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Short communication

Porous nanostructured ZnO films deposited by picosecond laser ablation

Cornelia Sima [a,b], Constantin Grigoriu [b,*], Cristina Besleaga [a], Tudor Mitran [a], Lucian Ion [a], Stefan Antohe [a]

[a] University of Bucharest, Faculty of Physics, 405 Atomistilor, P.O. Box MG-11, 077125, Bucharest-Magurele, Romania
[b] National Institute for Laser, Plasma and Radiation Physics, Laser Department, 409 Atomistilor, P.O. Box MG-36, 077125, Bucharest-Magurele, Romania

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ABSTRACT

Porous nanostructured polycrystalline ZnO films, free of large particulates, were deposited by picosecond laser ablation. Using a Zn target, zinc oxide films were deposited on indium tin oxide (ITO) substrates using a picosecond Nd:YVO_4 laser (8 ps, 50 kHz, 532 nm, 0.17 J/cm^2) in an oxygen atmosphere at room temperature (RT). The morpho-structural characteristics of ZnO films deposited at different oxygen pressures (150–900 mTorr) and gas flow rates (0.25 and 10 sccm) were studied. The post-deposition influence of annealing (250–550 °C) in oxygen on the film characteristics was also investigated. At RT, a mixture of Zn and ZnO formed. At substrate temperatures above 350 °C, the films were completely oxidized, containing a ZnO wurtzite phase with crystallite sizes of 12.2–40.1 nm. At pressures of up to 450 mTorr, the porous films consisted of well-distinguished primary nanoparticles with average sizes of 45–58 nm, while at higher pressures, larger clusters (3.1–14.7 μm) were dominant, leading to thicker films; higher flow rates favored clustering.

1. Introduction

Zinc oxide is a wide-bandgap semiconductor with many applications in electronics, optoelectronics, sensors, and solar cells. In solar cells, it can be used as a transparent conductive film or, as an alternative to TiO_2, as a nanocrystalline photoelectrode in dye-sensitized solar cells (DSSCs) [1–7]. It is an n-type semiconductor material with physical properties similar to TiO_2 but offers the advantage of higher electron mobility [2]. To achieve efficient light harvesting using DSSC technology, the photoelectrode consisting of dispersed particles must have a high surface-area-to-volume ratio and good porosity to allow the liquid electrolyte to penetrate the film and fill the pores [1,4,7,8]. Additionally, good physical and electrical contact between the nanoparticles is required to ensure efficient charge transport [3].

Another promising application of ZnO films is in gas sensors [9–11]. In surface acoustic wave sensors of all the detection mechanisms, changes in the wave velocity due to addition or removal of mass at the surface (by adsorption or absorption) is most important. That is why deposition of high-surface area granular adsorbents on piezoelectric substrate can provide good sensitivity for detection of vapor phase species [12]. At the same time the thin sensitive film (maximum thickness ~100 nm) must be free of large solid particulates. Such imperfections reflect acoustic waves, thereby incurring additional signal loss (sensor lower response) and increased noise that negatively affect the sensor's limit of detection (defined as the ratio between response when analyte is present and the noise level when there is no analyte).

ZnO films have been prepared using various methods, such as magnetron sputtering [13–16], molecular beam epitaxy [17,18], chemical vapor deposition (CVD) [19–21], sol gel [22–25], and pulsed laser ablation (PLA) [26–39]. Most preparation methods produce compact films, except sol gel and PLA.

The majority of PLA work devoted to ZnO films has been performed with nanosecond lasers (Nd-YAG or excimer). Generally, such research has focused on the influence of oxygen pressure and temperature on film crystallinity, morphology, grain size, optical properties, and photoluminescence without reference to porosity or the existence of particulates/outgrowths/droplets (size and density), which frequently occur during ablation with nanosecond lasers [26,27,29,34,35]. Wei et al. [39] reported the presence of micro-sized particulates on ZnO films deposited at low pressure with a nanosecond laser and tried to improve the surface quality and luminescence properties by annealing. Laser ablation at low oxygen pressure [27,31–33] produces compact columnar ZnO films that are nonporous; such films are inadequate for applications in DSSCs or gas sensors. Lemlikchi et al. [30] studied deposition with nanosecond lasers at high pressures (up to 3.7 Torr). The films exhibited a macroporous structure with honeycomb morphology. Chau et al. [28], Millon et al. [36], and Perriere et al. [37] prevented the formation of large particulates by using femtosecond lasers. They deposited smooth ZnO films with a compact, dense structure at low oxygen pressure.

* Corresponding author. Tel.: +40 21 4574027; fax: +40 21 4574027.
E-mail addresses: grigoriu@ifin.nipne.ro, constantingrigoriu@yahoo.com (C. Grigoriu).

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Lansiart et al. [38] using picosecond laser deposited nonporous, droplet free, dense and columnar ZnO films.

However, to the best of our knowledge, very little work has focused on producing nanoporous films that are free of particulates.

In this study, we report the successful preparation of nanostructured ZnO films using a picosecond laser with a high repetition rate (kHz–MHz) and low energy/pulse (μJ). Compared to ablation with nanosecond lasers, the individual picosecond pulses ablate a smaller mass, generating nanoparticles in relatively large quantities due to the high pulse repetition rate, resulting in films that are free of droplets.

The influence of deposition parameters and annealing treatment on the morpho-structural characteristics of the ZnO films deposited on ITO by pulsed laser ablation was studied. In particular, the objective was to obtain highly porous nanostructured ZnO films free of large particulates.

