутствующей в нанокристаллах ZnO:Mn, на магнитные свойства образцов.

Отримання нанопорошків оксиду цинку, легованих марганцем, які мають феромагнітні властивості при кімнатній температурі. *В.Ю.Воровський, О.В.Коваленко, О.І.Кушнерьов, О.В.Хмеленко*

Досліджено магнітні властивості, кристалічну структуру та спектри ЕПР нанокристалів ZnO:Mn, отриманих методом ультразвукового піролізу аерозолю. Досліджено вплив газу-носія (повітря, азот) на магнітні властивості нанокристалів при кімнатній температурі. Визначено вплив термообробки при T = 800°C та фази Mn_2O_3, яка присутня у нанокристалах ZnO:Mn, на магнітні властивості зразків.

1. Introduction

Zinc oxide (ZnO) doped with transition metals, for example, with manganese (Mn) belongs to the Diluted Magnetic Semiconductors (DMS) that are drawn attention due to possibility of construction spintronic devices for storing and recording of information on their basis. Such DMS as ZnO:Mn combines electric and ferromagnetic properties with optical transparency, thermal and radiation resistance, that is promising for practical use. After theoretical prediction of the ferromagnetic properties existence at the Curie temperature above room temperature in ZnO:Mn based DMS [1], zinc oxide began to draw even more attention of researchers. For the first time, experimental confirmation of this prediction was made on the samples obtained by the ceramic method [2]. It was found ferromagnetic properties at room temperature that disappeared after heat treatment at temperature $T > 500$°C. Specific magnetization value in the saturation state was not significant — $M_s = 0.007$ Gs·cm^3/g.

Different methods of synthesis were used to obtain DMS at the Curie room temperature. Thus, by the liquid ceramic method [3] there were obtained films of ZnO:Mn with concentration of manganese up to 2 atom.

% which after annealing at temperature $T = 400$°C exhibited ferromagnetism at the room temperature. The specific magnetization in the saturation state was $M_s = 2.5$ Gs·cm^3/g. Annealing of the samples at temperature $T > 500$°C also led to disappearance of ferromagnetic properties. In [4], nanocrystals (hereinafter NC) of ZnO:Mn with manganese concentration of 1 atom. % with ferromagnetic properties at the room temperature were synthesized by the colloidal method at temperature $T = 60$°C. The specific magnetization of such samples in the saturation state was $M_s = 0.65$ Gs·cm^3/g. The magnetic properties of the samples were disappeared after annealing at temperature $T = 500$°C inside oxygen or argon. In [5], the NC of ZnO:Mn at temperature $T = 80$°C was obtained by the compatible chemical deposition method from zinc nitrate and manganese chloride solutions in methanol. The sample with manganese concentration of 2 atom. % had ferromagnetic properties at the room temperature — $M_s = 0.09$ Gs·cm^3/g. The above mentioned literature sources analysis indicates that ferromagnetic properties at the room temperature in the NC of ZnO:Mn occurs in conditions of the low-temperature synthesis at concentrations of manganese up to 2 atom %. Increase of the synthesis temperature up to $T_s = 500$°C or annealing of the samples at temperature $T > 500$°C results in decrease or loss of the magnetic properties.

