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Porous and dense ZnO films produced by femtosecond and picosecond pulsed laser deposition

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This paper describes our preliminary results for controlling the structure of ZnO thin films grown on Si(100) at room temperature by PLD. The laser was operated at λ=810nm and pulse durations ranging from 30fs to 275ps were used. A laser fluence of 2J/cm^2 was used for pulse durations of 50fs, 200fs, 1ps and 10ps, which produced porous films that were found to increase in density with increasing pulse duration. Experiments were also conducted with 7.5J/cm^2, which resulted in denser films. The areal density and the size of the droplets were found to increase with decreasing pulse duration.

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Keywords: Pulsed Laser Deposition, Femtosecond, Picosecond, ZnO thin film

1. Introduction

As a thin film, ZnO is a material that exhibits piezoelectric [1] and photoelectric properties [2] that could be used in MEMS related devices [3], for acoustic wave sensors [4], for metal-semiconductor-metal photodetectors [5], for UV detectors [6-8] and for blue LEDs [9]. The aim of this research is to use pulse duration and pulse energy in a pulsed laser deposition (PLD) process to control the structure and characteristics of the deposited film. In this set of experiments, we characterize thin films of ZnO produced by femtosecond and picosecond PLD for a variety of different laser pulse durations and beam energies. The 10Hz/10TW line at the Advanced Laser Light Source (ALLS), located at INRS-EMT in Varennes (QC), allows for control over pulse duration in the range of 30fs to 275ps and can produce energies of 4.5mJ to 45mJ. This provides the means for growing thin ZnO films by PLD in the fs and ps-regimes with the same laser.

2. Experimental Conditions

A vacuum chamber was assembled to enable the PLD of a 99.9% pure ZnO target. The target was continuously rotated by an electric motor and was held at room temperature. A pure Si(100) substrate was placed opposite the target at a distance of 6 cm. The chamber pressure was reduced to 9.33×10^{-4} Pa (7×10^{-6} Torr) using a turbomolecular pump. The femtosecond source laser produces an 810nm laser beam at a repetition rate of 10Hz and with a 35fs pulse duration in stable operation. A series of crystals elongate the pulse to 275ps and a compressor, acting in air, was used to adjust the pulse duration between 50fs and 10ps. Measurements of pulse duration were made with an intensity autocorrelator (Thales).

A lens of focal length 50cm was used to reduce the beam dimension to a spot size of less than 0.5mm^2 on the target surface. A micrometer stage was used to move the lens along the optic axis and inspection of the beam print on a Si wafer, with an optical microscope, determined the optimal lens position, leading to a spot size of approximately 0.41mm^2. An anti-reflective window was used to minimize energy loss at the air/vacuum interface. The laser pulse duration and energy were measured before the beam reached the window, just prior to the deposition process. The films were produced by depositions lasting 5 hours, totaling 180 000 pulses. During these experiments, no background gases were introduced into the chamber.

3. Results and discussion

The surfaces of the deposited ZnO films were investigated using a scanning electron microscope (JEOL JSM 6300F), which was also used to determine the film thickness on cross-sections of the films. With 8.2 ± 0.2mJ of beam energy, a laser fluence of 2.01 ± 0.04 J/cm^2, depositions were made for 50fs, 200fs, 1ps and 10ps pulse durations. The thickness of the films was found to decrease with increasing pulse duration (Fig. 1), attributed to a visible increase in film density (Fig. 2). A possible mechanism is that increasing the pulse duration does not increase the density of the particles in the plume; rather, it raises the energy per particle and thus increases the density. This is consistent with spectroscopic studies of the laser plume, which indicate that increasing pulse duration does not affect ion density, but does increase temperature [10]. This mechanism is also in agreement with the observation of a relatively constant ablation rate in the fs-regime [11].

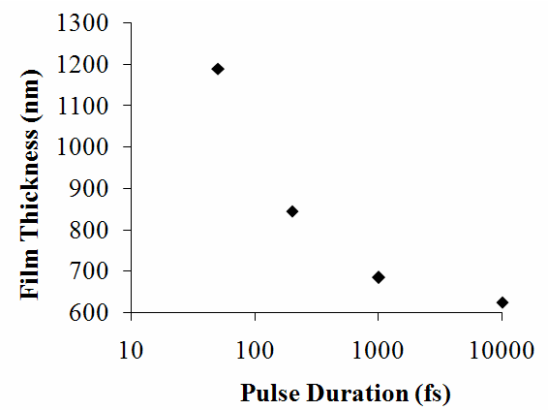
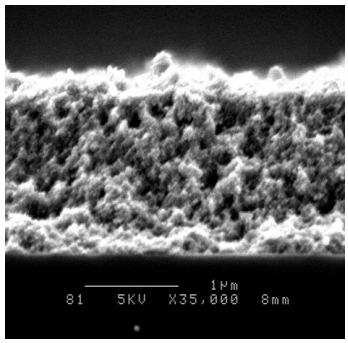


Fig. 1. Thickness of PLD grown ZnO films produced at a laser beam energy of 8mJ and measured on SEM cross-section images as a function of the laser pulse duration.



