Photoluminescent Enhancement by Effect of Incorporation Nickel in ZnO Films Grown

Delfino R. Gutiérrez-Olvera, Tomás Díaz-Becerril, Godofredo García-Salgado,
Antonio Coyopol-Solís, Enrique Rosendo-Andrés, Reina Galeazzi-Isasmendi, Ramón Peña-Sierra,
Crisóforo Morales-Ruiz, Roman Romano-Trujillo, and Fabiola G. Nieto-Caballero

Abstract — Microstructured films of undoped zinc oxide (ZnO) and ZnO doped with nickel (ZnO:Ni) were grown by hot filament chemical vapor deposition (HFCVD) technique on Si (100) substrates at 500 °C. Pellets of ZnO and ZnO:NiO as oxidant agent were used. A shift to the right around 0.17 degree of the X-Ray Diffraction pattern of the ZnO:Ni film was observed with respect to undoped ZnO films. Morphologically by Scanning Electron Microscopy was noticed a Core-Shell type growth in ZnO undoped and a nanostructured type (Nano-wire) in ZnO doped with Ni. Photoluminescence measurements showed an increase in the intensity of the green emission band of ZnO:Ni. It was attributed to defects of oxygen vacancies (V_O), zinc vacancies (V_{Zn}), zinc interstitials (Zn_i), oxygen interstitials (O_i), and oxygen vacancies complex (V_O complex) in the structure of the film. The incorporation of Ni atoms in the ZnO structure stresses the crystal lattice, leaving behind a large number of surface defects that increase the emission of PL.

Key word — Core-Shell, HFCVD, Nano-wires, Sea urchin, ZnO, ZnO:Ni.

I. INTRODUCTION

ZnO commonly crystallizes in a Wurtzite-type hexagonal structure at 300 K. It has a direct bandgap (E_g) of 3.3 eV as bulk material. It is a semiconductor with an n-type conductivity at room temperature [1]. This is mainly attributed to a large number of defects as oxygen vacancies (V_O) [2], zinc vacancies (V_{Zn}) [3], zinc interstitials (Zn_i) [4], and oxygen interstitials (O_i) [5]. Several authors have reported a p-type conductivity obtained, only in laboratories,

by doping ZnO with different elements of the periodic table and with different deposition techniques. For example, by pulse laser deposition (PLD), metalorganic molecular-beam epitaxy (MOMBE), radiofrequency magnetron sputtering (RF Magnetron Sputtering), and metalorganic chemical vapor deposition (MOCVD); ZnO was doped with Arsenic [6], Nitrogen [6], Phosphorus [7], and Nitrogen [7], respectively. However, these results have been difficult to replicate in order to achieve the desired homojunction. By another hand, different morphological growths have been reported, such as microwires [8], microribbons [9], microspheres [9], and even nanometric structures as nanoparticles [10], nanorods [11], and nanowires [12] of ZnO with the aim of manufacture different types of devices as gas sensors [13], light-emitting diodes [14] photodetectors [15], high electron mobility transistors (HEMT) [16], [17], field-effect transistors (FET) [18] and thin-film transistors (TFT) [19]. In this work, microsphere and sea urchin-type structures were found; the last structure is obtained when ZnO films are doped with Nickel. The obtaining process consists of the interactions of Ho with ZnO:NiO pellets for the generation of gaseous precursors and their subsequent deposit on silicon substrate using the HFCVD technique. This with the aim of improving the photoluminescence of ZnO for a possible application as light-emitting devices.

II. MATERIALS AND METHODS

ZnO films doped with Ni were grown from ZnO:NiO pellets with a mass ratio of 1:1, such pellets were used as a solid source which was obtained by compressing powders of ZnO (Mallinckrodt Chemical CAS 1314-13-2, St. Louis, MO, USA), and NiO (ALDRICH CAS 1313-99-1, St. Louis, MO, USA) at a pressure of 600 Kgf/cm. For the deposited films of undoped ZnO, the compressed powders of ZnO were used as solid sources. For deposits of the films, p-type silicon substrates of 1.5 cm², with a resistivity of 5-10 Ω -cm and <100> oriented were used. Films of ZnO:Ni were grown by the HFCVD method. Such technique involves heating up to 2000 °C a tungsten filament. The substrate is exposed to a region where H₂ species have higher kinetic energy because H₂ is thermally activated in the filament. This configuration can lead to greater interaction between the growth of ZnO and the H₂ species.

The following chemical reaction is proposed:

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Delfino R. Gutiérrez-Olvera, Universidad Autónoma de Puebla, México.

(e-mail: delfino.rgo@gmail.com).