To the above mentioned it should be added that conclusions made in the study [1] indicates that the ferromagnetic properties in the NC of ZnO:Mn can occur when creating *p*-type of conductivity in them. The difficulty of obtaining ZnO with the *p*-type of conductivity is that zinc oxide has high number of natural spot defects that determine the *n*-type of conductivity. It is also prone to the effect of self-compensating impurities which determine the *p*-type of conductivity. In the study [6], a possibility of creating the *p*-type of conductivity in films ZnO:Mn was shown due to their nitrogen doping. The method of ultrasonic aerosol pyrolysis (UAP) was used to obtain such films. In this case, an aqueous solution of zinc and manganese acetate with concentration of 0.5 mole (0.5 M) was used, in which to form the acceptor impurity the ammonium acetate concentration of 2.5 M was added to the nitrogen. According to the authors, doping with nitrogen leads to substitution of ZnO oxygen ions in the crystal cell by nitrogen ions and occurrence in the NC of ZnO:Mn the *p*-type conductivity. However, the study of the obtained films showed that they do not have ferromagnetic properties at the room temperature. The ferromagnetism in such samples arises at temperatures of liquid nitrogen and lower temperatures. The UAP method was also used to synthesize the ZnO:Mn films in other studies [7, 8] but the magnetic properties at the room temperature in such samples were not detected. In the films of ZnO:Mn obtained by this method at $T_s = 400$°C from solutions of zinc nitrates and manganese with concentrations of manganese of 7 atom. %, the ferromagnetic properties were observed at the temperature of liquid helium. The value of the specific magnetization in the saturation state for such samples was relatively low: $M_s = 3 \cdot 10^{-5}$ Gs·cm^3/g.

It is known that the UAP method is based on thermal decomposition of solution of corresponding components [9]. The solid phase is created over the short period of time due to evaporation of the solvent and thermolysis of the salts of the source components in atmosphere of the carrier gas and in the most cases the air is used as carrier gas. Therefore, in such a method, there are possibilities of influencing the physical properties of synthesized NC of ZnO by changing the carrier gas type of. In the study [10], possibility of the *p*-type of conductivity formation in the NC of ZnO:Mn was shown by the UAP method when used nitrogen as the carrier gas due to occurrence of acceptor-type defects in the formation in inert atmosphere of the ZnO crystal cell. Influence of this factor on the conditions for the NC of ZnO doping with the acceptor impurities and on magnetic properties of the samples requires further researches.

The purpose of this work is to obtain by UAP method the NC of ZnO:Mn with ferromagnetic properties at room temperature and study their magnetic characteristics.

2. Experimental

We carried out the NC synthesis of pure ZnO and ZnO:Mn in the form of nanopowder when air or nitrogen was used as carrier gas. In this synthesis it was used an aqueous solution of zinc nitrates (0.3 M) and manganese (0.01 M). The solution was sprayed with an ultrasonic emitter at frequency of 1.7 MHz. The aerosol particles of 1–5 μm in diameter in the carrier gas stream were fed into an oven heated to the synthesis temperature where solvent evapo-

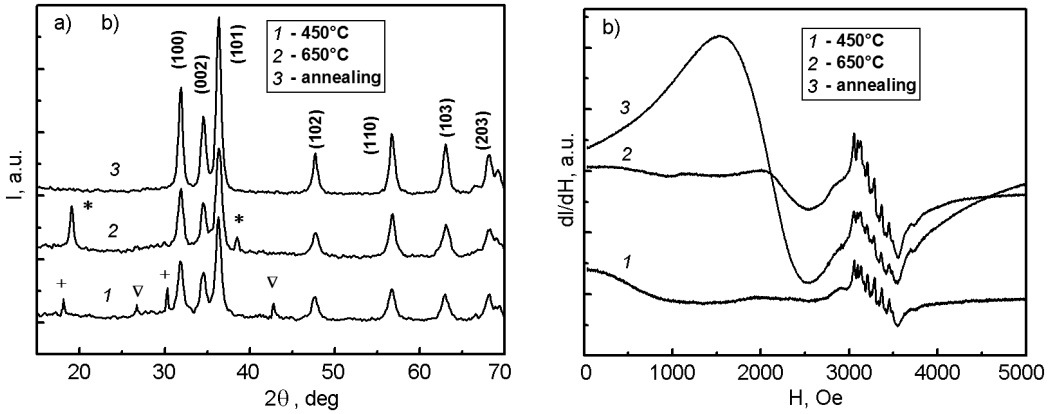

Fig. 1. Data of XRD (a) of ZnO:Mn NC and their spectra of EPR; (b) — samples obtained using nitrogen as carrier gas at T_s = 450°C (*1*), T_s = 650°C (*2*) and after annealing in air at T = 800°C (*3*). In XRD diagrams of the, the mark "+" is phase of $ZnMn_2O_4$, the mark ∇ is phase of MnO_2, the mark * the — phase Mn_2O_3.

