Structural and optical characterization of ZnO layers grown by chemical bath deposition activated by means microwaves

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Abstract: ZnO has received increasing attention and been recognized as a promising candidate for applications due to its optoelectronic properties in the UV range. The ZnO is grown by the technique of Chemical Bath Deposition activated by microwaves (CBD-µW). X-rays scattering yields a hexagonal polycrystalline wurtzite type structure. The Raman spectra present four main peaks at 444, 338, 104 and 78 cm⁻¹ associated to the modes $E_{2}^{\text{high}}$, $(E_{2}^{\text{high}} - E_{2}^{\text{low}})$, $E_{2}^{\text{low}}$ and an unidentified band. The 300 K photoluminescence presents visible/UV radiative bands associated to vacancies of zinc and oxygen. In addition, it was carried out energy dispersive spectroscopy (EDS) measurements on the films to determine their stoichiometry, relating the intensity of radiative bands associated to oxygen and zinc vacancies.

Key Words: ZnO, CBD-µW, Raman scattering, X-Ray diffraction, photoluminescence, Energy dispersive spectroscopy

1 Introduction

Zinc oxide (ZnO) is an important semiconducting oxide because it has a wide range of applications [1]. ZnO can be used in piezoelectric devices or in optoelectronic applications, especially as a transparent electrode [2, 3]. Its high electrical conductivity and optical transmittance in the visible region makes it useful for transparent conducting electrodes in flat panel displays or as optical windows in electroluminescent devices [4]. Among the various deposition techniques for ZnO thin films, DC reactive magnetron sputtering has received much attention, because of its flexibility, and because it offers good chemical composition control over extended areas. Furthermore the deposition technique offers the possibility to select the deposition rates in a wide range of values [5]. For more complex alloys, the stoichiometry of the films can be modified by changing the substrate temperature, the pressure and the reactive atmosphere used during the deposition process. Moreover the properties of the films depend too on the sputtering power and post annealing processes on the films [5,6,7].

We used the CBD technique activated with microwaves (CBD-µW). The ZnO films are grown on glass substrates. The used precursor reagents are analytic grade with purity about 99.9%.

2 Experimental details

As result of the chemical reactions in the CBD-µW the ZnO is obtained in thin film form. The solutions of the precursor reagents are prepared at room temperature using deionized water of 18.2 MΩ cm of resistivity with the purpose of diminishing the residual impurity concentration in the material. The used molar ratios are the following: Zn(NO₃)₂-0.1 M, Urea-0.1, 0.2,..., 1.0 M. The samples are submerged in the solution and NH₄OH is added to it. Afterwards, they are undergoing microwave irradiation during 5 min at maximum power keeping the temperature constant and after irradiating them at lowest power for 40 min. Finally, they are rinsed with strong agitation and are dried with gaseous nitrogen.

Structural characterization of the samples is carried out by means of X-ray diffraction (XRD) in a Bruker D8 Discover diffractometer, parallel beam geometry and monochromator of gobel mirror, CuKα radiation, 1.5406 Å, in the range of 20° <2θ <80° by step of 0.02°. The XRD data were refined using the programs POWDERX and DICVOL04 to determine the crystalline system, the parameters of unit cell and the density $\rho$. On the other hand the measurements of energy dispersive spectroscopy (EDS) were carried out in an LEO 438VP system, with W.D. of 26 mm using a pressure of 20 Pa to obtain the chemical
stoichiometry. Raman scattering experiments were performed at room temperature using the 6328 Å line of a He-Ne laser at normal incidence for excitation. The light was focused to a diameter of 6 µm at the sample using a 50x (numerical aperture 0.9) microscope objective. The nominal laser power used in these measurements was 20 mW. Care was taken to avoid the heating of the sample inadvertently to the point of changing its Raman spectrum. Scattered light was analyzed using a micro-Raman system (Lambram model of Dilor), a holographic notch filter made by Kaiser Optical System, Inc. (model superNotch-Plus), a 256x1024-pixel CCD used as detector cooled to 140 K using liquid nitrogen, and two interchangeable gratings (600 and 1800 g/mm). Typical spectrum acquisition time was limited to 30 s to minimize the sample heating effects discussed above. Absolute spectral feature position calibration to better than 0.5 cm\(^{-1}\) was performed using the observed position of Si which is shifted by 521.2 cm\(^{-1}\) from the excitation line. 300 K Photoluminescence was taken with a solid state laser 325 nm with 60mW as excitation source and a SCIENCETECH 9040 monochromator was used to perform the sweep of wavelength at room and low temperature in a cryostat CRYOGENICS.

3 Problem Solution

Figure 1 shows the diffractograms of the ZnO films. The experimental diffractograms indicate that in all the nitrate and urea ratios, the synthesized material is ZnO and besides there is not a change of crystalline phase. ZnO has hexagonal polycrystalline wurzite type structure and the variation in the solutions concentrations is not remarkably observed in the diffractograms. Besides, from the X-ray patterns was not possible to determine the influence of the urea concentration in the growing direction of the films.

