Influence of variation in the concentration of ammonium hydroxide on the size of ZnO crystal obtained by Microwave Chemical Bath Deposition

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Abstract. Films of good crystalline quality of ZnO were successfully prepared using the microwave chemical bath deposition method at a temperature of 80 °C. Concentration of the basic precursor was varied systematically in order to obtain different degrees of acidity in the precursor solutions. Increasing the pH causes an increase in yield. This increase is reflected on the thickness of the deposit. The results of atomic force microscopy (AFM) show an increase in particle size with increasing pH in agreement with the results obtained by profilometry.

Introduction

The metal oxides are currently the vehicles to achieve multifunctional heterostructures, nanostructures, and multilayer and thin films that are the basis of new optical devices whose electrical and magnetic properties interact one other. Furthermore, the metal oxides have extraordinary properties such as high electronic conductivity, optical transparency, superconductivity, thermoelectricity, etc. Therefore, the knowledge in the production of films obtained by altering its physical and chemical properties and by changing the processes of production is extremely important for the development of new applications for these materials.

The importance of ZnO is specifically based on its wide direct band gap that is 3.37 eV at room temperature and the large exciton binding energy of 60 meV. The significance of the ZnO films is such that various techniques have been employed to obtain it, such as RF magnetron sputtering at various temperatures [1], thermal oxidation of Zn ion beam sputtered films [2] Zn-vapor release in argon atmosphere and subsequent oxidation in air [3], vapor-deposition method (PVD) [4], chemical vapor deposition (CVD) [5], etc.
It has also been reported the synthesis of nanoparticles of ZnO in aqueous medium under microwave irradiation conditions, deposited on different substrates from zinc salts and various solvents [6]. However, no other report related to the variation in pH has been found. Chung-Hsin Lu et al. [7], performed an analysis related to obtain ZnO precipitates varying the pH of the solutions under hydrothermal conditions.

In this work we present the study on the variation on the concentration of ammonium hydroxide on the size and crystalline quality of ZnO obtained by microwave chemical bath deposition (MWCBD). The importance on the study and characterization on the properties of the films obtained by varying the pH of precursor solutions is that, the results obtained might help us to a better understanding of the physicochemical changes of ZnO obtained under these growth conditions.

1. Material and methods

As result of the chemical reactions in this deposition technique using microwave radiation as a way of heating, the material was obtained as a film and as precipitated powders. Because there are some reports on the behavioral grain size of ZnO precipitated powders [8], in this report we only mention the results obtained which are related to films.

Zinc nitrate hexahydrate salts (Zn(NO$_3$)$_2$·6H$_2$O, J. T. Baker) were used as a source for zinc ions, urea (CH$_4$N$_2$O, Sigma Ultra) was also used as a complexing agent, ammonium hydroxide (NH$_4$OH, E. M. Science) as oxidizing medium and Corning glass slides were used as substrates.

The solutions of the precursor reagents were prepared at room temperature using deionized water of 18.2 MΩ of resistivity with the purpose of diminishing the residual impurity quantity. Five solutions were prepared with molar ratio of 2:1 (0.2 M/0.1 M) of Zn(NO$_3$)$_2$/Urea, and NH$_4$OH was added to achieve pH of 9.25, 9.88, 10.39, 10.94 and 11.14. Three glass substrates were immersed into each solution, and then, they were placed in the microwave oven. The initial heating time was 4 minutes at maximum power reaching a temperature of 80 ºC, after this, heating was maintained at this temperature for 40 minutes, using the minimum power up to terminate the reaction. Finally, the films were rinsed with strong agitation and dried with gaseous nitrogen.

