

PECULIARITIES OF DOPING OF ZnO:Mn NANOCRYSTALS DURING THEIR SYNTHESIS BY THE AEROSOL PYROLYSIS METHOD

O.V. Kovalenko, V.Yu. Vorovsky, O.V. Khmelenko, Ye.G. Plakhtii

*Oles Honchar Dnipro National University, Dnipro, Ukraine
e-mail:kovalenko.dnu@gmail.com*

Samples of ZnO:Mn nanocrystals with Mn concentrations of 2 and 4 at.% were synthesized by ultrasonic aerosol pyrolysis. The synthesis was carried out at 550°C using aqueous solutions of zinc and manganese nitrates. The samples obtained were subjected to heat treatment at 550°C and 850°C in air for 1 hour. The study of the samples by XRD and EPR methods shows that during the synthesis the process of doping ZnO nanocrystals with manganese occurs only partially, on the surface, in the near-surface layer. Residues of the Mn impurity are located on the surface of nanocrystals and appear during annealing at 550°C in the form of manganese oxides (Mn₂O₃). During heat treatment at 850°C, decomposition of Mn₂O₃ and bulk doping of ZnO:Mn nanocrystals occur.

Keywords: zinc oxide, manganese, ultrasonic aerosol pyrolysis, nanocrystal, heat treatment.

Received 19.10.2020; Received in revised form 23.11.2020; Accepted 02.12.2020

1. Introduction

In recent years, dilute magnetic semiconductors (DMS) have attracted special attention of researchers in connection with the possibility of their use in spintronics [1]. A large number of works have been devoted to the study of DMS obtained by doping ZnO with transition metals. This is due to the fact that in [2] the ferromagnetic properties of Mn-doped ZnO nanocrystals (NC) at room temperatures were predicted theoretically. Experimentally this prediction was proved in [3]. The results were obtained [4], which showed the existence of ferromagnetic properties in ZnO:Mn NC samples synthesized by aerosol spray pyrolysis (ASP) at room temperatures. These properties disappeared after annealing the samples in air at $T = 800^\circ\text{C}$ and depended on the technological conditions of synthesis.

The ASP method compares favorably with all other methods for the preparation of DMS in that it is simple, it allows one to obtain nanomaterials in the form of both powder and films. This method is based on the thermal decomposition of aerosol droplets of the initial solution as they pass through the thermal zone. A feature of the synthesis of NC by the ASP method is that NC are formed within a short period of time in the volume of a microdroplet, under nonequilibrium conditions. This leads to the appearance of a large number of defects in NC, which significantly affect the physical properties of the synthesized product. In this case, it is important to study the possibility of doping NC with impurities in a short time, under nonequilibrium crystallization conditions during synthesis. The paper presents the results of studying the doping process of ZnO:Mn NC obtained by the ASP method before and after annealing.

2. Materials and methods

Samples of ZnO:Mn NC were obtained by the ASP method with Mn concentrations of 2 and 4 at.%. Zinc nitrates (Zn(NO₃)₂·6H₂O) and manganese nitrates Mn(NO₃)₂·6H₂O were used as precursors in the synthesis. A prepared aqueous 10% solution of zinc nitrate with the required amount of manganese nitrate was sprayed onto aerosol droplets $d = 1\text{--}2\ \mu\text{m}$ in size. These drops were transported with the help of a carrier gas (air) through the reaction zone of the furnace heated to a temperature of 550°C where, for a limited time ($7 \div 10\ \text{s}$), the processes of droplet drying and synthesis of ZnO:Mn NC. The synthesized product in the form of spherical granules was accumulated on the filter at a temperature of 250°C [5]. Heat treatment of the obtained samples was carried out in air at $T_1 = 550^\circ\text{C}$ and $T_2 = 850^\circ\text{C}$ for one hour. The study of the crystal structure and phase composition of the samples was carried out

by the method of X-ray diffraction analysis (XRD) on a DRON-2 diffractometer using Co K_{α} radiation ($\lambda = 0.17902$ nm). The EPR study of the samples was carried out on a RADIOPAN SE/X 2543 radio spectrometer. The magnetic properties of the samples were studied by vibration magnetometry.