ration and thermal decomposition of the components occurred, which resulted in the synthesis of the final product. The carrier gas flow was set at value of 4.5–4.6 liters per hour with help of gas variable area flow meter. The synthesis term was about 7–10 seconds. The particles were obtained in the form of spherical granules and were isolated from water vapor and other synthesis products by means of filter heated up to T = 200–250°C. The samples of pure ZnO NC were obtained at temperature T_s = 650°C and ZnO:Mn with concentration of manganese of 2.0 atom % at synthesis temperature T_s = 450°C and 650°C. The effect of annealing in air at T = 800°C within 1 h on physical properties of the samples was analyzed. The samples were examined by X-ray diffraction analysis (XRD), EPR and vibration magnetometry methods.

3. Results and discussion

Analysis of obtained XRD data (see Fig. 1) showed that the studied samples had crystal cell of the wurtzite type. The average crystal size that calculated by the Scherrer equation [11], for the NC of ZnO synthesized at T_s = 650°C is 38 nm and for NC of ZnO:Mn synthesized at T_s = 450°C and T_s = 650°C, respectively, 36 and 38 nm.

To obtain the one-phase NC of ZnO:Mn by UAP method is quite complicated. Under the given synthesis conditions and concentration of the dopant — manganese of 2 atom %, according to the XRD results, it was found that at the synthesis temperature T_s = 450°C in the samples there is an additional phase of zinc spinel $ZnMn_2O_4$ (2θ = 18.3°C and 29.3°C) and MnO_2 phase (2θ = 26.7° and 42.5°), and at the synthesis temperature T_s = 650°C in the samples the Mn_2O_3 phase (2θ = 19.0° and 38.5°) was present. After annealing the samples in air at T = 800°C within 1 h in the NC of ZnO:Mn, these phases disappear and the NC size increases up to 110 nm.

By EPR method there were found that resonance absorption lines in the NC of ZnO are missing. In the spectra of EPR the NC of ZnO:Mn obtained at T_s = 650°C (Fig. 1), there were two broad absorption lines. The first one is intensive, nonstructural and situated in the field of low magnetic field values with g = 4.287. Based on the value of g factor, the presence of such line may indicate that big amount of acceptor type defects have appeared in the NC of ZnO:Mn. This, in turn, can be condition for appearance of the *p*-type conductivity. This EPR line disappears after annealing of the NC at T = 800°C in air within 1 h. It is clear that such heat treatment due to peroxidation and recrystallization processes reduces the amount of the acceptor type defects and reproduces in the NC of ZnO:Mn the *n*-type of conductivity. The second intensive and structured line of the EPR spectrum is located in the area of H = 3250 oersteds. It consists of six components characteristic for the ultra-fine structure of the EPR spectra of Mn^{2+} ions. The spectroscopic splitting factor of this line is equal to g = 2.001 and the constant of the superfine structure A = 65.94 oersted. This is confirmed by the fact that ZnO doping with manganese ions Mn^{2+} during the synthesis. The same characteristic lines were present in the spectra of EPR of the ZnO:Mn NC and after annealing.