Tomás Díaz-Becerril, Universidad Autónoma de Puebla, México.

(e-mail: tomas.diaz.be@gmail.com).

Godofredo García-Salgado, Universidad Autónoma de Puebla, México.

(e-mail: godgarcia@yahoo.com).

Antonio Coyopol-Solís, Universidad Autónoma de Puebla, México.

(e-mail: acoyopol@gmail.com).

Enrique Rosendo-Andrés, Universidad Autónoma de Puebla, México.

(e-mail: enrique171204@gmail.com).

Reina Galeazzi-Isasmendi, Universidad Autónoma de Puebla, México.

(e-mail: ingquim25@gmail.com).

Ramón Peña-Sierra, Centro de Investigación de estudios Avanzados del IPN, México.

(e-mail: rpsierra@cinvestav.mx).

Crisóforo Morales-Ruiz, Universidad Autónoma de Puebla, México.

(e-mail: crisomr@yahoo.com.mx).

Roman Romano-Trujillo, Universidad Autónoma de Puebla, México.

(e-mail: roman.romano@gmail.com).

Fabiola G. Nieto-Caballero, Universidad Autónoma de Puebla, México.

(e-mail: ruscaballero@yahoo.com.mx).

where MO is a Metal Oxide (ZnO or Nickel Oxide (NiO)), H_2 is molecular hydrogen, M is a Metal and, H_2O water molecule [20]. According to equation (1), it was expected that both metal Nickel (Ni) and Zinc (Zn) with lower melting points (mp) (1455 and 420 °C, respectively) than NiO and ZnO (1955 and 1974 °C, respectively) can be easily sublimed. Into the gaseous phase and under an oxidant atmosphere, NiO and ZnO films are expected to be grown over the substrate. The distance between the filament and the source was calibrated to reach a temperature of 500 °C on the substrate surface. The growth process was carried out as a result of the reactivity of the atmosphere into the HFCVD reactor which increases and promotes the precursor gas formation. In the experiment, a flow of hydrogen gas at a constant rate of 50 sccm through the filament for 60 s was used [21]. The hydrogen gaseous atmosphere used was of chromatographic grade supplied by INFRA. H_2 reacted with a ZnO: NiO source generates gas precursors.

Fig. 1. The experimental arrangement at the center of the HFCVD system.

To study the effect of doping in ZnO with Nickel, experiments were performed under the same conditions using an undoped ZnO pellet. The X-ray diffraction measurements were carried out on a Bruker AXS D8 Discovery (Billerica, MA, USA) diffractometer. Copper radiation with a wavelength of 1.54 Å, was used. PL spectra was obtained using a Fluoro max 3 system (HORIBA, Ltd., Kyoto, Japan), with an excitation wavelength of 330 nm. Morphological characterization of the microstructures was made with an AURIGA 3916-FESEM scanning electron microscope (Zeiss, Jena, Germany).

TABLE I: EXPERIMENTAL DETAILS FOR THE GROWTH OF THE FILMS

Label	The Weight percentage ratio of ZnO:NiO	Substrate temperature	The time process
S0	1:0	500	1 min
S1	1:1	500	1min

III. RESULTS AND DISCUSSION

A. X-ray Diffraction Analysis

Fig. 2 shows the diffractograms of the samples grown at 500 °C. The diffraction peaks located at $2(\theta)$ =32°, 34.6°, 47.8°, 56.8°, 63.1°, 68° and 69.3° corresponding to the

planes (100) (002) (101) (102) (110) (103) (112) and (201) of the hexagonal crystal structure of ZnO (ICDD #00-036-1451), indicated by a vertical red line. The peaks located at $2(\theta)$ =36.4°, 39.2°, 43.3°, 54.5° and 70.8° match to the planes (002), (100), (101), (102) and (110) corresponding to Zn in the hexagonal phase (ICDD # 00-001-1244), indicated by a vertical green line.

Fig. 2. XRD pattern of the deposited at 500 °C S0 and S1.

In XRD patterns from undoped ZnO film (labeled as S0) and ZnO:NiO films (labeled as S1) the hexagonal phase of ZnO and Zn were observed. The analysis of the patterns showed a small shift to the left in the peaks of ZnO:NiO with respect to the diffraction peaks of the ZnO film. The effect is probably caused by a compression-type micro-stress attributed to the Ni atoms, that substitute Zn atoms inside the ZnO structure [22] or to the fact that the ionic radius of Ni (0.68 Å) is slightly bigger than the ionic radius of Zn (0.60 Å) [23].