2. Material and methods

For deposition of ZnO films, a Nd:YVO_4 picosecond laser (8 ps pulse duration, 532 nm wavelength, 1 W average power, 5×10^4 pps pulse repetition rate, 20 μJ/pulse, 0.17 J/cm^2 fluence) was used. ZnO films were obtained by ablation of a pure zinc target (99.95%) in an oxygen atmosphere in the range of 150–900 mTorr with 0.25 and 10 sccm gas flow rates. Deposition was carried out for 4 h. ITO deposited on glass (Kintec, 25 mm × 25 mm, 18 ohm/sq) was used as a substrate. The target–substrate distance was 3.5 cm. Before deposition, the chamber was evacuated to a base pressure of 7.4×10^{-4} Torr.

The experimental setup is shown in Fig. 1.

After deposition, the films were annealed (250–550 °C) for 2 h in an oxygen atmosphere. X-ray diffraction (XRD) was used to characterize the crystalline structure (Bruker D8 Discover diffractometer, Cu $K_{\alpha 1}$ radiation). The XRD was recorded at grazing incidence since this provides a longer path through the film and increases the intensity of diffraction; even more importantly for such films, grains with all crystalline orientations are probed, not only those aligned parallel to the surface of the sample.

The surface morphology, cross-sectional structure, porosity, nanoparticle and cluster sizes, and film thickness were characterized by scanning electron microscopy (SEM, Tescan Vega XM microscope).

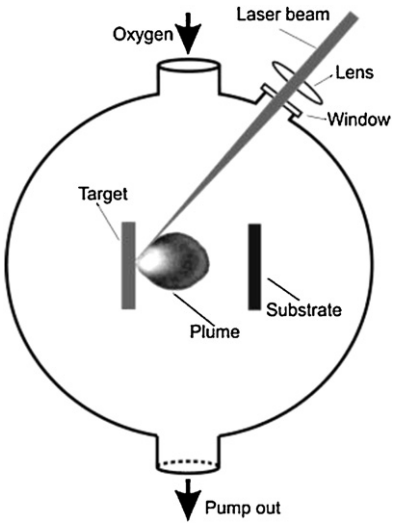

Fig. 1. Experimental setup.

3. Results and discussion

XRD spectra were acquired for films deposited at room temperature (RT) between 150 and 900 mTorr of oxygen at flow rates of 0.25 and 10 sccm (Fig. 2). At RT, pure ZnO could not be synthesized, but a mixture of Zn and ZnO formed.

To completely oxidize the Zn phase, the samples were annealed for 2 h in an oxygen atmosphere at temperatures ranging from 250 to 550 °C; Fig. 3 shows the XRD spectra of the films deposited at 450 mTorr and two flow rates, after annealing. The crystallite sizes determined using Scherrer's formula are presented in Table 1. Although the size evolution of the crystalline coherent zones was approximately monotonic with oxygen pressure during deposition, as expected (see Table 1), the intensity of the observed peaks was not (Figs. 2 and 3). The diffraction intensity corresponding to the ($h\,k\,l$) peak of a crystalline phase α can be expressed in a form appropriate for quantitative evaluation as [40]:

$$I^{(\alpha)}_{h\,k\,l} = C_e \frac{P^{(\alpha)}_{h\,k\,l} x^{(\alpha)}}{\rho^{(\alpha)}(\mu/\rho)_s} \quad (1)$$

where $x^{(\alpha)}$ and $\rho^{(\alpha)}$ are, respectively, the weight fraction and the density of the phase α, $(\mu/\rho)_s$ being the mass absorption coefficient

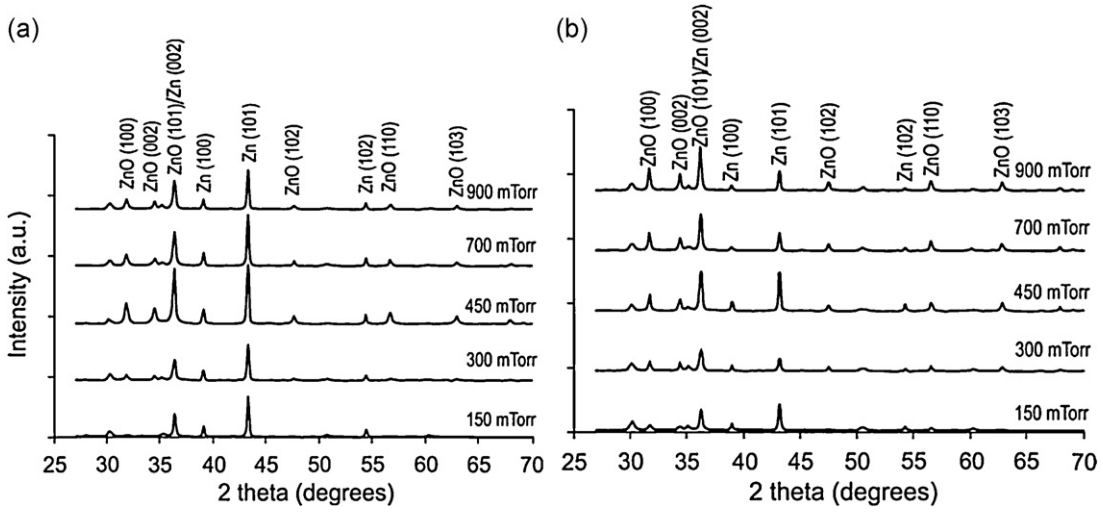

Fig. 2. X-ray diffraction patterns for samples deposited at RT and various oxygen pressures; flow rate 0.25 sccm (a) and 10 sccm (b).