Effects of post-growth thermal annealing on room temperature pulsed laser deposited ZnO thin films

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Abstract. ZnO thin films have been elaborated by Pulsed Laser Deposition (PLD) onto glass substrates, at room temperature. Post-growth annealing treatment was applied to the films in air background. Morphology, chemical composition and optical characteristics of ZnO films were evaluated as a function of annealing temperature. With the increase in annealing temperature, the 002 axis peak intensity is improved and optical band gap is shifted to lower values. The PL peak positions shift are associated at stoichiometry change, it is confirmed with the experimental results. The films elaborated with this experimental setup could be used to applications in short wavelength optoelectronic devices, chemical and optical sensors.

1. Introduction
In the last years, ZnO thin films have become more important because of their special properties compared with the bulk material. ZnO is a semiconductor with a direct wide band gap of 3.37eV at room temperature [1-5], with unique properties and wide range of applications [1-6]. Pulsed Laser Deposition allows tailoring the deposition conditions [3-5] to obtain films with good stoichiometry, multilayered samples and the possibility of using substrates with low thermal tolerance like polymers or glass [7,8]. In this paper, we present the influence of post-growth annealing developed in air atmosphere on the morphological, chemical and optical properties of PLD ZnO thin films prepared at room temperature over glass substrate.

2. Experimental setup
The PLD deposition system and as-growth film growth parameters have been described previously [7]. Substrates are hydrolytic class D263M1 glass slides (10mm in diameter, 0.1mm thick). As-growth films were treated with a post-growth thermal annealing process (100-600°C), for 1 hour, in a conventional furnace in air atmosphere over on flat surface; the samples were allowed to cool down to room temperature in air atmosphere. Photoluminescence data were acquired at room temperature using a Cary Eclipse fluorometer (λexc=310nm; λemi=330–750nm, spectral resolution 2nm). Before test measurements, films were exposed for 1h to dry air. UV-Vis absorption spectroscopy was performed on a Cary Eclipse 50 UV-Vis Spectrophotometer. SEM analysis was made with SEM microscope JEOL JSM-840. AFM data were recorded in a Veeco Nanoscope V in contact mode over an area of 2μm×2μm. Diffractograms were recorded with a Philips X’Pert PRO-MPD with a Cu Kα (1.5406Å) source. X-ray photon spectroscopy (XPS) was performed on a Physical Electronics PHI model 5700 equipped with Mg Kα radiation (1253.6eV) in combination with 4keV Ar+ gun sputtering.
3. Results and discussion

As-growth films are homogeneous, transparent and colourless, smooth surface with clusters, the average roughness is 10nm. With annealing process is observed reduction of cluster on film surface; increment in grain size and roughness, in agree with other authors (Figure 1 and 2) [2-5]. Coalescence effects in film structure is not observed.

![Figure 1. SEM images (A) As-growth (B) annealed film at 400°C.](image1)

![Figure 2. AFM images (A) as-growth (B) annealed film at 400°C.](image2)

As-growth films are polycrystalline; the peaks (100), (002) and (101) axes are detected; (002) peaks show the highest intensity, at regardless of previous reports of amorphous films (Figure 3) [2]. The (002) peak shifting indicates an increase of interplanar spacing; there is a transformation from press stress to strain stress causing by the annealing as shown the calculated values (Table 1) [1,4,5,9]. The press stress may be derived from lattice mismatch between glass substrate and ZnO film from differences in thermal expansion coefficients [4,5,9] or owing to observed increasing crystalline grain size [1,9]; the strain stress is attributed at surface contraction owing to the elimination of defects (interstitial or vacancy) [4,5,9,10] or the elimination of chemisorbed O [3]. The increment in annealing temperature stimulates the diffusion of the atoms at more advantageous positions in the structure, it improve the film orientation in c-axis direction and reduce the crystalline defects [4-6,10].

XPS photoelectron peaks (O 1s, Zn 2p3/2 and Zn LMM) exhibited a shifting in peak position (spectra do not show), it has been associated at films defects as interstitial or vacancies of Zn and O [3,9,11]. Film stoichiometry is modified with the increment in annealing temperature. This indicates atomic redistribution and variations in film defects, it can be associated at changes in the film stress observed with XRD results.

