Optical Materials 58 (2016) 317–322

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Raman study of surface optical phonons in hydrothermally obtained ZnO(Mn) nanoparticles

B. Hadžić [a, *], N. Romčević [a], M. Romčević [a], I. Kuryliszyn-Kudelska [b], W. Dobrowolski [b], U. Narkiewicz [c], D. Sibera [c]

[a] Institute of Physics, University of Belgrade, Pregrevica 118, 11 080 Belgrade, Serbia
[b] Institute of Physics, Polish Academy of Science, al. Lotnikow 32/46, 02-668 Warszawa, Poland
[c] West Pomeranian University of Technology, Institute of Chemical and Environment Engineering, Pulaskiego 10, 70-322 Szczecin, Poland

ARTICLE INFO

Article history:
Received 25 January 2016
Received in revised form
16 March 2016
Accepted 18 March 2016
Available online 7 June 2016

Keywords:
Nanostructured materials
Optical properties
Light absorption and reflection

ABSTRACT

Nanocrystalline samples of ZnO(Mn) were synthesized by hydrothermal method. The morphology of the samples was studied by HRTEM and SEM. X-ray diffraction was used to determine composition of the samples (ZnO and $ZnMn_2O_4$) and the mean crystalline size (from 16 to 99 nm). In this paper we report the experimental spectra of Raman scattering (from 100 to 1600 cm^{-1}) with surface optical phonons (SOP) in range of 497–538 cm^{-1} as well as formation of new phases MnO, Mn_3O_4 and $ZnMnO_3$. The phonon of registered phase's exhibit effects connected to phase concentration, while the SOP phonon mode exhibit significant confinement effect.

1. Introduction

Even though research interest in semiconductor ZnO goes back many decades, the renewed interest over the past few years is fueled by its wide range of properties that depend on doping, high transparency, piezoelectricity, wide-bandgap semiconductivity, huge magneto-optic and chemical-sensing effects. ZnO is material with a biggest potential for room-temperature ferromagnetism for spintronic applications when it is alloyed with 3d transition metals (Mn, Ni, Co, etc.) [1–4]. ZnO is a direct wide band gap (3.37 eV) material with a large exciton binding energy (60 meV) at room temperature. This makes it interesting as a next-generation applications material, such as in the low-voltage and short-wavelength electro-optical devices, transparent ultraviolet protection films and gas sensors, as well as laser material also. The interest in nanostructured semiconductors increased drastically in recent years due to their novel electronic, mechanical, optical and vibrational properties which are a consequence of surface and quantum confinement effects [1–4].

Raman spectroscopy is widely employed to characterize and study the optical and vibrational properties of bulk crystals, thin film, micro/nano structured samples and heterostructures. As a powerful, non-destructive, rapid, sensitive analytic technique, with minimal or no sample preparation, Raman spectroscopy has been method of choice for many investigation. Position, shift and broadening of the Raman peaks can be used to obtain valuable information about structure, morphology and chemical composition of investigated materials, isotopic effects and phonon lifetimes [5], position of doping ions in the host lattice, presence of impurities which are undetectable by X-ray analysis [6], as well as on the photon-electron and electron–phonon interactions occurring in these materials [7,8].

Due to its reduced dimensionality and large surface-to-volume ratio, in ZnO nanostructure, appearance of surface optical phonon (SOP) modes in Raman spectra is expected. When dimensions becomes extremely small surface modes are only modes that persist, that's why the state of surface atoms is important in determining their properties. With loss of long-range order and symmetry breakdown in ZnO shell appearance of Raman forbidden SOP modes is expected [9] as well as predicted theoretically and/or detected experimentally for ZnO nanostructures [10].

In our previous paper [11] we have detail study SOP modes in ZnO(Mn) prepared by calcination 333 method while with this paper we want to continue completing the picture about the impact of doping with the transition elements on vibrational properties of doped ZnO as well as influence of preparation method.

The aim of this work is to study influence of preparation method

* Corresponding author.
E-mail address: branka@ipb.ac.rs (B. Hadžić).

http://dx.doi.org/10.1016/j.optmat.2016.03.033
0925-3467/

on samples characteristics, by applying micro-Raman spectroscopy to study SOP mode, the Mn ion position in ZnO lattice, the formation of existing phases, and the samples quality in dependence of MnO concentration.

2. Technology

The nanocrystalline samples of ZnO doped with MnO were obtained by use of hydrothermal synthesis. In this method a mixture of manganese and zinc hydroxides was obtained by addition of an ammonia solution or 2M solution of KOH to the 20% solution of a proper amount of $Zn(NO_3)^*6H_2O$ and $Mn(NO_3)^*4H_2O$ in water:

$$Zn(NO_3)_2 + 2NH_4OH = Zn(OH)_2 + 2NH_4NO_3$$

$$Mn(NO_3)_2 + 2NH_4OH = Mn(OH)_2 + 2NH_4NO_3$$

Next, the obtained hydroxides were put in the reactor with microwave emission. The microwave assisted synthesis was conducted under a pressure of 3.8 MPa during 15 min. The synthesized product was filtered and dried. Nanopowders obtained on this way were pressed into indium panel.

