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THE MORPHOSTRUCTURAL CHARACTERISTICS OF ZnO THIN FILMS DEPOSITED BY ULTRAVIOLET LASER ABLATION WHICH MAY BE USED IN DYE SENSITIZED SOLAR CELLS

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We investigated the experimental deposition characteristics of zinc oxide (ZnO) films obtained by laser ablation method using an ultraviolet wavelength, with the intention of ensuring that the films meet the requirements of a photoelectrode in dye-sensitized solar cells (DSSC). Films were deposited using a picosecond Nd:YVO_4 laser at a 355-nm wavelength, starting from a pure zinc target on an optical glass substrate covered with a thin indium tin oxide (ITO) layer at ambient temperature. After deposition, the films were annealed at 350ºC in an oxygen atmosphere. The structure and morphology of the films were investigated using X-ray diffraction and scanning electron microscopy. The results demonstrated that polycrystalline ZnO films with anisotropic coherent regions were obtained after annealing treatment at 350ºC for oxygen pressures higher than 150 mTorr. The porosity and thickness of the films increased with oxygen pressure.

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Keywords: ZnO, laser ablation, ultraviolet wavelength, nanostructures, porous film

1. Introduction

Due to its specific semi-conducting properties, zinc oxide (ZnO) has been intensively studied for different transparent electronics applications [1] including transparent conducting films [2], sensors [3] and optoelectronic devices such as solar cells [4-10]. ZnO can be cast in thin films by chemical methods [11-13], atomic layer deposition [14], magnetron sputtering [15] and pulsed laser deposition (PLD) [16-26]. Thin porous ZnO films may have applications in surface acoustic wave sensors [1] or as nanostructured electrodes in hybrid or DSSC [8; 9; 27].

Numerous studies have focused on the required experimental parameters for different applications. Singh et al [16] reported the influence of different oxygen pressures and substrates on the film characteristics and showed a clear dependence of the oxygen pressure on the grain size. The grain size tended to increase with temperature, which is in agreement with the results of Vinodkumar et al [17]. In a previous study, C. Sima et al [26] demonstrated the obtaining of porous nanostructured ZnO films for possible DSSC applications using a 532-nm wavelength of Nd:YVO_4 picosecond laser.

Herein, we study the influence of using pulsed laser ablation with an ultraviolet-wavelength picosecond laser (355 nm) on the morpho-structural characteristics of ZnO porous films deposited on optical glass substrates covered with indium tin oxide (ITO), and examine whether the film characteristics are suitable for DSSC.

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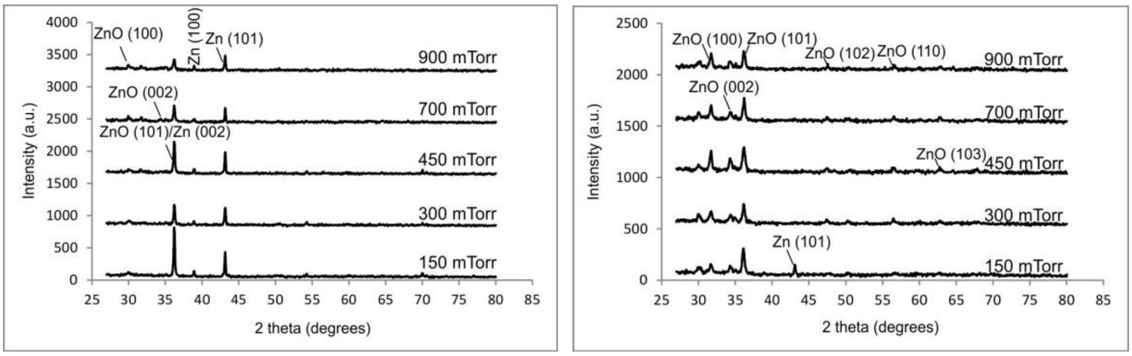
2. Experimental

A Nd:YVO_4 picosecond laser (8 ps pulse duration, 355-nm wavelength, 0.2 W average power, 1×10^4 pps pulse repetition rate, 20 μJ/pulse, 0.17 J/cm^2 fluence) in a typical PLD setup was used. The zinc target (99.95%) was ablated in an oxygen atmosphere (150–900 m Torr) at a 10-sccm gas-flow rate. Optical glass covered with ITO (125 nm thickness, Kintec) was used as substrate and placed at a distance of 3.5 cm from target. 10^{-4} Torr was the pressure before to introduce the oxygen in the deposition chamber. The experimental set up was described in a previous study by C. Sima et al [26].

