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ZnMnO diluted magnetic semiconductor nanoparticles: Synthesis by laser ablation in liquids, optical and magneto-optical properties

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ABSTRACT

Nanoparticles of ZnO and $Zn_{1-x}Mn_xO$ were synthesized by pulsed laser ablation in liquid medium (PLAL). Metal zinc target was used for preparing of pure ZnO nanostructures and $Zn_{1-x}Mn_xO$ ceramic plates served for preparing of ternary nanoparticles. As synthesized nanomaterials are characterized using scanning electron microscopy (SEM), energy dispersive spectroscopy analysis (EDS), atomic force microscopy (AFM), UV-vis absorption, photoluminescence and Faraday rotation spectroscopy. SEM images showed a well-defined flower-like nanostructures. Absorption edge of $Zn_{0.95}Mn_{0.05}O$ nanoparticles in colloid solution exhibits blue shift due to confinement effect. The observed photoluminescence peaks are attributed to the band-edge transitions and vacancies or defects. The Faraday rotation as a function of photon energy demonstrates behavior typical for diluted magnetic semiconductors (DMSs) in paramagnetic state.

1. Introduction

In recent decades diluted magnetic semiconductors (DMSs) have been studied extensively due to their unique properties and perspectives for applications in optoelectronic and spintronic devices. In this wide family of materials, transition metal (TM) doped ZnO in form of bulk samples and nanostructures have attracted much attention because they were predicted to have Curie temperature above room temperature [1,2]. As a rule, many researchers associate the revealed ferromagnetism with the localized magnetic moment of 3d-impurities. In particular, manganese is the most studied such an impurity and its d-electrons have zero orbital moment but a very stable 5/2 spin which can interact with s- and p-type electrons of host semiconductor [3]. However, there are suggestions that defects or vacancies may induce room temperature ferromagnetism in TM doped ZnO [4,5]. It was shown in numerous experiments that exhibition of different magnetic behaviors depends on the fabrication conditions and sample processing. There were used different synthesis routes for preparing of ZnO-based DMS nanostructures, including chemical vapor deposition, electrochemical approach, sol–gel method, co-precipitation, hydrothermal route, magnetron sputtering, pulsed laser deposition, etc. In particular, pulsed laser ablation in vacuum or in gas atmosphere, has been already applied in our previous papers [6–8] to prepare ZnO:TM thin films. On the other hand, pulsed laser ablation in liquids (PLAL) is comparatively new technique for the synthesis of nanosized semiconductor materials [9–16]. PLAL technique has many advantages compared to the other growth routes such as a large number of available ablation parameters for controlling the size and shape of nanoparticles and ability of producing nanomaterials having surface free from chemical contamination. To our knowledge, application of PLAL to fabricate undoped ZnO nanoparticles was reported in papers [11–15], but similar data on doped ZnO:TM nanoparticles are absent. Recently experimental results on rare earth Eu^{3+} doped ZnO nanoparticles fabricated by PLAL were published [17] and proved usefulness of this technique for doping active centers into nanoparticles. In the present work, experimental investigations on structural, optical and magneto-optical properties of $Zn_{1-x}Mn_xO$ nanoparticles synthesized by PLAL are reported. The DMS nanostructures are found to be paramagnetic at room temperature and exhibited blue shift of the absorption edge as compared with bulk films.

2. Experimental

Pure ZnO nanoparticles were produced by laser ablation of a metal zinc target (99.99% purity foil, from Alfa Aesar) in

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deionized water (with a resistivity of 15 MΩ cm at 20 °C). The target was irradiated using a frequency-quadrupled Q-switched Nd:YAG pulse laser (Continuum, Powerlite-8010). This laser was capable of producing 100 mJ of 266 nm light per pulse, laser fluence about 1.5 J/cm^2, operating at 10 Hz with pulse width of 7 ns. To prepare ZnO based DMS nanoparticles laser parameters were mainly similar to the mentioned ones. However, $Zn_{1-x}Mn_xO$ (x = 0.05; 0.1) ceramic plates as targets were applied in this case. The ceramic plates were prepared by pressing and using for this purpose ZnO and Mn_3O_4 pure powders (from Sigma Aldrich) as initial components. Experimental setup for deposition of thin films has been in part reported earlier [18]. However, for the synthesis of nanoparticles, a target was fixed at the bottom of a glass vessel on Al foil and covered by the deionized water (about 10 ml). The laser beam was steered vertically by dichroic mirror and focused by a quartz lens with focal length of 250 mm in order to get sufficient laser intensity for ablation. The reaction vessel was continuously rotated to avoid crater formation and to expose the new surface of target. The ablation process duration was typically about 40 min. Technological experiments were carried out at room temperature and atmospheric pressure. After laser ablation the colloidal aqueous solution with the produced nanoparticles or the dropped layer onto Al substrate were the samples under investigations. Additionally, polyvinylalcohol (PVA) was used as a stabilizer of colloidal solution. Scanning electron microscopy (SEM, model JEOL-6480LV) and atomic force microscopy (AFM, standard model NT MDT – NSG03) were main techniques for structural and morphological analysis of the fabricated nanostructures. The optical absorption and photoluminescence (PL) spectra of the formed colloidal nanomaterials and nanoparticles on Al substrates were measured by a UV-visible spectrophotometer at room temperature. The PL spectra were studied under He–Cd laser excitation at 325 nm. Faraday rotation measurements (spectral and magnetic field dependence) were carried out in spectral range of 350–700 nm at magnetic fields up to 5 T using a home-designed setup. These magneto-optical studies have been used to get information about magnetic behavior of the prepared colloidal nanoparticles.