Structural characterization of the layers was carried out using X-ray diffraction (XRD). The measurements were performed on a Bruker D8 Discover diffractometer, with a geometry of parallel beams and a gobel mirror monochromator, The diffractometer worked with Cu Kα radiation = 1.5406 Å, a tube conditions of 40 KV an 40 mA, the measurement interval was from 20° to 80°, with a step size 0.02°. The topographical characterization was performed in an Atomic Force Microscope AMBIOS. The data were processed with the program WSxM 5.0 [9]. The thickness of the films was measured in a profilometer Dektak Stylus 150 with a diamond tip of 12.5 μm in diameter at the base at a resolution of 10 nm.
2. Results and discussion

It is known that during the Chemical Bath process two types of reactions are carried out: One of them produces precipitates of the material. The other one produces film on the substrate. Both of them are in competition and depend on the concentration of the precursors agent. The scope of this work is dealing with the second one.

Furthermore, we assume that the deposition process is performed according MWCBD to model Stranski-Krastanov [10] that is characterized by the growth of layers (2D films) and islands (3D microstructure). The transition layer-by-layer growth to island occurs after a critical thickness of the layer, which is highly dependent on the surface energy and lattice parameters of the substrate and the film. Figure 1 reports the growth measurement of the total thickness (2D and 3D). Where it can be seen that the thickness of the deposit increases as the pH in the solution increases. In this case, NH$_4$OH is the reactive limiting of the process. When increasing the amount of this reactive, increases the reaction yield, which is reflected on the thickness of the deposit.

![Figure 1. Graph of the ZnO film average thickness on the pH of the precursor solution](image-url)
XRD patterns from the samples synthesized with solutions of 2:1 molar ratios and different pH values are presented in Figure 2. It shows that ZnO has a polycrystalline hexagonal structure wurtzite type, according to the pattern 36-1451 of the database of PDF-2 of ICDD. The results evidence the pH influence on the nucleation and growth process.

The diffraction pattern of material having a pH = 9.25 (Figure 2) has the peak (0002) more intense, suggesting that preferential growth is present along the direction [0001], the peak observed may be due to a first deposit (2D) highly crystalline.

Through the change in pH, it is possible to control the ratio of the growth rate between Zn$^{+2}$ ions and OH$^{-}$ ions [11]. The increase of OH$^{-}$ ions inhibits growth in the plane direction (0001) and induces the growth in the family of planes [1010], [12, 13].

Figure 2. Diffraction patterns of ZnO films obtained from solutions with molar ratio 2:1, with different pH.
Table 1. Crystal size calculated from the diffraction patterns obtained from samples with different pH.

| pH   | Crystal size in different directions | Average crystal size |
|------|-------------------------------------|----------------------|
|      | (100) | (002) | (101) |                     |
| 9.25 |       | 46.53 |       | 46.53               |
| 9.88 | 21.86 | 22.61 | 24.005| 22.82               |
| 10.39| 25.45 | 29.76 | 27.84 | 27.68               |
| 10.94| 25.09 | 29.42 | 27.26 | 27.25               |

The average crystal sizes in the main orientations were calculated by using the Scherrer equation; the results are shown in Table 1. Films obtained with pH of 9.25 have a preferential growth in the orientation (002) and a size of 46.53 nm. For polycrystalline films the obtained average crystal size is between 20 and 30 nm, at higher pH.

Atomic Force Microscopy (AFM) was used for to obtain the topography of the deposits (Figure 4). Deposits with larger particle size were obtained at higher concentration of the dissolution [14] in concordance with the results obtained by profilometry. In the Figure 4, it is seen the evolution on the surface of the films in relation to the increase in the pH in the precursor solution.

![Figure 4](image_url)
4 Conclusions

ZnO films with good quality crystalline were obtained by microwave chemical bath deposition technique, which was demonstrated by XRD characterization, this analysis demonstrated that the films have the hexagonal wurtzite structure and by the Scherrer equation we found that the crystal size of the films decreases by increasing the pH. As a result of increasing pH, the topography of the films and the deposit thickness increases. It is possible to obtain films with a preferential growth orientation, as well as polycrystalline deposits by adjusting the pH in the solution used for its growth.

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