The films were deposited at room temperature (RT) and annealed at 350ºC for 2 h in an oxygen atmosphere. The crystalline structure of the films was investigated by X-ray diffraction (XRD) using a Bruker D8 Discover diffractometer (Cu $K_{\alpha1}$ radiation). Scanning electron microscopy (SEM; Tescan Vega XM microscope) was used for investigation of surface morphology, cross-sectional structure, film thickness, porosity and cluster sizes.

3. Results and discussion

Fig. 1 shows XRD spectra of the films deposited at RT and annealed at 350ºC in oxygen atmosphere. Regardless of the oxygen pressure, a mixture of Zn and ZnO formed at RT. In accordance with results reported in a previous study by C. Sima et al [26], the films were annealed at 350ºC for a completely oxidation. Using the 355-nm wavelength laser, after annealing, the films were also oxidized except the case when the films were deposited at 150 mTorr oxygen pressure, where Zn is also present.



(a) RT/10 sccm (b) 350ºC /10 sccm

Fig. 1. X-ray diffraction patterns for samples (a) deposited at various oxygen pressures and 10-sccm flow rate at RT and (b) annealed at 350ºC.

Quantitative analysis of the XRD data was performed on all samples using MAUD software L. Lutteroti et al [28] to determine the percentage of ZnO phase present in the film and the average crystalline coherent zones. The results suggest a significant microstructure anisotropy because the fit was significantly improved when used the texture-strain anisotropic model developed by Popa [29] during refinement.

Table 1 Dimensions of the crystalline coherent zones of ZnO phase in the films before (RT) and after annealing at 350°C in an oxygen atmosphere.

Pressure (mTorr)	Anisotropic sizes for RT films (nm)			Anisotropic sizes for films annealed at 350°C (nm)		
	<002>	<100>	<101>	<002>	<100>	<101>
150	20.6	12.9	14.3	20.4	26.8	27.9
300	28.5	18.3	20.7	53.8	45.7	48.6
450	52.1	34.7	38.9	50.8	47.2	48.4
700	57.1	40.2	45.9	50.0	36.5	38.9
900	55.3	29.7	34.9	96.8	94.8	88.7

The size dependence of the ZnO average crystalline coherent zones on the oxygen pressure and thermal treatment are summarized in Table 1. The crystallite sizes were between 12.9 and 96.8 nm, unlike those obtained using a 532-nm wavelength at a 10-sccm oxygen flow rate (18.2–40.1 nm) (C. Sima et al [26]). The size of coherent crystalline zones tended to increase after annealing, especially for <100> and <101> reflections.

The values of the ZnO and Zn crystalline phase weight fractions are summarised in Table 2; a weight fraction up to 100% represents ITO. As expected, after annealing, the ZnO fraction became substantially higher than that of Zn.

Table 2 Weight fractions of the ZnO and Zn crystalline phases in the films, before (RT) and after annealing in oxygen at 350°C.

Volume fraction (%)					
Temperature		RT		350 ^{0}C	
		ZnO	Zn	ZnO	Zn
Pressure (mTorr)	150	5.9	82.4	70.8	16.9
	300	21.7	63.9	81.9	-
	450	53.3	36.2	94.6	-
	700	47.5	39.5	77.5	-
	900	55.3	42.1	80.1	-

SEM images (Fig. 2) showed clear modifications of the film surface with increasing oxygen pressure. However, in the present study, the film surface was more homogeneous compared to previously reported results C. Sima et al [26]. The clustering process described previously C. Sima et al [26], also occurred; however, at an oxygen pressure of 900 mTorr, there were fewer clusters compared to films deposited using a 532-nm laser wavelength. Because absorption decreases with wavelength in metals [30], resulting in thinner films, a less pronounced clustering phenomenon occurs when an ultraviolet wavelength is used.

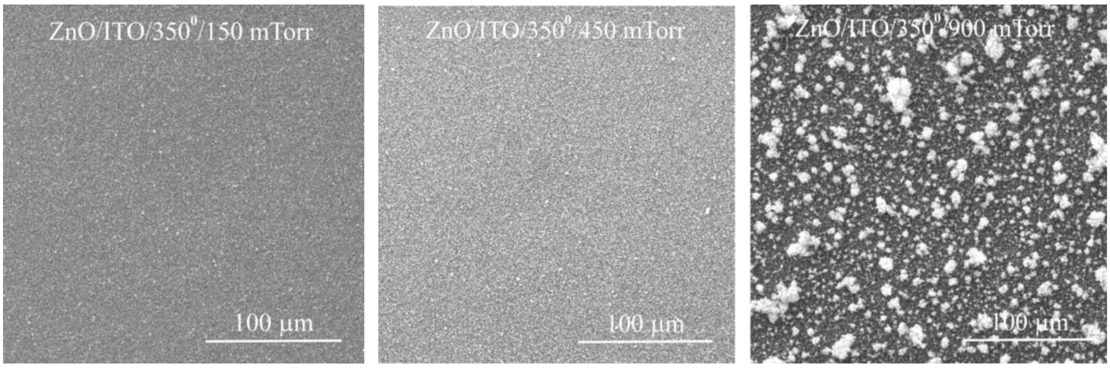


Fig. 2. SEM images of ZnO films deposited at 10 sccm and 150, 450, and 900 m Torr, after annealing at 350°C.

