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THE ANNEALING EFFECT ON STRUCTURAL AND OPTICAL PROPERTIES OF ZnO THIN FILMS PRODUCED BY RF SPUTTERING

A. G. Rolo, J. Ayres de Campos, T. Viseu, T. de Lacerda-Arôso and M.F. Cerqueira

Departamento de Física, Universidade do Minho, Campus de Gualtar 4710-057 Braga, Portugal

In this work, a study of the structure and optical properties of undoped ZnO thin films produced by r.f. magnetron sputtering technique as a function of the growth parameters is reported. Modification under annealing conditions is also analysed. Raman spectroscopy, X-ray photoelectron spectroscopy, X-ray diffraction and optical transmittance have been used. From the position of the (002) X-ray diffraction peak and the E_2 (high) mode detected in Raman spectra, the residual stress both in the as-grown and in the annealed samples has been estimated.

Keywords: *ZnO; Thin films; X-ray; Raman; Stress*

1. Introduction

Zinc oxide (ZnO) is a II–VI wide direct-gap semiconductor with a band gap of 3.37 eV at room temperature which makes it interesting for optoelectronic applications in the near ultraviolet (UV) region. Mostly in bulk, ZnO has been intensively studied for the past fifty years. A renewed interest in ZnO derived materials arose in the mid nineties of the last century, due to its potential technological applications. Since then, ZnO thin films, quantum wells, nano-rods and quantum dots have been produced and studied hoping to apply them in optoelectronics, electronic devices as alternative to ITO and spintronics.

In this study, experimental results of crystalline structure, stress, refractive index and chemical composition of ZnO thin films before and after annealing treatment are discussed.

2. Experimental

ZnO thin films have been grown on glass substrates within a mixture of O_2 and Ar gases at a constant working pressure of 0.7 Pa and a 50°C constant substrate temperature, in an

Alcatel SCM 650 sputtering system. The target consisted of a hyper-pure (99.99%) metal zinc wafer spaced 60 mm away from the substrates.

Films thickness and optical parameters have been determined by optical transmittance in near ultra-violet - visible -near infra-red range. The micro-structure of the films has been analysed by X-ray diffraction and Raman scattering. Optical transmittance spectra have been measured in a Shimadzu UV 3101 PC spectrometer. X-ray experiments (Bragg-Bretano geometry) have been performed in a Philips PW 1710 spectrometer using CuK_α radiation. Micro-Raman spectra have been measured on a Jobin-Yvon T64000 spectrometer equipped with a cooled CCD detector, using the 514.5 nm excitation line of an Ar^+ laser in the back scattering geometry.

Growth conditions, thickness, refractive index, and structural parameters obtained by X-ray are shown in table I.

3. Results and discussion

All films are highly transparent in the visible and NIR range, as illustrated by the example in figure 1. Thickness and optical parameters of the films have been determined by fitting the spectra using the Minkov^[1] method and adopting the unified treatment of Forouhi and Bloomer^[2] for the dispersion behaviour of the dielectric constant. A fit to the experimental spectrum is also shown in figure 1. The thickness of the films ranges from 230 to 830 nm which can be related to deposition conditions. Unexpectedly, the calculated refractive index of the as-grown films is slightly higher than the bulk value. Assuming as Fang et al^[3], that refractive index and packing density are correlated, it may be inferred that the high material density is to be due to the film stress. In order to better understand this behaviour, films have undergone thermal treatment at 500°C in air, for three hours. The refractive index dispersion of ZnO monocrystal^[4] and of a typical film, before and after annealing, are depicted in the inset of figure 1. On all annealed samples the refractive index is lower than the bulk value.

Table 1

Growth conditions, thickness, refractive index (n), and structural parameters obtained by XRD of as-grown (S#) and annealed (S#-A) ZnO thin films

Sample	$F(O_2)$	RF power (W)	Thickness (nm)	n (633 nm)	D (Å)	σ (GPa)
S1	0.28	50	289.2	2.03	146.6	-7.9
S2	0.13	50	561.0	2.03	197.0	-6.1
S3	0.28	50	342.3	2.08	178.2	-6.9
S4	0.50	50	262.4	2.04	63.0	-10.9
S5	0.62	50	228.3	1.99	62.1	-8.5
S6	0.13	80	826.5	2.03	108.1	-7.5
S7	0.50	80	523.1	2.08	32.2	-10.2
S8	0.23	50	418.1	2.04	69.1	-11.1
S2-A				1.95	271.2	-1.0
S4-A				1.94	257.3	-1.0
S8-A				2.00	246.4	-1.5

$F(O_2) = pO_2/(pAr + pO_2)$ means the relative oxygen fraction.

