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Zinc oxide nanoparticles with incorporated silver: Structural, morphological, optical and vibrational properties

Edgar Mosquera[a,*], Carolina Rojas-Michea[b], Mauricio Morel[a], Francisco Gracia[b], Víctor Fuenzalida[c], Ramón A. Zárate[d]

[a] Departamento de Ciencia de los Materiales, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Av. Tupper 2069, Santiago, Chile
[b] Departamento de Ingeniería Química y Biotecnología, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Av. Tupper 2007, Santiago, Chile
[c] Departamento de Física, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Av. Blanco Encalada 2008, Santiago, Chile
[d] Departamento de Física, Facultad de Ciencias, Universidad Católica del Norte, Casilla 1280, Antofagasta, Chile

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ABSTRACT

Zinc oxide nanoparticles with different amounts of incorporated silver (ZnO:Ag; 0.6, 3, 6, and 9 at.% Ag) have been successfully synthesized by a simple sol gel method. The effect of Ag content on the properties of ZnO nanoparticles have been studied by various characterization techniques. The results from X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy (RS) suggest that elemental silver is present as a second phase. The UV–visible absorption and photoluminescence (PL) properties of the samples were also studied. PL data at room temperature reveals a strong blue emission. In addition, Raman spectroscopy results indicate a very strong A_1(LO) mode resulting from oxygen vacancies and zinc interstitials. A new local vibrational mode (LVM) at 480 cm^{-1} induced by silver can also be observed in the Raman spectra, suggesting silver incorporation into the ZnO lattice compensating the Zn vacancies, which is consistent with the XRD results.

1. Introduction

Metal oxide semiconductor nanostructures have attracted considerable research interest during the last several years in terms of new technological applications, mainly because of their unique properties observed only at nanosized dimensions. Zinc oxide (ZnO) is a large band gap semiconducting metal oxide with a high-exciton binding energy (60 meV) [1–3]. This binding energy allows the excitonic transitions to occur even at room temperature (RT), which could mean higher radiative recombination efficiency for spontaneous emissions as well as a lower threshold voltage for laser emission. ZnO has been investigated in the past decade due to its interesting optical and electrical properties [4,5]. Recently, doped ZnO nanostructures have attracted significant attention for photocatalytic applications [6,7], where the effect of doping could greatly improve the luminescent properties of this material, as well as the photocatalytic degradation activity [1,2,8–10]. In particular, the influence of Ag-doping on the optical properties of ZnO for enhancing luminescence efficiency and producing p-type conductivity is an exciting research area wherein silver acts as an electron acceptor in the material [11]. In addition, it has been reported that the photocatalytic degradation activity of ZnO is improved by silver addition, which has been attributed to the doping induced modification of surface properties [12].

Several methods [13] have been reported to synthesize nanostructures of Ag doped ZnO [1,12,14–16]. However, the oxidation states, structural and optical properties of Ag incorporated ZnO nanoparticles have not been extensively studied.

The present work shows that ZnO nanoparticles modified with silver, posses interesting properties, due to various defects present in the lattice. XRD, XPS and Raman spectroscopy were used as powerful techniques for the nondestructive study of dopant incorporation. The surface plasmon resonance (SPR) property has been monitored in the UV–visible regime of 400–500 nm using UV–visible absorbance. Effects of silver dopant incorporation on the PL behavior of the nanoparticles are studied in detail. This investigation was undertaken to study the effect of silver incorporation on the structural, optical and vibrational properties of the samples.

* Corresponding author. Tel.: +56 2 2978 4795/2978 4222; fax: +56 2 2699 4119.
E-mail addresses: edemova@ing.uchile.cl (E. Mosquera), rojasmichea@gmail.com (C. Rojas-Michea), mmorel@ing.uchile.cl (M. Morel), Fgracia@ing.uchile.cl (F. Gracia), vfuenzal@ing.uchile.cl (V. Fuenzalida), rzarate@ucn.cl (R.A. Zárate).

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2. Experimental

2.1. Materials

High purity zinc nitrate ($Zn(NO_3)_2{\cdot}6H_20$), silver nitrate ($AgNO_3$), and polyvinyl alcohol (PVA, Mw: 89,000–98,000 g/mol) were obtained from Sigma Aldrich, and used as received without any further purification. Absolute ethanol with purity of 99.5% was obtained from Merck, Germany. The solvent used in the experiments was a mixture of deionized water and ethanol (50:50 volume).

2.2. Synthesis of ZnO and ZnO:Ag

A sol–gel process was used to prepare ZnO, and ZnO:Ag nanoparticles. Typically zinc nitrate (4 g) and silver nitrate (x = 13.9, 69.1, 138, and 207 mg, respectively) were dissolved in a mixture of deionized water and ethanol (50:50), and 8 g of PVA were added to prepare the corresponding gel solution. For the preparation of ZnO nanoparticles, an ethanol–water mixture (50:50) was used to dissolve 4 g of zinc nitrate and 8 g of PVA. All formulations were stirred at 80 °C in order to get a good mixture. Finally, the gels of ZnO and ZnO:Ag were calcined at 600 °C for 8 h in air. The molar ratios and molar composition of all samples are reported in Table 1.