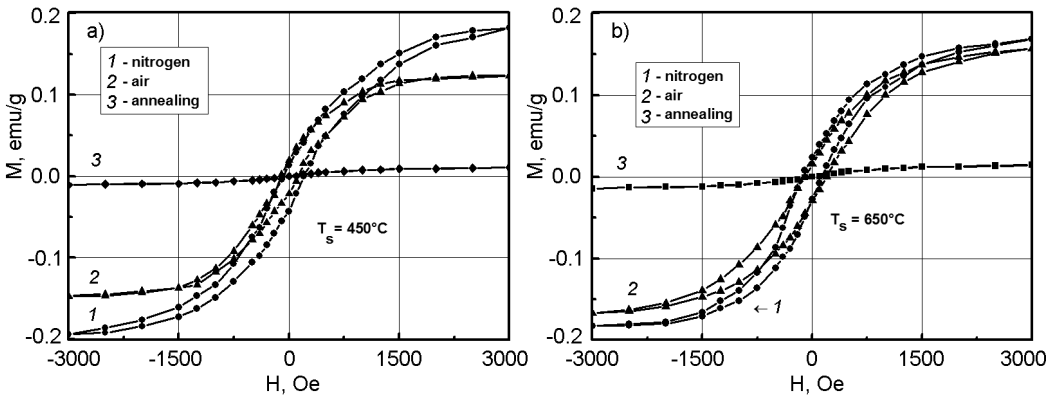

Fig. 2. ZnO:Mn NC magnetization curves obtained at T_s = 450°C (a) and T_s = 650°C (b) in nitrogen (*1*), air (*2*) as carrier gases before and after annealing in air at T = 800°C (*3*).

In the EPR spectrum of the ZnO:Mn NC obtained at T_s = 450°C, the first absorption line in the field of low values of the magnetic field is missing. The second structured EPR line which is associated with the presence of paramagnetic admixture of Mn^{2+} ions in the NC of ZnO:Mn is present and similar in comparison with the samples obtained at T_s = 650°C. After annealing, the EPR spectra of these samples become the same (Fig. 1). In them only the EPR line of Mn^{2+} ions remains. Its intensity increases, which indicates an increase in the concentration of Mn^{2+} ions in the samples. This, in turn, may be connected with disintegration of $ZnMn_2O_4$, MnO_2 and Mn_2O_3 phases at annealing and additional dissolution of Mn^{2+} ions in ZnO cell. These results can be explained by the peculiarities of the synthesis by UAP method. The formation of the basic phase of ZnO NC and impurity phases occurs in non-equilibrium conditions for several seconds with formation of the big amount of defects in the crystal cell. In such conditions only small portion of manganese has the ability to diffuse into the crystalline cell of ZnO, mainly on the surface. The main part of manganese generates phases of $ZnMn_2O_4$, MnO_2 and Mn_2O_3, which are located between the NC of ZnO.

These studies have shown that the NC of ZnO:Mn synthesized by us have ferromagnetic properties at room temperature, while the NC of pure ZnO do not exhibit such properties. The magnetization curves of ZnO:Mn NC, the value of specific magnetization in the state of saturation σ_s and the value of coercive force H_c (Fig. 2) were obtained using a vibration magnetometer. The obtained values of the specific magnetization in the saturation state M_s for the NC

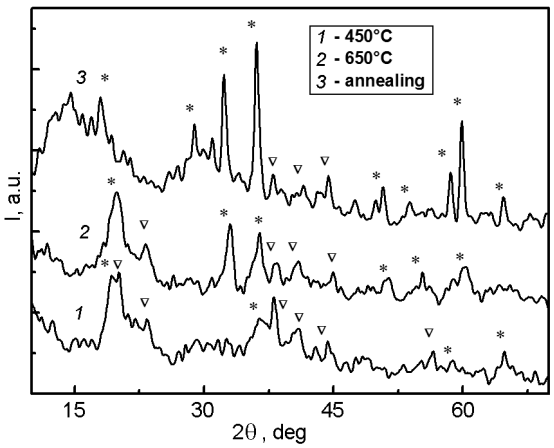

Fig. 3. The data of XRD samples obtained by UAP method from manganese nitrate with air as carrier gas at T_s = 450°C (*1*), T_s = 650°C (*2*) and after annealing in air at T = 800°C (*3*). On XRD diagrams, the mark ∇ is the MnO_2 phase, the mark * is Mn_2O_3 phase.

of ZnO:Mn synthesized at T_s = 450°C are 0.18 and 0.12 Gs·cm^3/g, respectively, for nitrogen and air as carrier gas. For synthesized samples at T_s = 650°C, the parameter M_s = 0.16 and 0.15 Gs·cm^3/g, respectively, for nitrogen and air as carrier gas. The coercive force average value for all samples is within the range of H_c = 120÷150 oersteds. Analyzing the above mentioned data it is possible to conclude that the type of carrier gases more influences on the magnetic characteristics of the samples that are synthesized at lower synthesis temperature. It should be emphasized that samples synthesized in nitrogen as the carrier gas are characterized by bigger values of the parameter M_s. Annealing in the air at T = 800°C results in disappearance of the ferromagnetic properties of the samples (see Fig. 2).

