DEFORMATION STRESSES IN ZNO:MN NANOCRYSTALS

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Two groups of ZnO and ZnO:Mn nanocrystals doped with Mn 2, 4, and 8 at.% using a zinc nitrate solution with a concentration of 5% and 10% were obtained by ultrasonic aerosol pyrolysis.By X-ray diffraction analysis, it was found that a decrease in the concentration of the initial solution leads to a decrease in the strain stresses in the crystal lattice of nanocrystals. This also improves the doping process and reduces the size of the NCs. During the doping of ZnO nanocrystals with Mn impurity, strain stresses increase more intensively in NCs obtained from a 10% zinc nitrate solution.

Keywords: method of ultrasonic aerosol pyrolysis, zinc oxide, crystal lattice, zinc nitrate, X-ray diffraction analysis, strain stresses..

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1. Introduction

Dilute magnetic semiconductors, which include manganese-doped ZnO, have recently been intensively studied in connection with the possibility of building spintronic devices for storing and recording information on their basis [1]. It is well known that the ferromagnetic properties of ZnO:Mn nanocrystals (NCs) largely depend on the presence of various types of defects in them [2]. During the synthesis of NCs by the method of ultrasonic aerosol pyrolysis (UPA), it is possible to influence the defective state of ZnO:Mn NCs by changing the duration of thermal exposure to aerosol droplets as they pass through the thermal zone of the furnace [3]. The synthesis process itself takes place in the volume of an aerosol solution droplet in a very short period – within 7–10 s. During such a short-term synthesis process, NCs with a defective crystal structure are formed, in which the parameters of the crystal lattice (CL) change and microstresses appear. Therefore, the study of strain stresses in NCs obtained under non-equilibrium conditions of synthesis by the UPA method is an important task.

Recently, it has been established that the strain stresses in NCs are due to the presence of their own defects, including oxygen vacancies [4], which significantly affect the physical properties of NCs. Until now, there have been no comprehensive studies of strain stresses in ZnO:Mn NC samples obtained by the UPA method in the scientific literature. In our work [5], we investigated the effect of Mn impurity on the values of strain stresses in ZnO:Mn NCs obtained by the UPA method. It has been shown that the strain stresses increase during the doping of ZnO with manganese from $5.9\cdot10^{-4}$ to $51.9\cdot10^{-4}$ with an increase in the concentration of Mn from 0 to 4 at.%. The unit cell volume of the ZnO:Mn NC samples is much smaller than that of single crystal ZnO.This indicates the disordered CL of the samples synthesized by the UPA method.

In [6], ZnO:Mn NCs were prepared by chemical precipitation from organic precursors – zinc and manganese acetates. It was shown that the doping of ZnO with Mn impurity leads to an increase in ε with an increase in the concentration of the Mn impurity from 1 to 5 at.%. At the same time, the value of ε increases from $2.2\cdot10^{-3}$ to $11.0\cdot10^{-3}$. Thus, it is clear that the value of ε in ZnO:Mn NCs depends on both the synthesis conditions and the concentration of Mn impurity.

One of the factors that affects the defective state of NCs during synthesis by the UPA method is the concentration of the initial solution. The studies in [7] showed that during the synthesis of ZnO:Mn NCs by the UPA method, a decrease in the concentration of zinc nitrate (ZN) solution from 10% to 5% leads to an improvement in the process of alloying with Mn

The aim of this work is to establish the regularity of the effect of the concentration of the initial solution on the strain stresses in the CL of ZnO:Mn NCs during their synthesis by the UPA method.

2. Research methods and calculation of crystal lattice deformation stresses

To conduct the study, ZnO NCs and ZnO:Mn NCs with aMn concentration of 2, 4, and 8 at.% were synthesized according to the technological modes described in [5].A solution of NCs with a concentration of 5% was used. Strain stresses were determined by X-ray diffraction analysis by analyzing the profile of the X-ray lines of the samples [8]. The X-ray diffraction patterns of the samples were obtained using a DRON-2M diffractometer with Co Kα radiation (λ = 1.7902 Å).

The analysis of the integrated width of diffraction lines of crystals is the most commonly used method for determining the structural parameters and strain stresses of CL. It is known that the integral width of a diffraction peak is the value of

$$\beta = \frac{\int f(x)dx}{f_{max}}, \quad (1)$$

where $f(x)$ is a function of the peak shape, f_{max} is the value of $f(x)$ at the maximum.

In polycrystals obtained under equilibrium synthesis conditions, the integrated width of the diffraction peak depends only on the size of the crystallite. In [9], it was shown that the integral width is inversely proportional to the size of the crystallites in the sample, according to the Debye-Scherrer formula:

$$D = \frac{K\lambda}{\beta_s \cos\theta}, \quad (2)$$

where θ is an angle between the incident beam and the reflection plane, λ is the X-ray wavelength, D is the effective size of crystallites, which depends on its shape and direction (hkl), K = 0.9, βS is the integral line width determined only by the size effect.

In NC samples obtained under non-equilibrium synthesis conditions, microstresses occur in the NC volume, which leads to the broadening of fractional peaks, and the integral width β will have an additional component:

$$\beta = \beta_S + \beta_D, \quad (3)$$

where βD is the integral width of the line due to the presence of strain stresses.

In [10], it is shown that such an additional expansion of the integrated diffraction line width β is due to an increase (d + Δd) or decrease (d – Δd) in the interplanar distances in the tensile and compressive zones of the NC. The interplanar distance d in the crystallographic direction (hkl) is determined from the Wulff – Bragg's equation:

$$2\,d(hkl)\sin\theta = n\lambda, \quad (4)$$

where θ is an angle between the incident beam and the reflection plane, n is an integer (reflection order).

Equation (4) leads to the important conclusion that the reflection of X-rays from the tensile zone leads to a shift in the reflex towards small angles θ, and the reflection from the compression zone, where tensile strain stresses act, shifts the reflex towards large angles θ.

Using the Wulff –Bragg's equation (4) and taking into account that the strain stresses are characterised by the parameter $\varepsilon = \left(\frac{\Delta d}{d}\right)$, it is possible to obtain the relation for β_D:

$$\beta_D = 4\varepsilon tg\theta \quad (5)$$

Thus, in the presence of strain stresses, the integral width β increases in direct proportion to tgθ. In their absence, in accordance with (2), the integral width β increases inversely with the value of cosθ. Equation (3) for the integral width β, taking into account (2) and (5), will be as follows:

$$\beta cos\theta = \frac{0.9\lambda}{D} + 4\varepsilon sin\theta \quad (6)$$

Equation (6) is a homogeneous strain model that assumes the same strain stresses in all crystallographic directions.

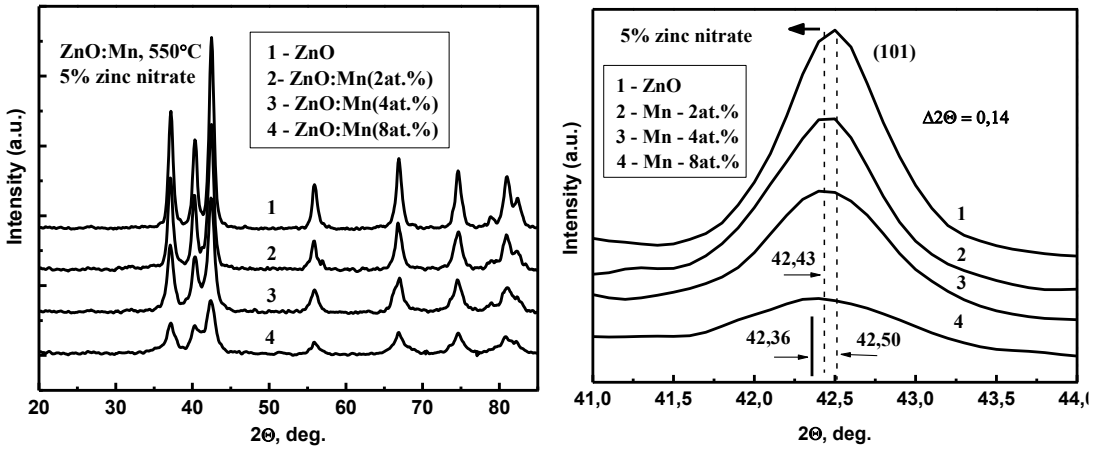
Williamson and Hall [11] proposed a graphical method for determining the value of using equation (6) for all diffraction peaks of the X-ray diffraction pattern of a sample. Equation (6) is the equation of a straight line (y=a+bx from the argument 4sinθ). If a straight line is drawn through a series of experimental values of for all diffraction peaks, the angle of inclination will determine the value of ε. The strain stresses ε CG of the ZnO:Mn NC samples were determined in accordance with equation (6). The integral line width β was calculated for the reflexes (100), (002), (101), (102), (110), (103).