2.3. Characterization techniques

The phase purity and the crystallite size of the prepared samples were characterized using a Bruker D8 X-ray diffractometer with CuK$\alpha_{1,2}$ radiation at room temperature (RT). The XRD instrument was operated at 40 kV and 30 mA. The Rietveld refinements were performed on XRD patterns obtained at a step size and scan rate of 0.01° and 0.1 s, respectively. A scanning electron microscope (SEM, FEI Quanta 250) was used to observe the surface morphology of the synthesized powders. Absorbance measurements of the prepared samples were obtained using a Rayleigh UV-1800 UV/vis spectrometer in the range 300–900 nm. Photoluminescence (PL) measurements of the synthesized samples were performed at room temperature in a Perkin Elmer spectrofluorometer LS-55, equipped with a Xenon lamp. Information about the oxidation states of the elements in the prepared samples was obtained from X-ray photoelectron spectroscopy (XPS, Physical Electronics system model 1257), using Al Kα emission, with working pressures in the range of 10^{-6}–10^{-7} Pa, using high resolution scans (pass energy 44.75 eV and step size 0.2 eV). All spectra were analyzed using Multipak and XPSpeak41. The energy scale was calibrated by assigning 284.8 eV to the C1s peak corresponding to adventitious carbon. Finally, Raman spectra were recorded at room temperature in a backscattering geometry using a WITec alpha300R spectrometer, model CRC200. Radiation of 632.8 nm (1.96 eV) from a He–Ne laser was focused on the sample using a 100× objective.

Table 1
Molar ratios and molar composition.

Sample (at.% Ag)	Weight $Zn(NO_3)_2$ (g)	Weight $AgNO_3$ (mg)	Moles Zn:Ag	XRF	
				Zn	Ag
0.6	4	13.9	99.43:0.57	98.894	0.517
3	4	69.1	97.23:2.77	97.148	2.432
6	4	138	94.14:5.86	94.031	5.695
9	4	207	91.06:8.94	91.782	7.921

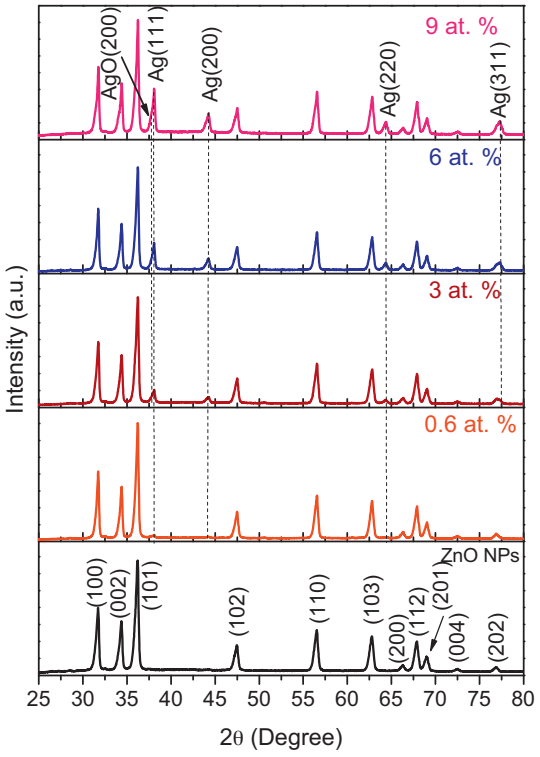

Fig. 1. X-ray diffraction patterns of ZnO and ZnO:Ag nanoparticles prepared by PVA-based sol gel synthesis.

3. Results and discussion

3.1. Structural studies and chemical states

The structural and chemical studies have been carried out through XRD and XPS analysis, for detecting the crystalline structure and silver oxidation state in these materials. The room temperature XRD patterns of the samples are shown in Fig. 1. XRD patterns of undoped ZnO exhibited the characteristic peaks of hexagonal wurtzite structure. The pattern from undoped ZnO nanoparticles is in good agreement with the JCPDS file no: 79-0208 and no other crystalline phases were detected. For the low percentage of silver additions (0.6 at.% Ag), the XRD pattern shows low-intensity diffraction peaks at 2θ values of 38.08°, 44.27°, and 64.38° revealing the presence of Ag (in agreement with JCPDS 4-0783) [17] in addition to ZnO diffraction peaks. For higher percentage of Ag addition (3, 6, and 9 at.% Ag), the XRD patterns of the samples contain four additional peaks at 2θ values of 38.08°, 44.27°, 64.38°, and 77.33°, assigned to elemental silver. These findings suggest that the as-grown ZnO:Ag nanoparticles exhibit the formation of elemental Ag entities as a second phase. An additional peak at 2θ = 37.89°, corresponding to AgO species, is also observed in the samples (see Table 2 and Fig. 3) [18].

Table 2
Position of the main diffraction peaks and average crystallite size calculated from the XRD patterns of the undoped and Ag incorported ZnO nanoparticles.

Sample (at.% Ag)	ZnO(1 0 1) peak position (°)	Ag(1 1 1) peak position (°)	AgO(2 0 0) peak position (°)	XRD crystallite size (nm)
0	36.2	–	–	23.45
0.6	36.22	38.08	–	27.35
3	36.23	38.09	37.89	25.26
6	36.23	38.08	37.90	25.92
9	36.24	38.09	37.88	25.26