Bull. Mater. Sci., Vol. 36, No. 3, June 2013, pp. 385–388. © Indian Academy of Sciences.

Oxidation of ZnO thin films during pulsed laser deposition process

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MS received 1 March 2012

Abstract. **Pulsed laser deposition of ZnO thin films, using KrF laser, is analysed. The films were deposited on (001) sapphire substrates at 400 °C, at two different oxygen pressures (0·3 and 0·4 mbar) and two different target–substrate distances (30 and 40 mm). It is observed that in order to obtain good quality in the photoluminescence of the films, associated with oxygen stoichiometry, it is needed to maximize the time during which the plasma remains in contact with the growing film (plasma residence time), which is achieved by selecting suitable combinations of oxygen pressures and target to substrate distances. It is also discussed that for the growth parameters used, the higher probability for ZnO films growth results from the oxidation of Zn deposited on the substrate and such process takes place during the time that the plasma is in contact with the substrate. Moreover, it is observed that maximizing the plasma residence time over the growing film reduces the rate of material deposition, favouring the surface diffusion of adatoms, which favours both Zn–O reaction and grain growth.**

Keywords. **Ablation; film deposition; ZnO thin film; semiconductors.**

1. Introduction

Pulsed laser deposition (PLD) is one of the widely used technique for growing thin films of multi-component materials. Among them, superconductor, ferroelectric and semiconductor materials like YBaCuO (Wang *et al* 1999), BaTiO (Xuan *et al* 1998) and ZnO (Wang *et al* 2003), respectively are some of the examples. ZnO is a well known material for its applications in solar cells and surface acoustic-wave devices. Recently, good results have been obtained using ZnO as a matrix for magnetic doping in the race for the development of so-called spin-electronic devices (Fukumura *et al* 1999) and it has emerged as an important material for developing near UV-semiconductor lasers (Tobin *et al* 2006) or opto-electrical devices (Li *et al* 2010).

The near UV-interband emission and its relation to the structural and surface properties of ZnO thin films, have been discussed in several papers in recent years (Tang *et al* 1998; Wu *et al* 2001). A detailed explanation on how and why *c*-oriented films are commonly obtained has been reported by Claeyssens *et al* (2005); while other studies have been devoted to the influence of the film thickness (Shim *et al* 2002), oxygen pressure (Im *et al* 2000; Shan *et al* 2005) and growth time (Vasco *et al* 2001) on the optical properties. In general, it is stated that the oxygen content is critical to obtain good quality films. Despite the amount of work devoted to the PLD of ZnO thin films, there is no clear picture about how material formation takes place, which is of prime importance in reaching a stoichiometric growth. This article combines the characterization results of both plasmas and thin films, obtained with different growth parameters, to identify the mechanism of ZnO formation during the PLD process.

2. Experimental

A KrF eximer laser, with a fluence of 1 J/cm^2 was used to ablate a 99·99% pure ZnO ceramic target for 10 min in an atmosphere of oxygen. The films were deposited on (001) sapphire substrates at 400 °C, using two different oxygen pressures and two different target–substrate distances (TSD). Some of the films were post-annealed in a deposition chamber, using the same substrate temperature and oxygen pressure as during the growth, with the aim of comparing structural and optical properties with the as-grown films.

The surface morphology of the films was examined using scanning electron microscopy (SEM) technique. A profilometer was used to measure the film thickness. X-ray diffractometer (XRD), equipped with a CuK$_\alpha$ source and θ–2θ configuration, was used to study the crystalline properties of the films. The photoluminescence of the films was measured with a HeCd ($\lambda = 325$ nm) laser, a monochromator and a photomultiplier tube cooled to −23 °C. All the sample spectra were acquired at room temperature using a 1 nm step size and an integration time of 1 s. The study of plasma expansion was performed using a planar Langmuir probe biased at −30 V and a gated ICCD. A delay generator

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was used to set both the ICCD integration time (3·8 ns) and the delay time after laser pulse arrival to target.

3. Results

XRD patterns of the grown ZnO samples are shown in figure 1, together with the growth parameters. The strong (002) and (004) peaks show that there is a preferential growth in the direction [00] with small quantity of [00] oriented material as can be drawn from the relatively weak intensity of the (100) peak.

It can also be observed that disregarding oxygen pressure films grown at a TSD of 30 mm presented poorer crystalline properties, showing higher intensity in the (100) peak and smaller grain size, as calculated using the Scherrer formula, than those obtained at a TSD of 40 mm. The annealing process carried out to the ZnO film, prepared with the same conditions of figure 1(d) film, did not reveal any significant improvement on the ZnO film structural quality, as shown in figure 1(e).