B. Scanning Electron Microscopy (SEM)

In the SEM micrograph of undoped ZnO film Fig. 3(a), microsphere morphology on the surface of this structure a chain-like framework is observed. In the same way, this growth is shown in the deep of the microstructure. In Fig. 3(b), of the sample of ZnO:NiO, the morphology of microsphere type is shown. On the surface of the microstructure, a nano-wires type structure can be seen over all the surfaces of the film. In both processes the growth mechanism for these microstructures is as follows, first, the Zn atoms are dispersed on the substrate surface which was heated at 500 °C. The hot filament simultaneously heats the substrate and the source maintaining a temperature gradient between them, which facilitates the transport of the material. The Zn powders mp = 420 °C are the first to melt and aggregate to form droplets on the surface of the substrate. The decomposition of the surface is generated an atmosphere rich in oxygen inside the reaction chamber [24]. During the nucleation, the oxygen bound with Zn droplet forming Zn and ZnO Core-Shell. The difference between these processes consists of the function of the Ni atoms, that act as a catalyst, favoring the growth of ZnO nano-wire on the surface of the microsphere, forming shapes like a sea urchin [25] (see Fig 3(b)).

Fig. 3. SEM micrographs of the sample (a) S0, (b) S1.

C. Energy Dispersive Spectroscopy (EDS) Analysis

EDS spectrum has been determined for different regions of the S0 and S1 films, see Table II. According to the analysis of the results, for undoped ZnO (S0) film the amount of Zn is bigger than the O. (on average 80 at% and 20 at%, respectively). The ZnO:Ni (S1) film can see a decrease in Zn and an increase in Ni (on average 80 at% and 0.3 at %, respectively). EDS analysis was performed inside the microsphere, S0 and S1 films rich in Zn were observed, (on average 80 at%). This ratifies the aforementioned.

TABLE II: THE ATOMIC PERCENTAGE OF UNDOPED ZnO AND ZnO:NI FILMS OBTAINED BY HFCVD TECHNIQUE

Atomic percentage of elements (%)				
Label	Zn	O	Ni	Total
S0	80.34	19.66	-	100
S1	80.05	19.66	0.29	100

D. Photoluminescence (PL)

Fig. 4(a), are shown the PL-spectrum for the films of S0 and S1 at room temperature. The most notable effect of the incorporation of Ni in the ZnO matrix is the increase in the PL intensity emission band located at 410 and 700 nm (1.77 eV-3.02 eV). In addition, the maximum emission shifts to higher energy in S1. This could mean that there is an increase and/or introduction of Ni radiative centers in the ZnO. In Fig. 4(b), the deconvolution of the spectrum S1 was

performed in order to obtain the bands that compose such spectrum. It was observed that the maximum emission is centered in the energy range of the green emission band, around 509-520 nm (2.45-2.39 eV). This optical behavior of ZnO is usually associated with the presence of several types of defects as V_O , V_{Zn} , Zn_i , O_i , O_{Zn} [26] or some metals transitions [24-26], generation recombination centers inside the bandgap (E_g) of the structure.

Hwang et al.[29] and Fedorov et al.[5], associate the green emission band to undoped ZnO with the presence of V_O and V_{Zn} [27],[30] that introduces deep acceptors in the E_g . Green luminescence is because of the electronic transition between shallow donors and deep acceptors.

The material Zn-rich guarantees the existence of V_O . The transition between those states and V_O (deep acceptor states) might be the origin of the increase in the green emission band. Additionally, a blue luminescence band emerges around 450 nm (2.21 eV) in the ZnO PL spectrum. Recently Zeng et al. [31] and Cao et al.[32], obtained visible dichromatic photoluminescence emitting in blue/violet, and green regions, introducing Zn_i defects in the ZnO structure.

Fig. 4. Photoluminescence spectrum of (a) ZnO undoped and ZnO:Ni; Deconvolution spectrum on (b) ZnO:Ni sample.

IV. CONCLUSION

ZnO and ZnO:Ni films were grown using the HFCVD technique and pellets of ZnO and ZnO:NiO as oxidant agents. Probably Ni atoms modify the crystalline structure

of ZnO since it causes a shift in the position of the diffraction peaks with respect to undoped ZnO. By SEM, shapes like a sea urchin due to the doping of ZnO were observed. The growth of these nanostructures resulted in a larger surface area, increasing the number of defects on the surface of the ZnO:Ni film compared to the undoped ZnO structures. The green-yellow emission band is due to defects in Zn_i , V_O , O_i , O_{Zn} , and some V_O complexes. This work shows the possibility of obtained ZnO:Ni films in a short time process that implies a lower cost for the manufacturing of the optoelectronic device.

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