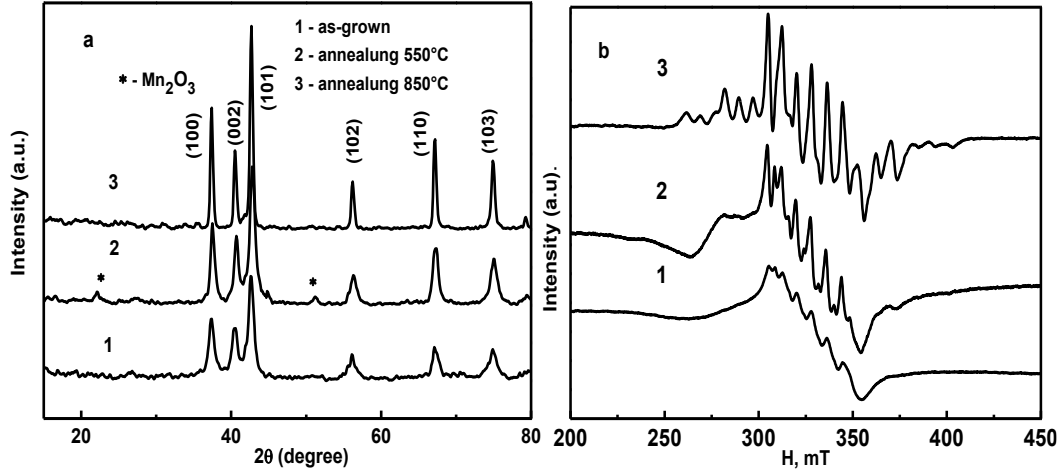


Fig. 1. X-ray diffraction patterns of a ZnO:Mn NC sample (4 at%) (a) and its EPR spectra (b): 1 - before annealing, 2 - after annealing at $T_1 = 550^\circ\text{C}$, 3 - after annealing at $T_2 = 850^\circ\text{C}$ in air for one hour. Symbol * indicates Mn_2O_3 phase.

The average size of NC ZnO:Mn was calculated by the Scherrer formula [6] with taking into account the expansion of the reflexes of radiographs:

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (1)$$

where $k = 0.9$ (const) is a dimensionless shape factor varies with the actual shape of the crystallite, λ is the X-ray wavelength ($\lambda = 0.17902$ nm), β is the line broadening at half the maximum intensity (FWHM), after subtracting the instrumental line broadening, in radians, θ is the Bragg angle.

For the hexagonal structure of ZnO, the interplanar spacing $d_{(hkl)}$ is related to the lattice constants a , c and Miller indices as follows:

$$\frac{1}{d_{(hkl)}^2} = \frac{4}{3} \left[\frac{h^2 + hk + k^2}{a^2} \right] + \frac{l^2}{c^2} \quad (2)$$

The values of the lattice parameters a and c for the samples are determined by the equations:

$$a = \frac{\lambda}{2 \sin\theta} \sqrt{\frac{4}{3} \left(h^2 + hk + \frac{l^2}{(c/a)^2} \right)}, \quad (3)$$

$$c = \frac{\lambda}{2 \sin\theta} \sqrt{\frac{4}{3(a/c)^2} (h^2 + hk + l^2)}. \quad (4)$$

The unit cell volume for the hexagonal system is calculated using the equation:

$$V = \frac{\sqrt{3}a^2c}{2} = 0.866a^2c. \quad (5)$$

The calculation results are shown in Table 1. Their analysis shows that the values of the crystal lattice parameters (a , c) and the unit cell volume (V) of the samples before annealing and after annealing at $T_1 = 550^\circ\text{C}$ practically do not differ from such values of

the non-doped NC ZnO [5]. This is a consequence of the fact that during the synthesis of ZnO:Mn NC under nonequilibrium conditions, Mn doping practically does not occur. An increase in these parameters after annealing the sample at a high temperature $T_2 = 850^\circ\text{C}$ indicates that under these conditions the process of bulk doping of ZnO NC occurs by replacing zinc ions Zn^{2+} with manganese ions Mn^{2+} , which have a larger ionic radius (in the wurtzite structure, the ionic radius Mn^{2+} is 0.83 \AA , and Zn^{2+} is 0.74 \AA). In the synthesized samples, an increase in the Mn concentration leads to a decrease in the average size of NC, because impurity atoms retard the growth of NC in the direction of the surface on which they are located.