Figure 3 shows cross-sectional images of the films deposited at different pressures after annealing, demonstrating that the film porosity increased with the oxygen pressure.

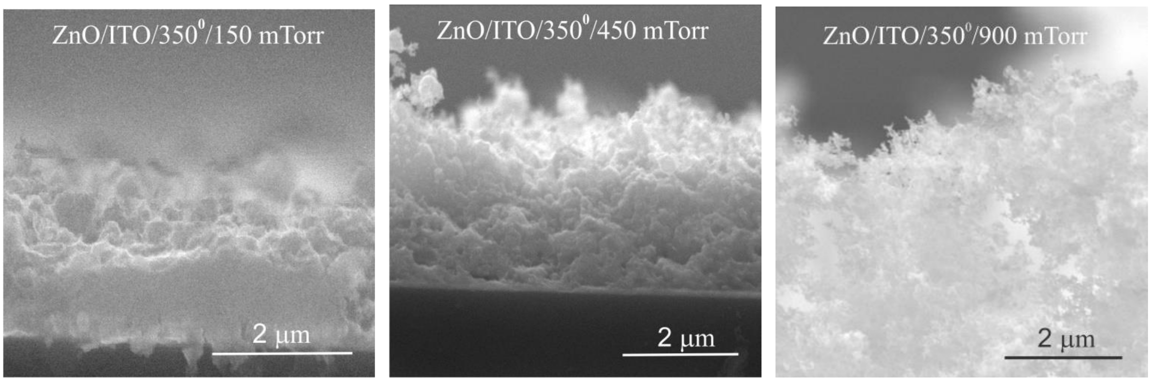


Fig. 3. Cross-sectional images of ZnO films deposited at 10 sccm and 150, 450, and 900 m Torr, after annealing at 350□*C in an oxygen atmosphere.*

The dependence of the film thickness on oxygen pressure, as observed in cross-sectional images, is shown in Fig. 4. The thickness increased with the oxygen pressure to a value of approximately 12 μm for the films deposited at 900 mTorr, about half of the value measured for the films deposited at the same conditions when using a 532-nm wavelength laser (C. Sima et al [26]). Because absorption decreases with wavelength [30], the ablation process was less efficient in the ultraviolet range compared to that obtained at a visible wavelength, resulting in thinner films, as shown in Fig. 4.

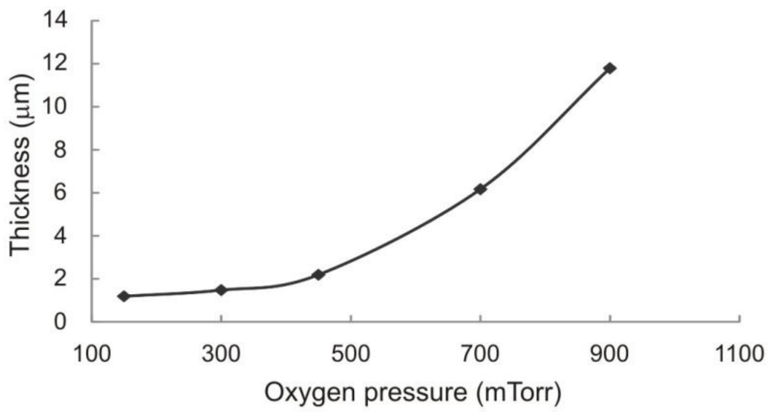


Fig. 4. Thickness of the annealed films as a function of oxygen pressure.

4. Conclusions

Porous ZnO films were produced by PLD using a Nd:YVO_4 picosecond laser operating at a 355-nm wavelength, at pressures higher than 300 m Torr and after annealing at 350ºC in an oxygen atmosphere. The morphology of the films depended on the oxygen pressure: at low oxygen pressure, the ZnO films consisted of nanoparticles, while at higher pressure, a clustering process was predominant. The clusterization phenomenon was less predominant for the 355-nm wavelength laser comparing with the films deposited using visible wavelength. The results obtained in this study will be useful for future research on photoelectrodes for DSSC applications.

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