Superlattices and Microstructures 51 (2012) 942–951

Contents lists available at SciVerse ScienceDirect

Superlattices and Microstructures

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

Synthesis by sol–gel process, structural and optical properties of nanoparticles of zinc oxide doped vanadium

J. El Ghoul [a,*], C. Barthou [b], L. El Mir [a,c]

[a] Laboratoire de Physique des Matériaux et des Nanomatériaux Appliquée à l'Environnement, Faculté des Sciences de Gabès, Cité Erriadh Manara Zrig, 6072 Gabès, Tunisia
[b] Institut des NanoSciences de Paris (INSP), UPMC Université Paris 6, CNRS UMR 7588, 140 rue de Lourmel, F-75015 Paris, France
[c] Al-Imam Muhammad Ibn Saud University, College of Sciences, Department of Physics, Riyadh 11623, Saudi Arabia

ARTICLE INFO

Article history:
Received 27 January 2012
Received in revised form 4 March 2012
Accepted 16 March 2012
Available online 23 March 2012

Keywords:
Zinc oxide
Nanoparticles
Photoluminescence
Optical materials
Sol–gel

ABSTRACT

We report the elaboration of vanadium-doped ZnO nanoparticles prepared by a sol–gel processing technique. In our approach, the water for hydrolysis was slowly released by esterification reaction followed by a supercritical drying in ethyl alcohol. Vanadium doping concentration of 10 at.% has been investigated. After treatment in air at different temperatures, the obtained nanopowder was characterised by various techniques such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and photoluminescence (PL). Analysis by scanning electron microscopy at high resolution shows that the grain size increases with increasing temperature. Thus, in the case of thermal treatment at 500 °C in air, the powder with an average particle size of 25 nm shows a strong luminescence band in the visible range. The intensity and energy position of the obtained PL band depends on the temperature measurement increase. The mechanism of this emission band is discussed.

1. Introduction

Zinc oxide (ZnO) is an attractive material for applications such as luminescent screens, varistors, lasers, optoelectronic devices and room temperature ferromagnetic materials [1–6]. ZnO powder can be prepared by many methods such as thermal oxidation of metallic zinc, hydrothermal methods, plasma chemical synthesis, laser ablation, vapour condensation and others. The morphology and the

* Corresponding author. Tel.: +216 97 86 35 99; fax: +216 75 39 24 21.
E-mail address: jaber.elghoul@fsg.rnu.tn (J. El Ghoul).

0749-6036/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.spmi.2012.03.013

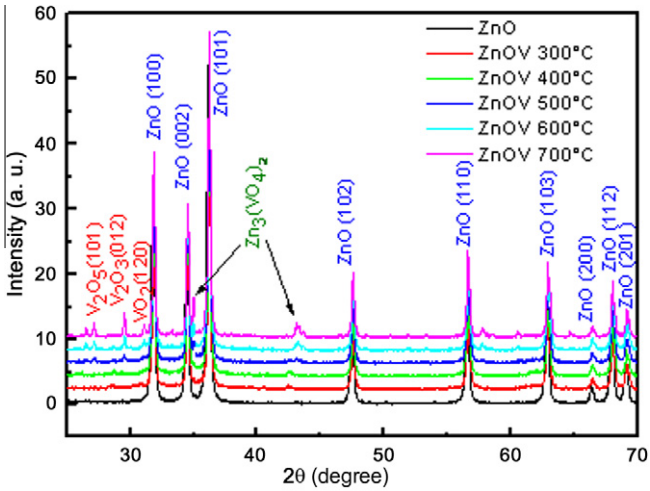

Fig. 1. X-ray diffraction spectrum of V doped ZnO nanoparticles for different treatment temperatures.

average size of the obtained nanocrystal powders strongly depend on the preparation method and synthesis conditions [6–10].

The luminescent properties are very sensitive to the defect content, stoichiometry, impurity type and concentration, grain size and powder morphology. Therefore, it is important to use X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) to study powders and to examine their effects on the luminescence properties. The main luminescence bands were observed in the 1.8–2.4 eV spectral region [11–14] (defect related luminescence) and at ~3.1–3.45 eV (excitonic states) in the ZnO crystals and the nanostructured systems at room temperature [15].

Also different approaches of transition metal (TM) doped ZnO nanocrystalline powders were investigated and the results different from those obtained on thin films have been reported [16–20]. In most of these studies, the synthesis and doping are achieved by a sol–gel process.

Thin films have equally been prepared from such powders by spin coating but the properties of the films can be different from those of the initial material. We report in this paper a new approach to obtain such powders based on hydrolysis of zinc acetate in methanol followed by supercritical drying in ethanol using modified sol–gel process.

The effect of vanadium as TM doping element on structural and optical properties of the powder is investigated for different annealing temperature in air.

2. Experimental details

Vanadium-doped ZnO nanocrystals were prepared by the sol–gel method using 16 g of zinc acetate dehydrate as precursor in a 112 ml of methanol. After 10 min of magnetic stirring at room temperature, 0.628 g of ammonium metavanadate corresponding to [V]/([Zn] + [V]) = 0.10 was added. After 15 min magnetic stirring, the solution was placed in an autoclave and dried under supercritical conditions of ethyl alcohol (EtOH). The obtained powder was then annealed in a furnace for 2 h at different temperatures in air.

X-ray diffraction (XRD) patterns of vanadium doped zinc oxide nanopowder were carried out by a Bruker D5005 diffractometer, using CuKα radiation (λ = 1.5418 Å). The synthesized products were also characterized using a JEOL JSM-6300 scanning electron microscopy (SEM) and a JEM-200CX transmission electron microscopy (TEM). The specimens for TEM were prepared by putting the as-grown products in EtOH and immersing them in an ultrasonic bath for 15 min, then dropping a few drops of the