

Accepted Manuscript

Full Length Article

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PII: S0169-4332(18)31738-0
DOI: <https://doi.org/10.1016/j.apsusc.2018.06.169>
Reference: APSUSC 39677

To appear in: *Applied Surface Science*

Received Date: 19 April 2018
Revised Date: 31 May 2018
Accepted Date: 19 June 2018

Please cite this article as: O. Marin, P. Alastuey, E. Tosi, J. Orive, E. Mosquera, G. Zampieri, S. Suárez, D. Comedi, M. Tirado, Suppression of the green emission, texturing, solute-atom diffusion and increased electron-phonon coupling induced by Ni in sol-gel ZnNiO thin films, *Applied Surface Science* (2018), doi: <https://doi.org/10.1016/j.apsusc.2018.06.169>

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Suppression of the green emission, texturing, solute-atom diffusion and increased electron-phonon coupling induced by Ni in sol-gel ZnNiO thin films

Oscar Marin^{1,*}, Patricio Alastuey², Ezequiel Tosi¹, Joseba Orive³, Edgar Mosquera^{4,5},
Guillermo Zampieri^{5,6}, Sergio Suárez^{5,6}, David Comedi^{1,‡} and Mónica Tirado^{2,⊗}

¹ Nanoproject – LAFISO, Facultad de Ciencias Exactas y Tecnologías, Universidad Nacional de Tucumán, and INFNOA (CONICET-UNT), San Miguel de Tucumán, Argentina.

² Nanoproject – LNPD, Facultad de Ciencias Exactas y Tecnología, Universidad Nacional de Tucumán, and INFNOA (CONICET-UNT), San Miguel de Tucumán, Argentina.

³ Laboratorio de Materiales Funcionales a Nanoescala, Departamento de Ingeniería Química, Biotecnología y Materiales, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Santiago de Chile.

⁴ Departamento de Física, Universidad del Valle, Cali, Colombia

⁵ Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Argentina.

⁶ Instituto Balseiro, Centro Atomico Bariloche, Bariloche, Argentina.

Corresponding authors:

*Oscar Marin: omarin@herrera.unt.edu.ar

‡David Comedi: dcomedi@herrera.unt.edu.ar

⊗Monica Tirado: mtirado@herrera.unt.edu.ar

Abstract

Zn_{1-x}Ni_xO thin films (nominal x=0, 0.01, 0.02, 0.04, 0.1 and 0.2) were synthesized on silicon substrates through a sol-gel/dip-coating technique. Samples were studied by X-ray diffraction, scanning electron microscopy, photoluminescence spectroscopy, Rutherford backscattering spectrometry and depth-profiling X-ray photoelectron spectroscopy. The results from X-ray diffraction show growth in the wurtzite crystal structure for all samples, with cubic NiO being detected as a secondary phase for x = 0.2. While for x = 0 (pure ZnO) no texture is present, for 0 ≤ x ≤ 0.1 strong preferential crystallization along the c-axis is observed. A tendency for Ni diffusion towards the film/Si substrate interface was observed. The formation of substitutional Zn_xNi_{1-x}O solid solution for 0.01 ≤ x ≤ 0.04 is suggested by the results. Photoluminescence spectra exhibit strong near band edge UV emission and suppression of deep defect-related emission in the visible upon Ni²⁺ incorporation into the ZnO lattice. As in pure ZnO, the UV emission in ZnNiO at room temperature is dominated by the first two phonon replica of the excitonic emission, however the LO phonon energy ($\hbar\omega_{LO}$) is reduced by up to ~ 15 meV in the 0 ≤ x ≤ 0.04 range. Due to this reduction of $\hbar\omega_{LO}$, the exciton-phonon coupling increases, in consistency with a corresponding expected increase of the Fröhlich coupling constant with decreasing $\hbar\omega_{LO}$.

Keywords: Sol-Gel synthesis; Zn_{1-x}Ni_xO; Rutherford Backscattering; Depth-profiling X-Ray Photoelectron Spectroscopy; Electron-phonon coupling; Fröhlich interaction.

1. Introduction

Nanostructured ZnO films are being intensively studied due to their important technological applications [1], including UV light sensors [2], transparent electrodes for solar cells [3] and chemical sensors [4]. In addition to being a wide band gap semiconductor (~ 3.37 eV), ZnO exhibits an exciton binding energy of 60 meV, i.e. much

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