



Simple room temperature synthesis and optical studies on Mg doped ZnO nanostructures

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ARTICLE INFO

Article history:

Received 21 June 2009

Received in revised form

14 July 2010

Accepted 19 July 2010

Available online 6 August 2010

Keywords:

Nanostructured materials

Optical properties

Sol–gel processes

Exciton

II–VI semiconductors

ABSTRACT

We report simple room temperature synthesis of Mg doped ZnO nanostructures through the sol–gel method. X-ray diffraction shows the prepared ZnO particles are in wurtzite structure and replacement of Zn^{2+} by Mg^{2+} alters the position of the X-ray diffraction peak slightly towards higher angle. Measured optical absorption spectra show the exciton peaks of ZnO present around 366, 296 and 235 nm. Room temperature photoluminescence measurements show strong peaks around 385, 394 nm are attributed to band edge exciton emission; other peaks found at 469 and 558 are attributed to oxygen ion vacancy and formation of Vo^+ and Vo^{++} centers in nanostructures.

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1. Introduction

Nanotechnology has a potential to create many new devices with a wide range of applications in the field of medicine [1], electronics [2] and energy production [3]. The increased surface area to volume ratio and quantum size effects are the properties that make these materials as a potential candidate for device applications. These properties can control their optical properties like absorption, fluorescence and light scattering. Recently biologists have borrowed these nano tools and apply them to a variety of applications ranging from diagnosis of disease to gene therapies [4,5]. Among the nanomaterials, ZnO has received much attention over the past few years because it has a wide range of properties that depend on shape and doping. Doping in ZnO will change its conductivity, room temperature ferromagnetism [6], piezoelectricity and sensing properties [7]. ZnO is naturally an n-type semiconductor due to its presence of intrinsic defects such as oxygen vacancies and Zn interstitials. It has a direct wide band gap (~ 3.3 eV) and has a large exciton binding energy of 60 meV.

Magnesium doped ZnO nanoparticles gains much interest in hydrogen storage [8], electroluminescence [9] and field effect transistors [10]. Apart from these, synthesis methods that yield different shapes show different optical behaviors [11–13]. Owing to the interest in metal doped ZnO nanostructures, we prepared

Mg doped ZnO nanoparticles through a simple method in ambient temperature and studied their optical properties.

2. Experimental

Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) and sodium hydroxide (NaOH) were purchased from Aldrich chemicals (USA) and high purity magnesium nitrate ($Mg(NO_3)_2 \cdot 6H_2O$) was used for the chemical reaction. The experimental procedure for the preparation of ZnO and Mg doped ZnO is as follows: 0.05 M zinc nitrate hexahydrate was dissolved in 100 ml double distilled water, 0.1 M NaOH was dissolved in 100 ml double distilled water and then this solution was added dropwise in the above solution; the slow addition yields a white gel. This white gel was kept at room temperature over a 12 h period and became a precipitate. Similarly, Mg doping on ZnO was done as follows: 0.001, 0.003 and 0.005 M of magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$) were added into the zinc nitrate solution of 0.049, 0.047 and 0.045 M, respectively. Then NaOH solution was added dropwise in the above mentioned solutions; it formed a white gel in a similar way as mentioned above. The formed white gel was kept at room temperature over a 12 h period. The precipitates were collected and dried in hot air oven at 60 °C for 4 h. To identify the crystal structure, X-ray powder diffraction (XRD) measurements were done by using a Rigaku X-ray diffractometer using $Cu K_{\alpha}$ radiation ($\lambda = 1.54 \text{ \AA}$). The morphology and size of the prepared powders were studied using scanning electron microscopy (FESEM Quanta). Optical absorption (UV–vis) studies were carried out by using a Perkin–Elmer spectrometer.

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Table 1
Sample composition, sample coding and first excitonic band gap.

Sl. no.	Sample code	Sample composition	Band gap of $n=1$ exciton (eV)
1	ZnMg0	0.05 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + 0.1$ M NaOH	2.54
2	ZnMg1	0.049 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + 0.1$ M NaOH + 0.001 M $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	1.96
3	ZnMg3	0.047 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + 0.1$ M NaOH + 0.003 M $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	2.73
4	ZnMg5	0.045 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + 0.1$ M NaOH + 0.005 M $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	2.89

The photoluminescence (PL) studies were performed by using a *Jobin Yvon* (Fluoromax) fluorimeter. The prepared sample compositions with sample code are presented in Table 1.

3. Results and discussion

Fig. 1 shows the XRD patterns of the prepared samples. Patterns show strong and sharp peaks, which confirm the wurtzite structure of ZnO [14]. The peaks are located at the angle (2θ) of 31.6° , 34.3° and 36.1° , which correspond to (1 0 0), (0 0 2) and (1 0 1) planes of the ZnO; similarly other peaks are found in the 2θ angles of 47.5° , 56.5° , 62.8° , 67.9° , 68.8° and 76.6° corresponding to (1 0 2), (1 0 3), (2 0 0), (1 1 2), (2 0 1) and (2 0 2) planes of the wurtzite structure, respectively. Interestingly Mg doped samples show no additional phase formation but there is a slight higher angle shift compared to undoped ZnO diffraction pattern. The ionic radius of Zn^{2+} is 0.74 \AA and for Mg^{2+} , 0.66 \AA . Replacement of Mg in the Zn site and the change in ionic radius will make the variation in 'd' induce this type of angle shift. The strong peaks in ZnMg3 are at 31.9° , 34.6° and 36.4° . The lattice constants 'a' and 'c' of wurtzite structure can be calculated by using the relation