Films present a good transmittance in the visible range, with an increment as function of annealing temperature (Figure 4). The band gap energy of ZnO films can be determined by Tauc’s plot...
\[ \ln(T) \propto \alpha \] (inset Figure 4) \[1,4,5,7,9,10\]. The calculated band gap values (Table 1) are similar to those already reported \[4,5\]. Some reports indicate that the optical properties are not modified by annealing process \[1\], although shifts in optical band gap energy is generally observed in the annealed direct-transition-type semiconductor films \[1,6\]. The effect of the annealing temperature in optical properties of films can be attributed at grain size variations \[4-5\], film stress alterations \[1,4,5,9\] or changes in the film stoichiometry \[9,10\]. In agree with our analysis; the incrementing in annealing temperature causes that press stress changes at tensile stress, indicating stoichiometry degradation, it explain the band gap shift observed as effect of O variations.

**Table 1.** Structural and optical parameters of ZnO films as function of annealing temperature.

| Annealing temperature (°C) | 002 Peak position (°) | FWHM (°) | d-spacing (Å) | Grain size (nm) | Stress (GPa) | Band gap (eV) |
|----------------------------|-----------------------|----------|---------------|-----------------|-------------|--------------|
| As-growth                  | 34,24                 | 0,409    | 2,61669       | 23              | -1,19753    | 3,27         |
| 100                        | 34,30                 | 0,305    | 2,61211       | 32              | -0,78761    | 3,31         |
| 200                        | 34,35                 | 0,246    | 2,60855       | 42              | -0,46899    | 3,27         |
| 300                        | 34,36                 | 0,191    | 2,60780       | 59              | -0,40186    | 3,26         |
| 400                        | 34,29                 | 0,225    | 2,61307       | 41              | -0,87353    | 3,25         |
| 500                        | 34,43                 | 0,216    | 2,60308       | 50              | 0,02059     | 3,24         |
| 600                        | 34,43                 | 0,222    | 2,60309       | 48              | 0,01969     | (a)          |

(a) Not evaluated

**Figure 3.** 002 XRD peak intensity and position as function of annealing temperature.

**Figure 4.** Spectra transmittance of ZnO films as function of annealing temperature. Inset: Tauc plot.

In Photoluminescence data, the peak position and intensity in PL spectra are function of the structure and stoichiometry: DLE band (500-650nm) is associated at defects like vacancies or interstitials atoms \[3,5,6,11,12\] and UV band is attributed to the near band edge emission (NBE), is originated from the recombination of free excitons \[1-3,6,7,11\]. Figure 5 shows peak position of UV and Visible PL bands as function of annealing temperature. The blue shift of DLE band as function of the rise in annealing temperature is associated at changes in crystalline defects \[O \rightarrow VO, O_{Zn}\] \[12\]; the red shift of UV peak is related with the increase in grain size \[6\], changes in O vacancies (film stoichiometry) \[2,3,7\] or type of film strain \[2\]. In agree with the experimental data, the stoichiometry degradation and crystallographic changes causing the peak shift observed.
4. Conclusions
In the present work, we showed that is possible to elaborate ZnO thin films using the PLD technique with IR laser over glass substrates at room temperature. Analysis showed defects in as-growth ZnO thin films. The effect of post-growth annealing treatment on film properties has been studied. Film morphology is strongly modified by annealing, film thickness is reduced and roughness is incremented; film cracking can be observed at highest temperature, by differences in thermal expansion coefficients between glass substrate and ZnO film. With the annealing the crystalline properties are improved in c-axis; 002 peak exhibited reduction of FWHM and increment in the intensity and grain size; all this is associated at correction of defects in the structure. The film stoichiometry study confirmed the increment in O vacancies with the annealing in agree with the shifting in the band gap and PL peak position of the UV and visible band. The post-growth annealing modifies the film properties and allows the preparation of films with tailored properties.

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