3. Experimental part

The X-ray diffraction patterns of the obtained samples of NC ZnO and NC ZnO:Mn with a concentration of Mn of 2, 4, and 8 at.% are shown in Fig. 1.a. They do not show reflexes of impurity phases, which indicate the preparation of single-phase compounds. In contrast, in ZnO:Mn NCs (4 at.%) obtained from a solution of 10% NCs, there is an impurity phase of MnO2 [5]. This fact indicates that a decrease in the concentration of the initial solution activates the process of doping ZnO NCs with Mn impurity. It was shown that the crystal structure of ZnO:Mn NCs is of hexagonal wurtzite type (according to the standard JCPDS card: 36-1451). By analysing the X-ray diffraction patterns, an important feature of the crystal structure of the NC samples was established: the positions of the reflexes are shifted relative to the standard values for single crystal ZnO towards large diffraction angles of 2Θ, which is due to the nonequilibrium state of their CL. The analysis of the reflexes (101) in Fig. 1.b shows that the shift of the X-ray diffraction pattern reflexes of the ZnO sample relative to the standard (2Θ 101 = 42.36°) is Δ(2Θ) = 0.14°. This shift is much smaller than in samples obtained from a 10% NC solution, which has a value of Δ(2Θ) = 0.34° [5].

Such a shift in the reflexes indicates a decrease in the interplane distances, which causes the appearance of tensile strain stresses in the CL. Thus, it is shown that a decrease in the concentration of NCs during the synthesis of ZnO:Mn NCs can lead to a decrease in strain stresses.

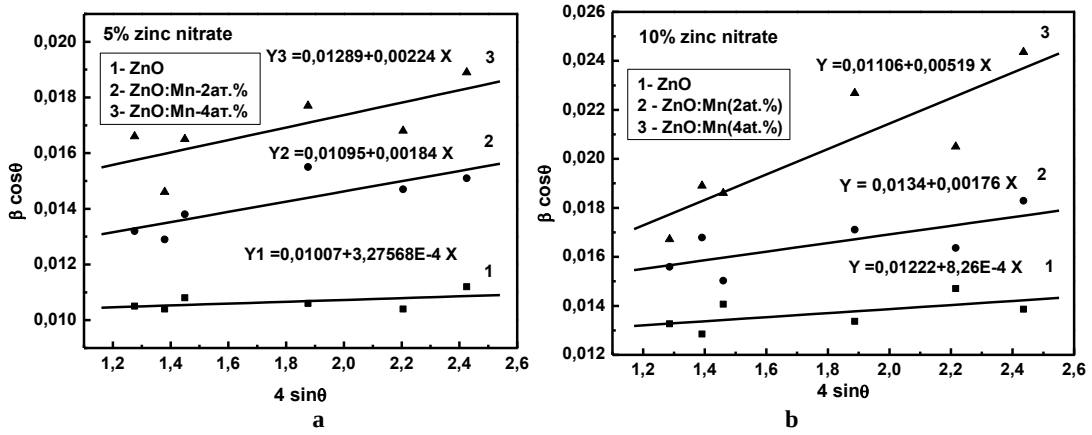
The XRD patterns also show a shift in the positions of the reflexes with increasing Mn concentration towards small diffraction angles relative to the NC ZnO sample. Thus, for the NC sample ZnO:Mn (4 at.%), the shift is Δ(2Θ) = 0.1°. This displacement is explained by the partial doping of the samples with Mn impurity, since the ionic radius of Mn2+ (0.83 Å) is larger than that of Zn2+ (0.74 Å).



a b

Fig 1. X-ray diffraction patterns of the samples synthesized at T = 550 °C (a), reflex shift (101) (b): 1 –ZnO sample, 2, 3, 4 –ZnO:Mn with an impurity concentration of 2, 4, and 8 at.%, respectively.

Fig. 2 shows the approximating lines of βcosθ dependence on the argument 4sinθ according to Equation (6) for the reflexes (100), (002), (101), (102), (110), (103).



a b

Fig. 2. Results of X-ray analysis of samples by the Williamson – Hall method (a) – samples synthesized from a solution of NC 5%, (b) – NC 10% [5]:1 –ZnO sample, 2,3 –ZnO:Mn samples with an impurity concentration of 2 and 4 at.%, respectively.