3. Results and discussion

Analysis of X-ray diffraction spectra (not shown here) of the $Zn_{1-x}Mn_xO$ nanoparticles suggests they are in agreement with the standard patterns of wurtzite structure. Fig. 1 shows the SEM micrograph of a typical $Zn_{0.95}Mn_{0.05}O$ nanostructure. The image confirms the formation of small particles on the surface of Al foil substrate. There are observed both isolated particles and

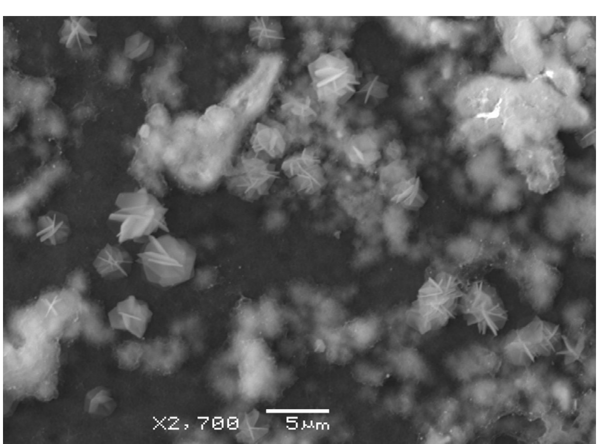

Fig. 1. SEM image of $Zn_{0.95}Mn_{0.05}O$ nanostructures grown by PLAL technique on Al substrate.

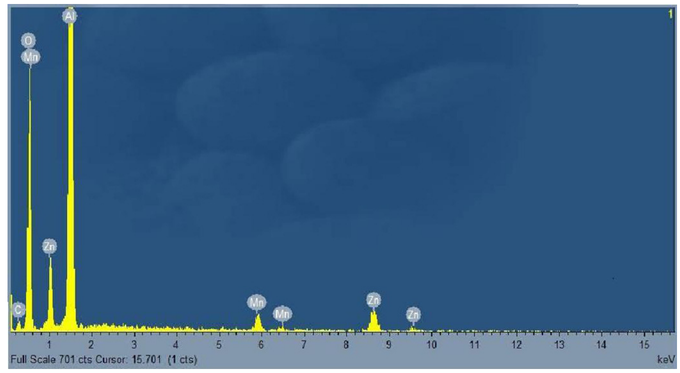

Fig. 2. EDS spectrum of $Zn_{0.95}Mn_{0.05}O$ nanostructures on Al substrate.

agglomerated chains with flower-like structure. The average diameter of the isolated particles is estimated to be in range of 300–700 nm. The observed flower-like structures consist of nanosheets with thickness about 20 nm. About similar flower-like ZnO nanostructures synthesized by chemical methods recently several research groups have reported [19–22]. The energy dispersive spectroscopy (EDS) analysis simultaneously was carried out in order to estimate the average concentration of elements. As shown in Fig. 2 carbon, zinc, aluminium, manganese and oxygen were detected. Obviously, the most intense peak is attributed to Al from foil substrate, Zn and O are from the formed ZnO particle layer. In addition, C contamination was also detected. The EDS results show that the amount of zinc oxide increased when number of laser pulses is increased and the amount of Mn impurity is less than in the used ZnMnO targets.

The 2D and 3D AFM images of the $Zn_{0.95}Mn_{0.05}O$ nanostructures shown in Fig. 3 demonstrates the variation in size distribution of the nanoparticles without details on their shape and structure. The estimated from these AFM images diameters of particles are in range of 200–500 nm.

Fig. 4 shows the absorption spectrum of colloidal $Zn_{0.95}Mn_{0.05}O$ nanoparticles dispersed in polyvinylalcohol (PVA) solution. It was found that the absorption edge is blue-shifted as compared to the bulk $Zn_{0.95}Mn_{0.05}O$ due to confinement effect. By measurements of the absorption edge for $Zn_{0.95}Mn_{0.05}O$ thin film (with thickness of 1.2 μm) deposited on sapphire substrate by PLD technique we have estimated the energy band gap value $E_g^{bulk} = 3.34$ eV, whereas the estimated from Fig. 4 value $E_g^{nano} = 3.45$ ev. In framework of the effective-mass approximation for spherical particles, the observed shift $\Delta E = E_g^{nano} - E_g^{bulk}$ is given by expression [23]

$$\Delta E \cong \frac{\hbar^2\pi^2}{2eR^2}\left[\frac{1}{m_e^*}+\frac{1}{m_h^*}\right] - \frac{1.8e}{4\pi\varepsilon\varepsilon_0 R} - \frac{0.124e^3}{\hbar^2(4\pi\varepsilon\varepsilon_0)^2}\left[\frac{1}{m_e^*}+\frac{1}{m_h^*}\right]^{-1}, \quad (1)$$

where R is the radius of the particle, m_e^* and m_h^* are the effective mass of electrons and holes respectively, ε_0 and ε are the free space and relative permittivity. For the calculations effective masses for electrons and heavy hole in pure ZnO were taken as 0.26 m_o and 0.59 m_o [24], respectively, where m_o is the free electron mass. The dielectric constant was taken also for ZnO as 8.3 [24]. By substitution of these values and the determined experimentally ΔE = 110 meV in the Eq. (1) we have estimated radius R = 9 nm. Therefore, the obtained average size of nanoparticles is associated with small fragments of the mentioned flower-like nanostructures.

Fig. 5 depicts PL spectra of ZnO and $Zn_{0.95}Mn_{0.05}O$ nanoparticles prepared by PLAL technique on Al substrate. Broad emission bands located at 2.39, 2.79 and 3.13 eV have been observed for undoped ZnO nanoparticles. Similar PL spectrum was reported recently