Table 1

Crystal lattice parameters (a , c), average crystal size (d), unit cell volume (V) of NC ZnO and ZnO:Mn

Sample	Mn concentration 2.0 at%				Mn concentration 4.0 at%			
	d , nm	a , \AA	c , \AA	V , \AA^3	d , nm	a , \AA	c , \AA	V , \AA^3
ZnO, pyrolysis [5]	$D = 56 \text{ nm}$, $a = 3.2415 \text{ \AA}$, $c = 5.1946 \text{ \AA}$, $V = 47.12 \text{ \AA}^3$							
Synthesized	35.8	3.2352	5.1951	47.08	33.6	3.2395	5.1873	47.14
Annealing at 550°C	38.6	3.2389	5.2014	47.19	34.9	3.2396	5.1876	47.15
Annealing at 850°C	93.7	3.2525	5.2105	47.73	104.2	3.2403	5.1917	47.21

An EPR study of the ZnO:Mn NC sample with a manganese concentration of 4 at% (Fig. 1b) also confirms the necessity of annealing the sample at a high temperature for doping it with Mn. The amplitude of the lines of the hyperfine structure (HFS) of the EPR spectrum after annealing at a temperature of $T_2 = 850^\circ\text{C}$ significantly increases, which is associated with a significant increase in the concentration of Mn^{2+} ions in the bulk of the ZnO NC. These studies also show that the EPR spectrum after annealing the sample at $T_1 = 550^\circ\text{C}$ has additional peaks (Fig. 1b). It is assumed that the presence of these peaks is due to the presence of Mn^{2+} ions in the sample in a different local environment. It is possible that this is facilitated by the formation of an impurity phase Mn_2O_3 (Fig. 1a). In addition, it is found that the amplitude of the HFS of the EPR spectrum after annealing the sample at $T_1 = 550^\circ\text{C}$ increases. It is most likely that, during the annealing of the sample, one part of the Mn impurity, which was in the amorphous state, diffuses into the surface layer of ZnO NC, increasing the concentration of Mn^{2+} ions, while the other part of this impurity crystallizes, forming the Mn_2O_3 phase.

The analysis of the EPR spectra of the ZnO:Mn NC sample with a Mn concentration of 4 at% (Fig. 2) shows that the maxima of the main lines of the HFS of the sample before (1) annealing and after (2) annealing coincide (group of lines SI). The maxima of the additional HFS (group of SII lines) in the sample after annealing at a temperature of $T_1 = 550^\circ\text{C}$ (2) are shifted relative to the maxima of the main HFS by the value of $\Delta H = 3.9 \text{ mT}$. The width values of the group of lines SI and SII for all EPR spectra are the same and equal to $\Delta H_1 = \Delta H_2 = 39.5 \text{ mT}$. The calculation of the average value of the hyperfine structure constant of the EPR spectra shows that they are approximately the same and equal to $A_1 = A_2 = A_3 \sim 7.9 \text{ mT}$. This value is close to the value $A = 7.6 \text{ mT}$, which corresponds to the tetrahedral environment of the Mn^{2+} ion in the ZnO NC. It is also found that the g -factor of the EPR spectra (1), (2), and (3) of the sample does not change, it is equal to $g_1 = g_2 = g_3 = 2.019$. For the EPR spectrum of additional peaks, to which the group of SII lines corresponds, the g -factor has the value $g_{\text{II}} = 1.998$. This value of the g -factor may indicate that after annealing the sample at a temperature of $T_1 = 550^\circ\text{C}$, the Mn^{2+} ions are in a deformed environment on the surface of the ZnO NC. These conclusions

coincide with the results of work [7]. In this paper, the authors showed that after annealing ZnO:Mn NC at a temperature $T \sim 500^\circ\text{C}$, an additional group of SII lines appears in their EPR spectrum, which is caused by Mn^{2+} ions located in a thin shell of zinc hydroxide $\text{Zn}(\text{OH})_2$, covering surface of NC ZnO.