ZnO commonly crystallizes in a hexagonal wurzite type structure in most of the synthesizing methods, with lattice parameters of unit cell of \(a = 3.2495 \, \text{Å}\) and \(c = 5.2069 \, \text{Å}\) and with a density \(\rho\) around 5.605 g/cm\(^3\) \cite{8}. By refinement of X-ray data one finds the unit cell parameters for all studied urea concentration, which are illustrated in Fig. 2. For the ZnO thin films the parameter average values are \(a = 3.253 \, \text{Å}\) and \(c = 5.212 \, \text{Å}\), with a tendency to increase in both parameters and a similar tendency to increase or decrease among their values starting from the molar relation 1:4 to 1:10. However, the tendency of lattice constants values in the molar relations 1:1, 1:2 and 1:3 is opposed, which can be explained if it is considered the stress when the film is deposited, this is valid for the three ratios. For the relation 1:4 the film is deposited with compressive stress and starting from the relation 1:5 again it is deposited with strain. From the refinement of experimental data the volume of the unit cell is obtained, besides of the lattice parameters, for which if it is considered that each unit cell of ZnO contains two zinc atoms and two oxygen atoms, then taking the atomic weight of the chemical elements one can determine the density \(\rho\) of this material. Fig. 3 shows the results of the densities of the ZnO films that were synthesized by CBD-\(\mu\)W. The Films density does not show a clear tendency as a function of the the urea concentration changes in the growth solution, that is why it could be considered an average value of approximately 5.662 g/cm\(^3\). However, if one only considers the ratios 1:1, 1:5 and 1:10 it could be observed that the tendency is to decrease, as the urea concentration increases in the solution.

Fig. 1. X-ray patterns of the ZnO films synthesized by CBD-\(\mu\)W, for all samples studied in this work.

![Fig. 1. X-ray patterns of the ZnO films synthesized by CBD-\(\mu\)W, for all samples studied in this work.](image1)

Fig. 2. Lattice parameters obtained by refinement of x-ray pattern data for ZnO films.

To have a more profound idea regarding the composition of the obtained ZnO thin films we carried out measurements of energy dispersive spectroscopy (EDS) to the samples with ratio: 1:1,
1:5 and 1:10. The results of such measurements are shown in Table 1, in which is included the atomic and mass percentages. From these results it is observed that the ratio 1:5 is the one that gives a good stoichiometric compound and that starting from it a higher urea concentration in the solution gives a greater presence of zinc in the material and an absence of oxygen. Continuing with the consideration that each unit cell contains two zinc atoms and two oxygen atoms, the atomic weight of the ideal unit cell is ~162.74 corresponding to 19.66% oxygen and 80.33% of zinc, then when a stoichiometric deviation of ideal unit cell occurs it could establish a correspondence between vacancies or interstices of some of the elements (V_O, V_Zn, Zn_i, O_i).

### Table 1. Result of the analysis by EDS of the samples with the relations 1:1, 1:5 and 1:10

<table>
<thead>
<tr>
<th>Ratio</th>
<th>O atomic percent (%)</th>
<th>Zn atomic percent (%)</th>
<th>O mass percent (%)</th>
<th>Zinc mass percent (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:10</td>
<td>47.01</td>
<td>52.99</td>
<td>17.83</td>
<td>82.17</td>
</tr>
<tr>
<td>1:5</td>
<td>50.08</td>
<td>49.92</td>
<td>19.71</td>
<td>80.29</td>
</tr>
<tr>
<td>1:1</td>
<td>52.43</td>
<td>47.57</td>
<td>21.24</td>
<td>78.76</td>
</tr>
</tbody>
</table>

Assuming that the volume of the unit cell remains around 47.78 Å³ for all cases and also because of the atomic weight of the zinc is four times greater that of oxygen, it could be expected that a great presence of zinc in the structure should correspond to a higher density and the contrary happens for a greater oxygen presence. However, when one analyzes the EDS results considering the densities one can see that for a greater zinc concentration in the material the density diminishes, which indicates that the zinc is present interstitially in the structure in such a way that relaxes the chemical bonds. From Table 1 is observed that the sample with ratio 1:10 contains higher zinc concentration, while the sample with ratio 1:1 contains zinc vacancies.

![Fig. 3. ZnO films density for the different ratios between the zinc salt and urea.](image1)

![Fig. 4. Curve fitting analysis of the Raman spectrum of ZnO film with ratio 1:4 grown by chemical bath.](image2)

![Fig. 5. Raman spectra of ZnO film for molar ratios 1:1, 1:4, 1:5, 1:6 and 1:10.](image3)