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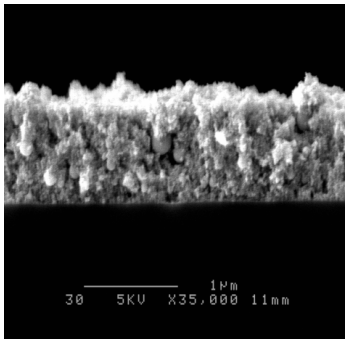

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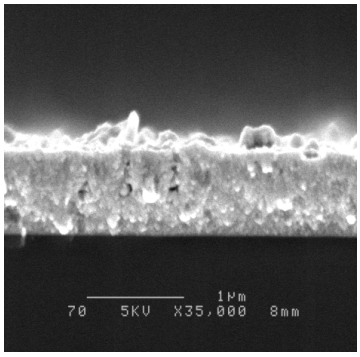

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Fig. 2. Cross-section SEM images of PLD grown ZnO films produced at a laser beam energy of 8mJ with laser pulse durations of (a) 50fs, (b) 200fs and (c) 10ps.

The X-ray diffraction (XRD) analysis of ZnO films produced by 50fs laser pulses revealed formation of polycrystalline films with a porous microstructure (Fig. 3). For a laser pulse duration of 10ps, denser polycrystalline films were produced, with a slight (100) or (002) texture. In all cases, the peaks in XRD measurements of the ZnO thin films were found to match the peaks of the ZnO ceramic target. At the shortest pulse durations and lower energy levels, more peaks were found, in accordance with the randomly oriented crystallites observed in these more porous films.

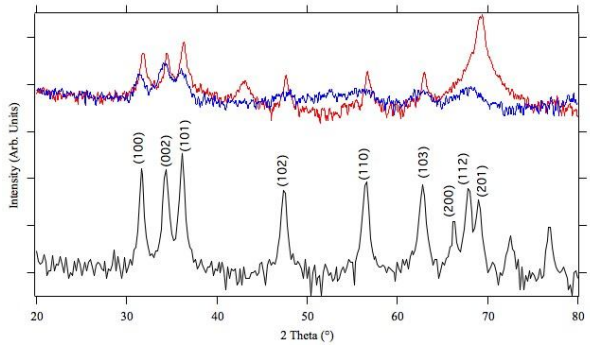

Fig. 3. XRD spectra of ZnO target (black) and thin films: 50fs pulse durations with 8mJ energy (red), 10ps pulse durations with 45mJ energy (blue).

Another series of measurements was made with a fixed pulse duration of 200fs and at laser beam energies of 4.6mJ, 8mJ, 20.4mJ and 45mJ (Fig. 4). At 4.6mJ, very little deposition occurred, as the corresponding fluence is just slightly over the ablation threshold. As the energy increased from 4.6mJ to 20.4mJ, the deposition rate increased, producing thicker films of similar porous nature. At 45mJ a dense film was produced, which exhibited a smooth surface with droplets ranging in diameter from 30nm to 500nm. As the laser fluence was increased, it is expected that more high-energy ionized species were emitted from the ZnO target's surface [12]. While this was responsible for producing the dense film, it appears that the increased fluence also produced large ZnO droplets. The nature of the thin film microstructures as well as their sequences and transitions conform, at least qualitatively, to the basic Thornton structure zone model [13]. In other words, as the energy of the depositing particles increases, the film tends to become denser. In this classic Thornton structure zone model, the higher energy is provided by the substrate temperature. In PLD, or other PVD techniques such as sputter deposition, the higher energy is provided by the kinetic energy of depositing particles.