In this paper we present the results of micro-Raman spectroscopy for major part of the samples from 5% till 70% as well as changes of relative intensity of modes with concentration of MnO.

3. Experimental

The morphology of samples was investigated using a high-resolution transmission electron microscope (HRTEM) FEI Tecnai F20 operating at 200 kV and scanning electron microscopy (SEM) LEO 1530.

The phase composition of the samples was determined by X-ray diffraction ($Co_{K\alpha}$radiation, X'Pert Philips).

Ar-ion laser 514.5 nm, green line, operating at 20 mW of laser power was used as excitation source, while with backscattering configuration the micro-Raman spectra of nanocrystalline samples were obtained with the Jobin Yvon T64000 spectrometer, which has nitrogen cooled charge-coupled-device detector.

4. Results

TEM and SEM was used for morphological studies of samples, while chemical compositions of samples was studied by XRD and Raman spectroscopy.

4.1. TEM

First we performed TEM measurements. In Fig. 1 are shown obtained TEM images for three representative samples doped with 5, 40 and 60 wt. % of MnO. In a case of sample doped with 5% of MnO (Fig. 1 a) and b)) it's clearly visible that particles size is bigger than 20 nm (Fig. 1a) and smaller than 50 nm (Fig. 1b), while particles size for samples doped with 40% of MnO are bigger than 10 nm (Fig. 1c) and for 60% of MnO are bigger than 20 nm (Fig. 1d). The particles in all samples shown in Fig. 1 are highly agglomerated. The agglomerates seen in Fig. 1 are composed of the crystallites. These results do not allow for any identification of individual nanocrystals. The agglomeration of the nanoparticles makes image analysis difficult and unable for identification of individual nanoparticles. However, we can suppose that hexagonal nanoparticles correspond to ZnO, while spherical nanocrystals to spinel $ZnMn_2O_4$ phase. It is also clearly visible that with the increase of Mn content, spherical nanocrystals are more pronounced.

4.2. SEM

Second method in the morphological study of the samples was by use of SEM. For samples with low content do MnO (5 wt.%) spherical and larger nonoval nanograins are observed. The agglomeration of the nanoparticles makes image analysis difficult. However, we can suppose that larger nonoval nanoparticles correspond to ZnO, while spherical nanocrystals to spinel $ZnMn_2O_4$ phase. It is also clearly visible that with the increase of Mn content, spherical nanocrystals becomes dominant. For samples with higher concentration of MnO the dominance of smaller spherical nanoparticles is clearly observed. Obtained SEM images for three representative samples doped with 5, 40 and 60 wt. % of MnO are shown in Fig. 2.

4.3. X-ray diffraction (XRD)

The detailed phase composition investigation, by XRD, revealed the presence of hexagonal ZnO and spinel structure of $ZnMn_2O_4$. In the purpose to demonstrate this fact, the characteristical X-ray diffractogram for representative samples is shown on Fig. 3 XRD data allowed determining a mean crystallite size in prepared samples by use of Scherrer's formula [12]. The mean crystalline size ã of these phases are between 33 and 99 nm for ZnO phases, while for $ZnMn_2O_4$ are between 16 and 29 nm. The results of XRD measurements are gather in Table 1. Sign "–" means that the presence of these particles haven't been register.

4.4. Raman spectroscopy

In Figs. 4 and 5 are presented Raman spectra's for all investigated samples of nanocrystalline ZnO doped with MnO. As we already have mention nanoparticles of ZnO and $ZnMn_2O_4$ are registered by XRD.

For analysis of Raman spectra usually two common type of lines are used Gaussian and Lorentzian [13]. Here for analysis of our spectra's we have assumed that all phonon lines are of Lorentzian type.

5. Discussion

Good knowledge of the vibrational properties of ZnO(MnO) nanocrystalline samples are essential to understand transport properties and photon–phonon interaction, both of which have great impact on future application in optoelectronic device performance. That's why we will give here brief report about structural and vibrational properties of all potentially present phases in the samples. We expect that bulk modes will be shifted and broadening as a consequence of miniaturization.

In our previous paper [14] we have mention characteristics of ZnO phase. Here we will, for clarity, repeat only most important details for ZnO structures.

The wurtzite-type semiconductor, ZnO, belongs to the space group C^4_{6v} with two formula units per primitive cell, where all atoms occupy C_{3v} sites. The Raman active zone-center optical phonons, predicted by the group theory are A_1, E_1, and $2E_2$. The phonons of A_1 and E_1 symmetry modes are polar phonons and hence, exhibit different frequencies for the transverse-optical (TO) and longitudinal-optical (LO) vibrations because of the macroscopic electric field associated with the LO phonons. On the other hand nonpolar and Raman active phonon modes with symmetry E_2 have two frequencies: E_2^{high} associated with oxygen atoms and E_2^{low} associated with Zn sublattice [14]. The ZnO Raman active modes have as the most typical frequencies for the corresponding assignation the values of 102 cm^{-1} for $E_2^{(1)}$ (low), 379 cm^{-1} for A_1(TO),