The results of the analysis of X-ray diffraction patterns of samples synthesised from a solution of NC 5% by the Williamson – Hall method showed that the obtained experimental values of βcosθ are approximated by the following linear functions:

$$Y_1 = 0{,}01007 + 0{,}00033X\text{–for the ZnOsample;}$$

$$Y_2 = 0{,}01095 + 0{,}00176X\text{–for the ZnOsample:Mn–2at%;} \quad (7)$$

$$Y_3 = 0{,}01289 + 0{,}00224X\text{–for the ZnOsample:Mn–4at%.}$$

From the linear approximations of equation (7) shown in Fig. 2a, the values of strain stresses ε were obtained (Table 1). The average size of NCs was calculated by formula (2). It was found that the value of D of NCs decreases with increasing Mn concentration from 49.4 to 30.6 nm when the impurity concentration changes from 0 to 4 at.%, respectively (Table 1). This tendency is characteristic of the growth process of ZnO NCs from a supersaturated

solution of NCs, since when an impurity atom enters the crystal surface of NCs, the growth rate in this direction decreases [12].

Table 1

Results of calculations of the average NC size *D* and strain stresses ε for different concentrations of NC solution

Mn impurity, at.%.	NC-5%		NC-10%, [5]	
	***D*,nm**	**ε, ×10^{-4}**	***D*,nm**	**ε, ×10^{-4}**
0	49,4	3,3	54,4	5,9
2	44,2	18,4	40,6	17,5
4	30,6	22,4	34,8	51,9

The obtained values of strain stresses ε increase with increasing concentration of Mn impurity from a valueof $3.3 \cdot 10^{-4}$ for ZnO NCs to a value of $22.4 \cdot 10^{-4}$ for a sample with a concentration of Mn of 4 at.%. These values are more than 2 time slower than those obtained in [5] from a 10% NC solution.

Such a decrease in ε may be due to the additional maintenance of the samples during their synthesis from NC of low concentration. It is known that a decrease in the concentration of NC leads to a decrease in the size of aerosol droplets [7]. With a decrease in the mass of the substance in a small droplet, the process of synthesis of ZnO:MnNCs is faster than in a large microdroplet. This increases the maintenance time during the passage of the pellet through the thermal zoneof thefurnace. A sign of such a process ofZnO:Mn NC formation, characterised by an extended heat treatment time, is the absence of impurity phases on X-ray diffraction pattern so samples obtained from a solutio nof NC 5% (Fig. 1.a).

This can also be confirmed by the EPR spectra of ZnO:MnNCs doped withMn 2 at.% obtained from solutions of different NC concentrations (Fig. 3).

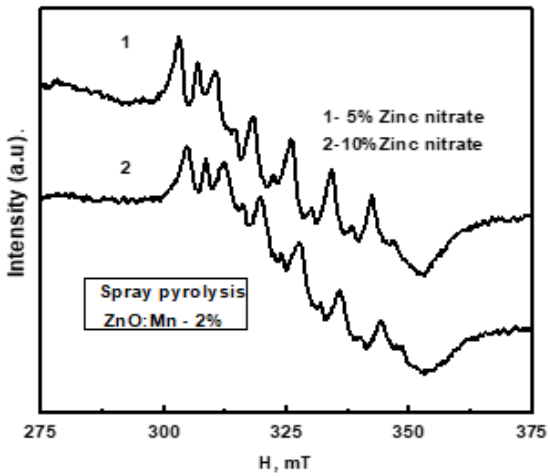


Fig. 3. EPR spectra of ZnO:Mn NC samples (2 at.%) obtained from NC solution 1 – 5%, 2 – 10%.

The higher intensity of the lines of the ultrafine structure of Mn^{2+} ions in the EPR spectrum for the sample obtained using a solution of NC 5% indicates a more intense process of doping with Mn impurity.

4. Conclusions

The studies have shown that during the synthesis of ZnO:MnNCs byt he UPA method a decrease in the concentration of the NC solution from 10% to 5% leads to a decrease in the strainstress ε in the CLofNCs. It also improves the process of doping with Mn and reduces the size of NCs. Taking into account that the size of NCs depends on the concentration of the initial solution, this mode of synthesis by the UPA method allows to control the size of the synthesized NCs.

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