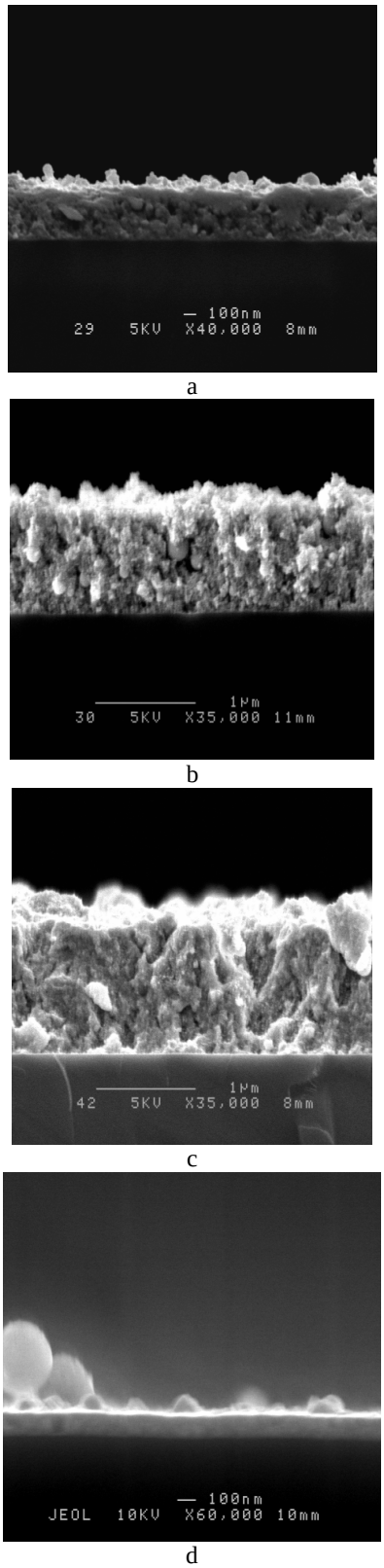

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Fig. 4. Cross-section SEM images of films produced with 200fs pulses and energies of (a) 4.6mJ, (b) 8mJ, (c) 20mJ and (d) 45mJ.

A series of 45mJ depositions were made for pulse durations of 200fs, 10ps and 275ps (Fig. 5). The 200fs pulse duration produced the greatest droplet density of the series, while the 275ps pulse duration produced the least droplets. The droplet size varied between 30nm and 500nm for a pulse duration of 200fs and from 30nm to less than 350nm for the other pulse durations. The increase in areal density as well as the increase in size of the droplets at lower pulse duration is likely due to the pulses' very high peak intensity. The high peak intensity is expected to cause a sub-surface heating of the target resulting in the ejection of larger droplets than those found with longer, less intense pulses [12].

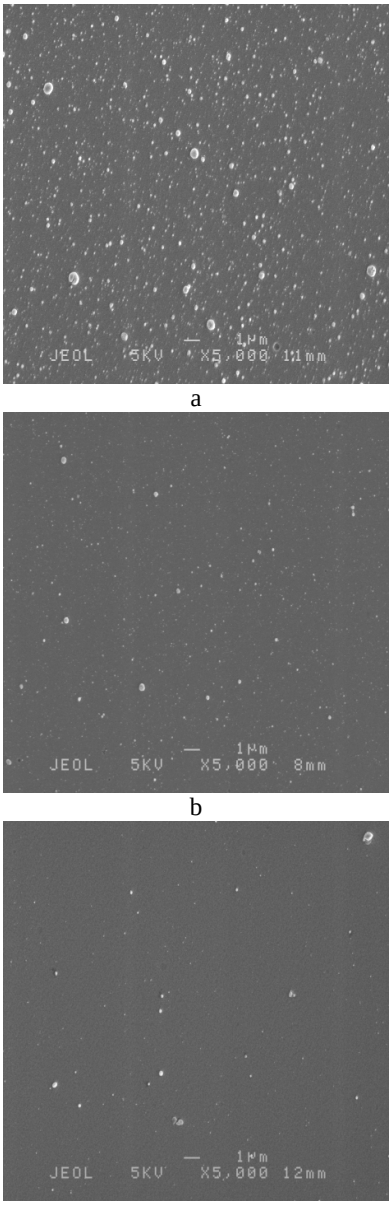

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Fig. 5 - SEM images of the surfaces of films produced with 45mJ and pulse durations of (a) 200fs, (b) 10ps and (c) 275ps.

4. Conclusions

In this paper, a new mode of control over thin film microstructure has been demonstrated. By adjusting pulse duration and laser fluence, dense and porous structures can be produced without the requirement of heated substrates or background pressures of gaseous species in the deposition chamber. This study reveals that simply reducing the pulse duration does not appear to reduce the production of droplets either in their size or in their areal density. To establish a clear correlation between the pulse duration and the density and size of droplets, a more detailed study with variation of the laser beam wavelength is also needed to fully understand the phenomenon. We can accomplish this by second harmonic generation in our laser beam line. Our future studies will also focus on studying the effects of film structure variation on electrical and optical properties of the deposited films.

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