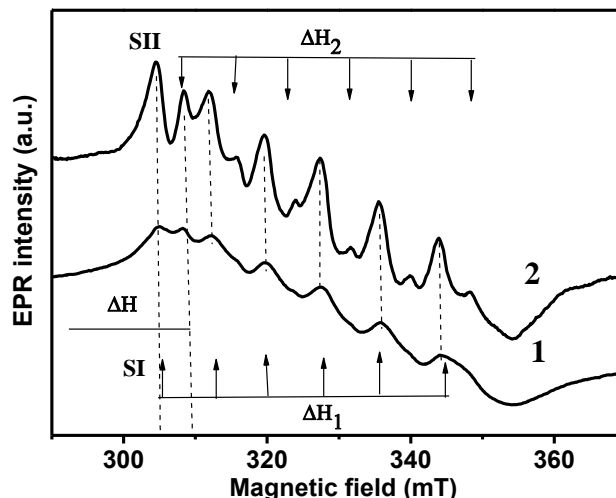


Fig. 2. EPR spectra of a ZnO:Mn NC sample with a manganese concentration of 4 at%:
1 - before annealing, 2 - after annealing at $T = 550^\circ\text{C}$.

4. Conclusion

It is shown that the main feature of doping ZnO NC with manganese during their synthesis by ultrasonic aerosol pyrolysis is the inhomogeneous arrangement of the Mn impurity in the volume of the NC. Under short-term, nonequilibrium conditions of NC formation, the Mn impurity does not spread over the entire volume of the ZnO NC, but is concentrated in its near-surface layer. Only annealing at a temperature of $T = 850^\circ\text{C}$ for 1 hour in air leads to the diffusion of Mn impurities into the bulk of the NC.

The obtained results are of practical importance. They can be used to optimize the modes of DMS synthesis by ultrasonic aerosol pyrolysis.

References

1. **Pogorily, A.M.** Spintronics. Basic Phenomena. Trends of development / A.M. Pogorily, S.M. Ryabchenko, A.I. Tovstolytkin // Ukr. J. Phys. Reviews. – 2010. – Vol. 6. – P. 37-97.
2. **Dietl, T.** Zener Model Description of Ferromagnetism in Zinc-Blende Magnetic Semiconductors / T. Dietl, H. Ohno, F. Matsukura, J. Cibert, D. Ferrand // J. Science. – 2000. – Vol. 287. – P. 1019-1022.
3. **Sharma, P.** Ferromagnetism above room temperature in bulk and transparent thin films of Mn-doped ZnO / P. Sharma, A. Gupta, K.V. Rao, F.J. Owens, R. Sharma, R. Ahuja, J.M. Osorio Guillen, B. Johansson, and G.A. Gehring // Nature Mater. – 2000. – Vol. 2. – P. 673-677.
4. **Vorovsky, V.Y.** Preparation of zincoxide nanopowders doped with manganese which have ferromagnetic properties at room temperature / V.Y. Vorovsky, A.V. Kovalenko, A.I. Kushneryov, O.V. Khmelenko // J. Functional Materials. – 2018. – Vol. 25, No. 1. – P. 61-66.
5. **Bulaniy, M.F.** Synthesis of Nanopowders ZnO and ZnO:Mn by Ultrasonic Spray Pyrolysis / M.F. Bulaniy, V.Yu. Vorovsky, A.V. Kovalenko, O.V. Khmelenko // J. Nano-Electron. Phys. – 2016. – Vol. 8, No. 2. – P. 02043-02048.
6. **Patterson, A.L.** The Scherrer Formula for X-Ray Particle Size Determination / A.L. Patterson // J. Phys. Rev. – 1939. – Vol. 56. – P. 978-982.
7. **Zhou, H.** Magnetic resonance investigation of Mn^{2+} in ZnO nanocrystals / H. Zhou, D.M. Hofmann, A. Hofstaetter, B.K. Meyer // J. Appl. Phys. – 2003. – Vol. 94 – P. 1965-1968.