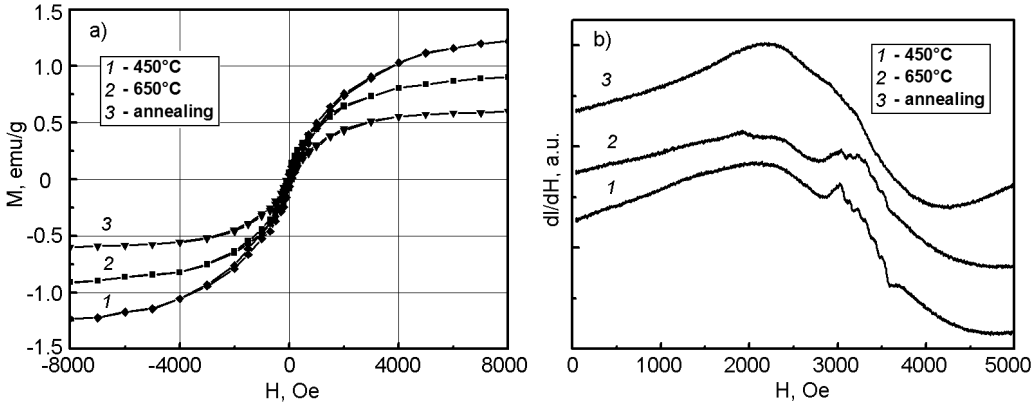

Fig. 4. Magnetization curves of samples consisting of NC phases of MnO_2 and Mn_2O_3 mixture (a) and their spectra of EPR (b): the samples are synthesized using air as carrier gas at T_s = 450°C (*1*), T_s = 650°C (*2*) and after annealing in air at T = 800°C (*3*).

It is known that manganese oxides with different levels of valence (MnO_2, Mn_2O_3) which can affect the ferromagnetic properties of synthesized materials [12] are formed by the thermal decomposition of manganese nitrate. Taking into account the presence of the MnO_2 phase in the NC of ZnO:Mn, we performed additional studies on the possible influence of this phase on the magnetic properties of the samples obtained. For this by UAP method it was synthesized the NC from solution of manganese nitrate with concentration of 0.06 M at the synthesis temperatures T_s = 450°C and T_s = 650°C with the use of air as the carrier gas. The XRD data showed that chemical composition of the obtained NC is heterogeneous. It consists of the MnO_2 and Mn_2O_3 phases (see Fig. 3).

The average size of the NC calculated by the Scherrer equation [11] did not exceed 28 nm. At the same time, in the NC obtained at temperature T_s = 450°C, the MnO_2 phase dominates and the synthesis at T_s = 650°C leads to increase in the amount of the Mn_2O_3 phase. This result is in agreement with the known process of thermal decomposition of MnO_2 polycrystalline powder, according to which the Mn_2O_3 phase begins to form at temperatures T_s > 530°C. The average size of the NC increased up to 37 nm after annealing in air at T = 800°C with the Mn_2O_3 phase in the samples becoming dominant (see Fig. 3).