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

with the first order approximation ($n=1$) for the (1 0 0) plane the lattice constant 'a' is obtained through the relation $a = \lambda / (\sqrt{3} \sin \theta)$ and the lattice constant 'c' can be derived for the plane (0 0 2) by the relation $c = \lambda / \sin \theta$. The calculated values of 'a' and 'c' for ZnMg0 are 3.26 , 5.22 \AA and for ZnMg3, 3.23 and 5.17 \AA . It shows shrink in lattice constants due to Mg doping. Scanning electron microscopic images (see Fig. 2) show that the particles are spherical in nature and there is a small size variation with doping concentration. Energy-dispersive X-ray spectrum (EDS) studies on ZnMg3 confirm the presence of Mg in the ZnO particles (shown in Fig. 3 along with the FESEM image).

The optical absorption measurements of the prepared samples were done by dispersing 1 mg of powder in 3 ml of water. Fig. 4a depicts the absorption spectra of all the prepared ZnO and Mg doped ZnO samples. There are three different peaks at the wavelengths of 366, 296 and 235 nm. These peaks are due to $n=1$, 2 and 3 excitonic absorption from ZnO nanostructures, respectively. Interestingly, when the doping concentration of Mg increases, all the peaks become sharp and intense. The optical properties of semiconductor nanoparticles depend on the shape and structure of the valence band and conduction band. Apart from this dopant also plays a role through the "Burstein–Moss" (BM) effect [9], while doping ions in semiconductors, will increase the band gap. Fig. 4b shows the blue shift in exciton peak maximum with the Mg concentration, which confirms the BM effect.

Considering the particles size, when the size is less than the "Bohr radius" (for ZnO Bohr radius is 2 nm) it is said to be in strong confinement regime and bigger than these, the particles are said to be in weak confinement regime. In this regime, the

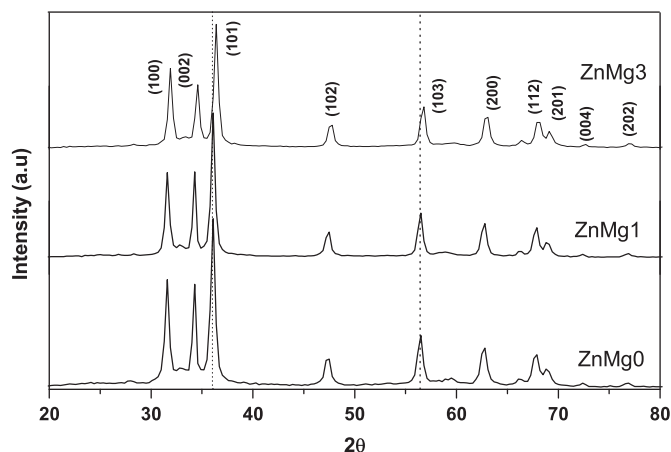


Fig. 1. X-ray diffraction patterns of ZnMg0, ZnMg1 and ZnMg3 samples. Dotted line indicates the shift in peak angle with level of doping concentration (see the sample naming).

Coulomb energy is much larger than the confinement effect [15]. In the present case, the prepared particles are well above the Bohr radius, so in these structures the electron–hole pair is confined as a whole and quantification of the movement of the center of mass is accomplished. The envelope wave function of the electron–hole pair (excitonic) is the product of two wave functions describing the movement of the electron–hole (e–h) pair with respect to the center of mass and the movement of the center of mass is assumed to be confined to the infinite spherical well.

By solving the Schrodinger equation the energies of the possible optical transition will be [16,17]

$$E_n = E_g - E_{exc} + \frac{\hbar^2 \pi^2 n^2}{2MR^2}$$

where $M = m'_e + m'_h$ is the total mass of the e–h pair, 'R' is radius of the nano-particle, ' E_g ' is the bulk band gap energy, ' E_{exc} ' is exciton binding energy and 'n' is the quantum number. Through this equation the size of the nanoparticles acts in the optical transitions even though it is bigger than the quantum size effect regime. This size variation may also be the combined effect of absorption shift of ZnO with Mg doping (from SEM studies). Fig. 5 depicts the calculated excitonic band gap (for the $n=1$ exciton) of the prepared materials. This is obtained from the optical absorption spectrum. It is clear that more level of doping (except ZnMg1) causes increase in excitonic band gap, proving the BM effect.

Gaussian de-composed fluorescence peak of ZnMg0 is shown in Fig. 6. The fit shows the complete profile is a combination of four bands. Wang et al. [18] found a similar kind of broad emission, which is attributed to the surface dangling bonds and oxygen vacancies in the surface. We also attribute the same to our system. Fujihara et al. [19] found the annealing atmosphere induced emission in Mg doped ZnO thin films showed a similar kind of band emission. Rakshit et al. [12] studied the photoluminescence of Mg doped ZnO nanostructures, which are oleate

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