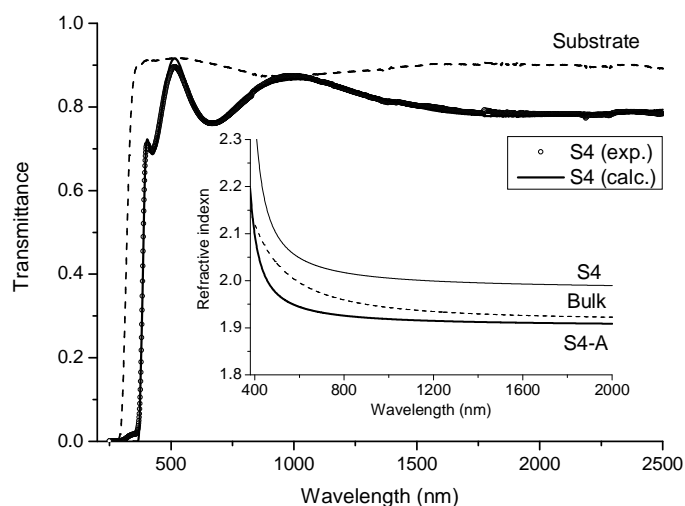


Figure 1 - Transmission spectra (experimental data and fit) of a typical ZnO sample. Inset shows the refractive index of the ZnO monocrystal and of the film, before and after annealing.

The X-ray diffraction spectra of ZnO thin films reveal the existence of a single phase with hexagonal wurtzite structure as in bulk ZnO. Only (002) peak or (002) and (004)

peaks are observed evincing a highly preferential orientation along the c-axis, perpendicular to the substrate surface, in consonance with literature^[5-7].

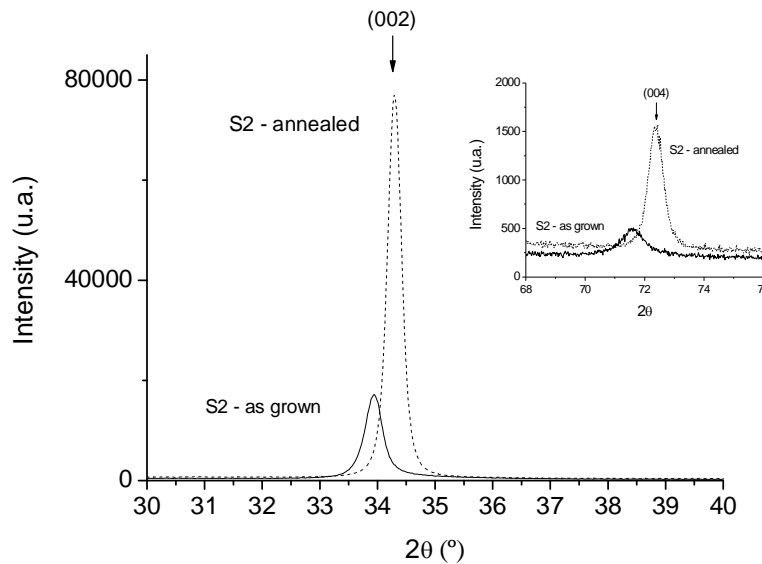


Figure 2 - XRD spectra of a typical ZnO thin film exhibiting (002) and (004) peaks, before and after annealing.

For all as-grown films the (002) peak is asymmetric and shifted from the bulk peak position towards smaller angles, revealing that the structure is stressed. Figure 2 shows the (002) and (004) peaks from the above sample, before and after annealing. With annealing peaks intensity increases and they shift towards the bulk position, demonstrating some improvement in the crystallinity of the film. The (002) peak position as a function of the asymmetry (measured as the ratio between the calculated symmetric curve and the experimental curve) for the as-grown and annealed films is plotted in figure 3. As shown, the asymmetry decreases as the peak position approaches that of the bulk, supporting that the stress has been relief during the thermal treatment. From the XRD data lattice parameter (c), domain size (D), as well as the strain along c-axis (e_{zz}), and the corresponding stress (σ) have been calculated according to the procedure described in literature^[5, 7-11] (table I). After annealing, all the samples exhibit the same average domain size (around 258 Å), independently of the as-grown microstructure (table I and figure3).