Figure 4 shows polarized Raman spectrum of the 1:4 ZnO film obtained at room temperature in backscattering configuration, which allows the observation of all active modes and the well-resolved ones for the deposited films studied in this work. The Raman spectrum is dominated by two intense, sharp E₂ modes at 104 and 444 cm⁻¹. The low-frequency E₂ mode, involving mainly Zn motion, displays an extremely narrow linewidth. The E₂(LO) mode displays a clear asymmetry toward low frequencies that we shall discuss in more detail below. The Raman spectrum can be deconvoluted in Lorentzian line shape signals through a standard fitting procedure performed in the whole studied interval and the results are plotted using solid lines, which are shown in Fig. 4. Reasonable fits are achieved with Lorentzian curves, whose centers are shown in figure and which allow to identify the vibrational bands.
present in the Raman spectrum. In contrast with previous works, where the \( A_1(LO) \) mode could not be detected for excitation wavelengths longer than 406.7 nm [9], we detect a weak \( A_1(LO) \) mode at 578 cm\(^{-1}\). In addition to the strong \( E_2 \) mode a new peak appears at 388 cm\(^{-1}\), which can be assigned to the \( A_1(\text{TO}) \) mode. We detect a strong mode, a low frequency one at 104 cm\(^{-1}\), which could be associated to the \( E_1^\text{low} \) mode. The \( 2E_2^\text{high} \) mode can be observed at 195 cm\(^{-1}\) in the Raman spectrum. Finally, there are two intense modes at 78 and 115 cm\(^{-1}\) that could not be identified.

One of the peaks in the intermediate-low-frequency region is observed at 338 cm\(^{-1}\). This mode had been previously assigned to transverse acoustic overtone at high pressure [13]. A similar situation occurs when the 534 cm\(^{-1}\) TO overtone [11]. The peak at 534 cm\(^{-1}\) −1 frequency is observed at 338 cm\(^{-1}\) and as the urea concentration is increased/diminished in the solution the spectra decrease though they are nearly similar.

According to the calculated phonon dispersion relations [12], the 338 cm\(^{-1}\) mode could also contain contributions from \([TO-TA]_{M.L.H} \) differences. Another prominent peak is observed at 195 cm\(^{-1}\), which exhibits \( A_1 \) symmetry and thus can be attributed to a TO overtone [11]. The peak at 534 cm\(^{-1}\) is of \( A_1 \) symmetry and can be attributed to \( 2B_1^\text{low} \) and LA overtones along \( L-M \) and \( H \).

We noted that the \( E_2^\text{high} \) mode exhibits a visibly asymmetric line shape with a low-frequency tail. This is quite apparent from Fig. 4 when one compares the line shapes of the \( E_2^\text{high} \) and \( A_1(\text{TO}) \) modes. The asymmetry of the \( E_2^\text{high} \) mode cannot be ascribed to lattice disorder. Furthermore, isotopic broadening is negligible for the \( E_2^\text{high} \) mode since it mainly involves O motion, and O is nearly isotropically pure. The line-shape broadening is then mostly determined by anharmonic phonon-phonon interactions. These can result in strongly distorted peaks when resonant interaction with a band of second-order combinations takes place (Fermi resonance), as is the case, for instance, for the GaP TO mode [13, 14], where the presence of van Hove-type singularities in the DOS of the TA+LA combination band gives rise to a highly asymmetric TO mode, which develops a side band at high pressure [13]. A similar situation occurs for the \( E_2^\text{high} \) mode of ZnO, as its frequency lies close to a ridge-like structure of the two-phonon DOS corresponding to TA+LA combinations in the vicinity of the \( K \) point [15].

Figure 5 shows the polarized Raman spectra of ZnO layers for five different urea ratios at room temperature. The spectra show a similar behaviour and only variations in the intensity of the bands. The sample 1:4 that is closely stoichiometric presents the more intense Raman spectrum and is better resolved in the urea concentration is increased/diminished in the solution the spectra decrease though they are nearly similar.
defects bound to neutral vacancies associated to oxygen and zinc [19]. As is observed in Fig. 6, band violet increases as the zinc interstitials are predominant and shifts lightly toward the blue. The green band is intense and dominant in the stoichiometric/nonstoichiometric samples and it does not shift appreciably. The violet band increases to increases the Zn interstitial concentration and it does not shift lightly to red.

4 Conclusion
ZnO was obtained by means of the activated by microwaves chemical bath deposition technique. The thin films were characterized structurally by means of X-ray diffraction, although could not determine the influence of the solution composition, considering to the zinc nitrate and urea. By EDS measurements obtained the chemical stoichiometry of the samples. To the consider that each unit cell contains two zinc atoms for two oxygen atoms is possible to establish that for a higher urea quantity the zinc incorporates interstitially and the chemical reaction is also slower.

We have carried out a detailed study of the Raman scattering of ZnO for concentrations ranging from 1:1 up to 1:10, one has discussed the origin and assigned the main bands sited at 444, 338 and 104 cm\(^{-1}\) that are associated at the modes \(E_{2}^{\text{high}}\), \((E_{2}^{\text{high}} - E_{2}^{\text{low}})\), \(E_{2}^{\text{low}}\).

Room temperature photoluminescence presents three radiative transitions labelled by green band and violet band, which are associated to vacancies and interstices of oxygen and zinc. For a higher concentration of Zinc observes that violet emission band shifts to higher energies improving the quality of the luminescence in the region UV with the presence of a lower oxygen quantity in the film.

References: