

Reaction processes in a ZnO + 1%Gd₂O₃ powder mixture during mechanical and laser processing

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ABSTRACT

X-ray diffraction, electron paramagnetic resonance, Fourier transform infrared spectroscopy and scanning electron microscopy were used to study the defect formation and reaction processes in a ZnO + 1%Gd₂O₃ powder mixture during its mechanical and laser processing. Mechanical treatment of the ZnO + 1%Gd₂O₃ powder mixture leads to a grinding of initial ZnO particles and formation of three types of superficial paramagnetic donor defect centers. The rise of the sample temperature with increasing processing time promotes a successive annealing of ZnO defects with small activation energies and of superficial defects in Gd₂O₃. The formation of a ZnO:Gd³⁺ solid solution in the used mechanical processing regimes has not been observed. Laser surface melting of the ZnO + 1%Gd₂O₃ pellets provokes formation of a surface layer exhibiting a texture. The crystallization directions in the superficial layers of different specimens have a random character. In the superficial layers and deep sub-surface layers, processes of solid-state interactions (formation of an inhomogeneous ZnO:Gd³⁺ solid solution) take place. The surplus charges of the Gd³⁺ ions are compensated by the formation of Zn vacancies or interstitial oxygen ions which in the laser-surface-melted layers are located closer to the Gd³⁺ ions than in the case of single-crystalline samples.

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1. Introduction

Zinc oxide (ZnO) is a wide-bandgap (3.37 eV) material that is used in semiconductor, optoelectronic, spintronic and other applications [1]. Doping ZnO by various impurities, in order to modify its electrical conductivity, is used to engineer nonlinear properties of varistor ceramics [2]. In the recent years, interest in doping ZnO with 3d and 4f transition metal ions has increased in connection with the advent of diluted magnetic semiconductors [3]. Some theoretical calculations [4,5] predicted room-temperature (RT) ferromagnetism in ZnO doped with transition metals. However, an additional problem is that normally only single-phase systems can be used in electronic devices. According to the calculations [4,5], to induce RT ferromagnetism in ZnO, the content of Mn²⁺ ions should exceed 5%, and the sample should contain about 3.5×10^{20} holes/cm³. A number of studies have shown a marked solubility of Mn atoms in ZnO when introduced by various doping techniques, and the obtained samples demonstrated high temperature ferromagnetism [6–15]. Even a much higher solubility (up to 35%) of Mn in the ZnO matrix was claimed in Refs. [7,8]. However, other

studies have shown the absence of high-temperature ferromagnetism in ZnO:Mn²⁺ single-phase samples [16–22]. So, it has been shown [16] that the solubility limit for Mn in the ZnO matrix is about 10% so that the high-temperature ferromagnetism [7,8] is attributable to the formation of second-phases. The authors of the review [19] concluded that the combination of microscopic defects and delicate point-like defects created upon energy impact in ZnO leads to weak ferromagnetic properties. Importantly, it has been shown in 1966 that the Mn solubility in ZnO is low, less than 2 mol% in the 600–1450 °C temperature range [23]. It is known that the basic interaction mechanism in mixtures of mutually insoluble (or low-solubility) substances is reactive diffusion [24]. So, during the thermal treatment at a relatively low pressure (ca. 10 atm.) of a powder ZnO–MnO₂ mixture the solid-state interphase interaction between ZnO and MnO₂ should proceed not through the formation of mutual solid solutions but through the formation of intermediate phase products.

Thus, the problem of the creation of magnetic semiconductors on the base of ZnO consists in the development of methods of increasing the solubility of paramagnetic impurities in ZnO and thus stabilizing its lattice. Such technological methods can be, e.g., the use of a high-pressure and high-temperature (>1450 °C) synthesis, or of the application of a high-intensity mechanical (or thermal) pulsed load, etc. Formation of the Mn²⁺ solid solution in ZnO during

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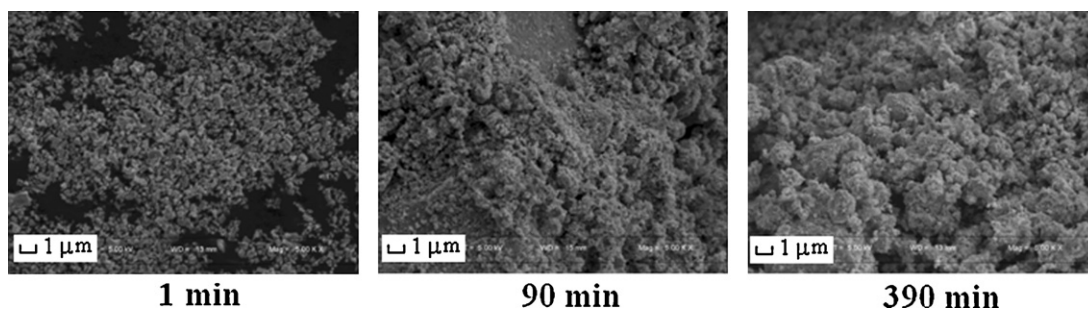


Fig. 1. SEM images of ZnO + 1%Gd₂O₃ samples depending on the duration of MP: (a) $t_{MP} = 1$ min, (b) $t_{MP} = 90$ min, (c) $t_{MP} = 390$ min.

an intense mechanical processing of ZnO- x MnO₂ ($x = 1.0$ – 10.0%) powder mixtures has been reported earlier [25,26].

Room-temperature ferromagnetism was observed in a Gd-doped ZnO powder which was obtained using a mixture of bi(acetylacetonato) zinc(II)hydrate and tri(dimethylglyoximato)gadolinium(III) complexes [27]. In the present work we shall consider reaction processes in a ZnO + 1%Gd₂O₃ powder mixture during mechanical and laser processing.

2. Experimental

A mixture of 99 wt.% ZnO (99% purity, Reasol, average particle size $d \approx 0.3 \mu\text{m}$) and 1 wt.% Gd₂O₃ (99.9% purity, Sigma–Aldrich, $d \approx 0.25 \mu\text{m}$) was selected as an initial material. Mechanical processing (MP) was performed with the same planetary ball-mill (PM 400/2, Retsch Inc.), equipped with tungsten carbide “comfort” grinding jars (volume 50 ml) and balls (3 of 20 mm and 10 of 10 mm), and in the same working conditions as in the previous study of the solid solution formation in the ZnO + 1% MnO₂ system [25,26]. The weight ratio between the balls and the powder sample was 28:1. Samples of the milled powders were removed from the milling jars after the following time intervals, t_{MP} : 1, 3, 9, 30, 90, and 390 min.

For the laser processing, two different powder mixtures (an initial and another one subjected to MP for $t_{MP} = 390$ min) were uniaxially pressed at ≈ 30 MPa into pellets of 8 mm in diameter and 5 mm in height. The laser surface melting (LSM) was carried out using a 10.6 μm CO₂ laser (CW-CO₂ Spectra Physics 820, output power 130 W). The laser spot size was about 0.3 mm. The scanning velocity was 0.7 mm/s. The laser treated surface was a square of 5 mm \times 5 mm. Three consecutive parallel linear processing scans were performed with a step (distance between lines of parallel laser beam passes) of 0.25 mm. Such a distance has been chosen to achieve an overlap of melting-crystallization zones on the surface of the samples dubbed in the following LSM_{init} and LSM_{MP}.

The techniques of scanning electron microscopy (SEM, LEO 1450-VP), X-ray diffraction (XRD, Siemens D-500 with CuK α radiation), electron paramagnetic resonance (EPR, Bruker ESP 300E) and infrared spectroscopy (IR, Specord M80 and Bruker Vector 22 FTIR, with a resolution of 4 cm⁻¹) were used in this study.

The average crystallite size was determined based on the XRD peak broadening (the (100) and (103) reflections were used for ZnO) using the Scherrer formula [28]. The EPR measurements were carried out as a function of the angle θ between the external magnetic field and the normal to the sample surface. The IR spectrophotometers were used in the transmission mode. The samples were mixed with KBr in a ratio of 2:60, and the resulting mixtures were pressed until obtaining transparent plates.

3. Results

It is observed that the color of the ZnO + 1%Gd₂O₃ samples varies during MP from white (initial) to gray ($t_{MP} = 390$ min). Fig. 1 shows SEM images of the ZnO + 1%Gd₂O₃ samples depending on the MP duration. The ZnO average particle size changes from ≈ 250 nm in the initial sample to ≈ 30 nm after MP for $t_{MP} = 390$ min.

Optical cross-section microscopy observation of the LSM samples shows the presence of three different states in them (see Fig. 2): (a) a surface layer, in which processes of melting-crystallization take place; the thickness of this layer is ≈ 0.2 mm; (b) a layer of sintered material; the thickness of this layer is ≈ 1 mm; (c) the virgin sample.

XRD patterns of the samples are shown in Fig. 3 as a function of the MP time. All of the observed peaks are characteristic of the hexagonal wurtzite structure of ZnO [29]. X-ray patterns in the initial and MP samples are typical of polycrystalline ZnO (Table 1). The increase of t_{MP} causes a broadening of the diffraction peaks and a diminution of their amplitude (Fig. 3). The average size of the crystallites was determined by means of the full width at half maximum (FWHM) of the ZnO (100) and (103) XRD peaks (Fig. 4). During MP the crystallite sizes in the ZnO powders change from $d_X \approx 240$ nm in the initial samples to $d_X \approx 30$ nm in the samples with $t_{MP} = 390$ min.

The observed diffraction intensities in the LSM_{init} and LSM_{MP} ZnO pellets (Fig. 3) are different from the “ideal” polycrystalline intensities and from the ones observed in the initial and MP samples (see Fig. 3 and Table 1). Such a situation is typical of samples with a preferential orientation of crystallites (appearance of a texture). One can see the preferred ZnO crystallite orientations along (101), (200) and (112) in sample LSM_{init} and the preferred crystallite orientations along (002), (101) and (200) in sample LSM_{MP} (Table 1). The crystallite sizes in the samples are almost the same as in the virgin one, $d_X \approx 240$ nm (Fig. 4).

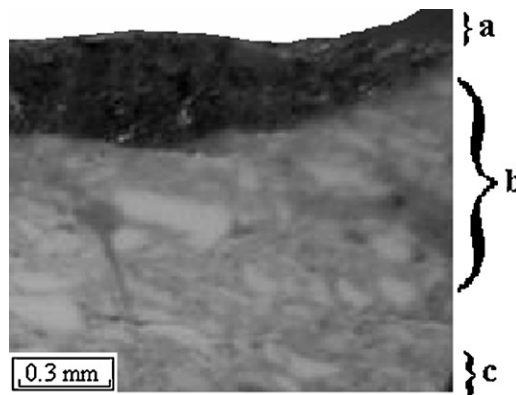


Fig. 2. Cross-section photograph of a LSM sample (ZnO + 1.0% Gd₂O₃). (a) Surface layer; (b) layer of sintered material; (c) the raw sample.

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