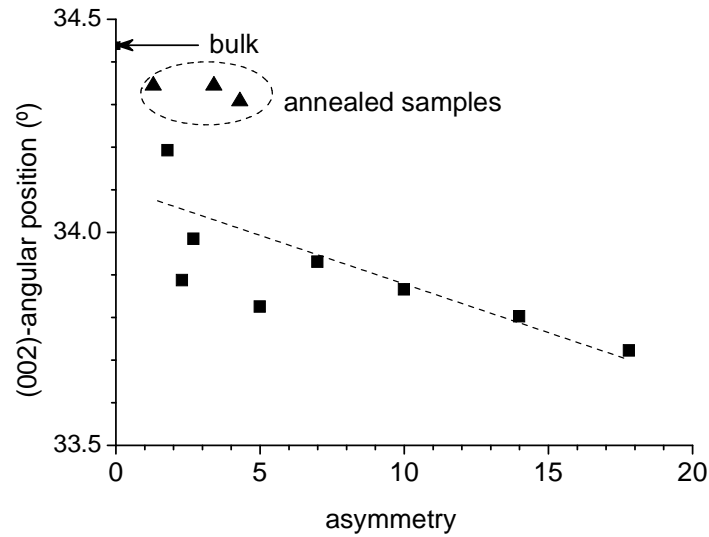


Figure 3 - The (002)-peak position as a function of its asymmetry (see text) for both as-grown and annealed samples.

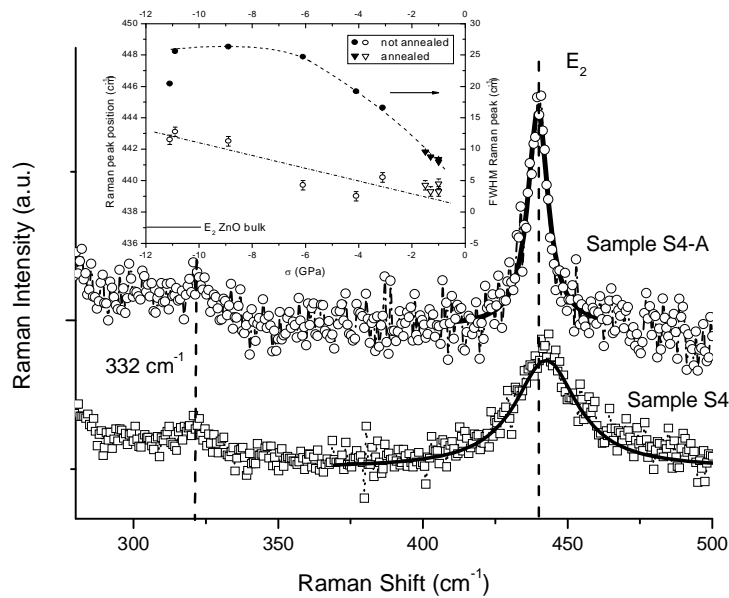


Figure 4 - Typical Raman spectra measured on as-grown and annealed ZnO films. Full lines represent Lorentzian fits. Inset: E_2 -peak position and its half-height width

as a function of stress as assessed by X-ray. Dashed lines are guides for the eyes.

The improvement of the ZnO crystallinity due to the annealing treatment has also been confirmed by Raman scattering. Figure 4 depicts a typical Raman spectra measured on both as-grown and annealed ZnO films. The experimental peak at about 435 cm^{-1} has been assigned to the non-polar optical phonons (E_2 -high) mode^[12]. After annealing, the intensity of this mode increases, the peak position shifts ($2.0\text{-}5.5\text{ cm}^{-1}$) towards the bulk position and the full width at half maximum (FWHM) decreases ($26.6\text{ to }8.4\text{ cm}^{-1}$), as it can be seen in the inset of Figure 4. This behaviour suggests a compressive stress in the non-annealed samples. The peak at 332 cm^{-1} , which can be seen in the Raman spectra both on the as-grown and on the annealed samples, has been assigned to multiple phonon scattering processes^[13]. The Raman measurements have thus proven to be a sensitive probe to stress relaxation and stoichiometry improvement in the film.

4. Final remarks

Undoped ZnO thin films have been grown by reactive magnetron r.f. sputtering under different Ar/O₂ atmospheres. Films with different crystal sizes, ranging from 3.2 nm to 19.7 nm in the as-grown form, have been obtained by changing the deposition parameters. The reported results have shown that the thermal treatment has conducted to a decrease of the refractive index from above to below the bulk value and to the improvement of film crystallinity. Since the refractive index and packing density are correlated, we have assumed that the high material density in the as-grown films is to be due to the film stress. This compressive stress has been relieved by annealing as it has been confirmed by our X-ray and Raman data.

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