Despite the fact that polycrystalline MnO_2 and Mn_2O_3 do not exhibit magnetic properties at room temperature, they have been detected in the NC synthesized by us (see Fig. 4). The value of the specific magnetization in the saturation state was M_s ~ 1.25 Gs·cm^3/g and practically in ten times exceeded the value of this parameter for NC of ZnO:Mn (σ_s ~ 0.15 Gs·cm^3/g). The average value of coercive force for all samples was within the range of H_c = 80÷100 oersted. In addition, the ferromagnetic properties of these samples after the annealing did not disappear but rather increased. This behavior of the MnO_2 and Mn_2O_3 NC phases requires further study. But these results make it possible to conclude that these phases can affect the magnetic properties of ZnO:Mn NC despite their low concentration. It should be noted that zinc spinel $ZnMn_2O_4$ in nanocrystalline state may also acquire ferromagnetic properties [13]. The fact of the ferromagnetism disappearance in the NC of ZnO:Mn after annealing can be associated with the disappearance of $ZnMn_2O_4$, MnO_2 and Mn_2O_3 phases due to dissolution of manganese in the crystal cell of ZnO.

The EPR spectra of the NC phase of MnO_2 and Mn_2O_3 phases (see Fig. 4) revealed the presence of superposition of two broad absorption lines which at annealing increase in intensity. In their behavior at heat treatment and in terms of *g*-factors, they are not related to the intensive line in EPR with g = 4.2874, which we observed in the NC of ZnO:Mn synthesized in nitrogen as the carrier gas (see Fig. 1). In the EPR spectra of the ZnO:Mn NC samples due to low concentration of the MnO_2 impurity phase, the first line of EPR which is located in the area of low magnetic field value, is not observed at all. The second line of EPR which is registered in the area of H = 3200÷3300 oersteds, at the low temperatures of the NC synthesis (T_s = 450°C) has weak structure of six lines. It may be

connected with presence of Mn^{2+} ions in the studied samples. With increasing the synthesis temperature (T_s = 650°C) and annealing of the samples (T = 800°C), this structure disappears.

4. Conclusions

The obtained experimental results make it possible to draw the following conclusions. By the UAP method NC of ZnO:Mn with ferromagnetic properties at room temperature were synthesized. These magnetic properties of the ZnO:Mn NC are not related to increase of concentration of the paramagnetic impurity Mn^{2+}, since at annealing the concentration of the Mn^{2+} ions increases and the magnetic properties of the ZnO:Mn NC disappears. The presence of MnO_2 and $ZnMn_2O_4$ phases in the NC of ZnO:Mn can affect the magnetic properties of the obtained samples. In the case of annealing with the disappearance of these phases and their influence on the magnetic properties the NC of ZnO:Mn disappears, which, in turn, causes an increase in the concentration of Mn^{2+} ions in the ZnO cell according to the EPR data. However, in our opinion, the above mentioned phases cannot determine the ferromagnetic properties of the ZnO:Mn NC in full scope to the fact that they are present in the synthesized samples in very low concentrations. The absorption line in the EPR spectrum with g = 4.287 is related to the NC of ZnO:Mn but not to the MnO_2 phase. It can testify the presence of the p-type conductivity in the NC of ZnO:Mn which are synthesized in non-equilibrium conditions with use nitrogen as carrier gas. This line disappears during annealing due to recrystallization and pre-oxidation processes. The presence of this line can be assumed as certain supposition for the appearance of ferromagnetic properties of the NC of ZnO:Mn but it does not determine the ferromagnetic properties of the samples since such properties are registered in the NC where there is no such line in the EPR spectra. Such line may indicate that big amount of the acceptor-type defects arises in the synthesized NC of ZnO:Mn under the non-equilibrium conditions, which, in turn, can redistribute electronic states on the surface of the NC. This can be attributed to the main contribution to the ferromagnetic properties appearance in the NC of ZnO:Mn. This assumption coincides with the hypothesis made in the study [14] that ferromagnetism is a general feature of non-magnetic oxides in nanosized state and its reason is the rise of exchange interactions between unpaired spins of electrons which are supplied by oxygen vacancies from the surface of the NC. During annealing in air the number of surface defects decreases and hence the number of oxygen vacancies decreases, resulting in disappearance of the ferromagnetic properties in the NC of ZnO:Mn.

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