Figure 2 shows photoluminescence (PL) spectra of the films. All the films show the expected blue band at ~370 nm that is associated with the band-edge transition (3·3 eV) characteristic of ZnO. Films grown at TSD of 30 mm showed wide yellow–green and orange bands in the range of 450–700 nm, which are understood to be associated with oxygen vacancies (Im *et al* 2000; Shan *et al* 2005). The above mentioned optical bands practically disappear in the ZnO film prepared at a TSD of 40 mm with 0·3 mbar oxygen pressure

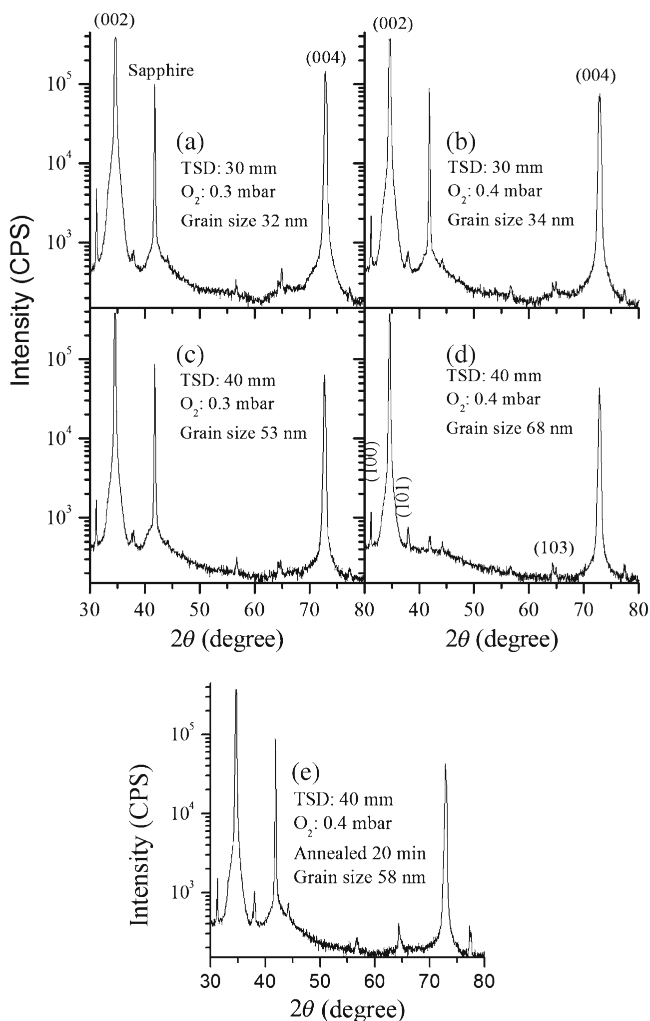


Figure 1. XRD pattern of *c*-oriented ZnO films and corresponding grain size, as calculated using Scherrer formula, together with growth parameters. Figures (**a–d**) correspond to as-grown films while figure (**e**) corresponds to a film annealed for 20 min with same oxygen pressure and temperature as used during its growth.

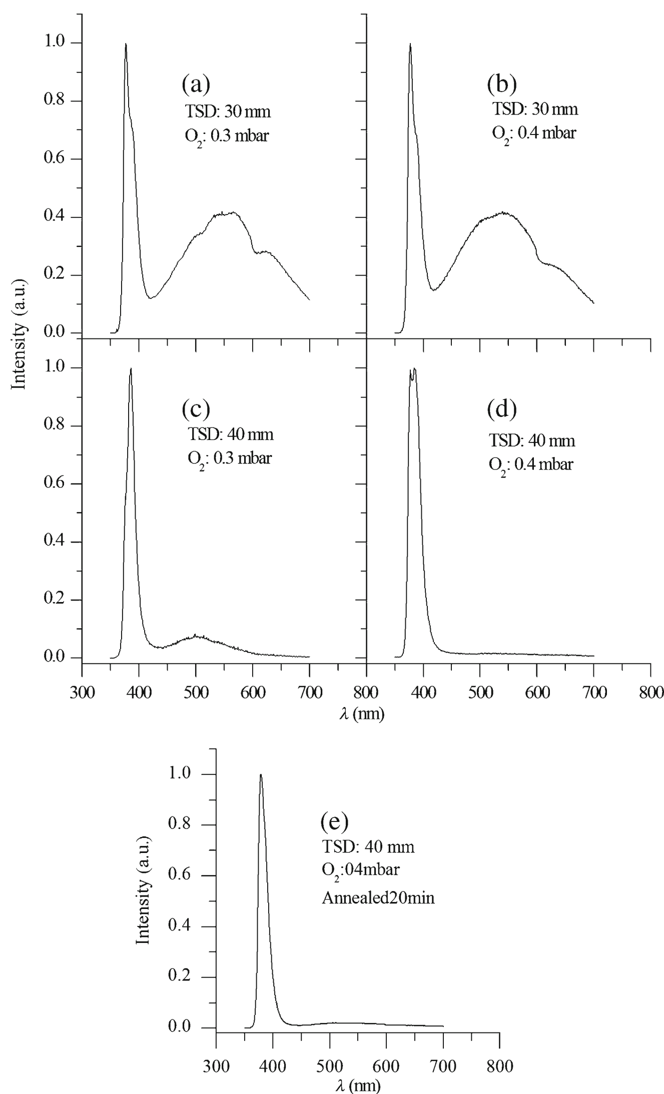


Figure 2. PL spectra of grown thin film with expected blue band-edge transition (about 370 nm). Some of films present yellow–green and orange bands of 450–700 nm associated to lack of oxygen. Figures (**a–d**) correspond to as-grown films while figure (**e**) corresponds to a film annealed for 20 min with same oxygen pressure and temperature as used during its growth.

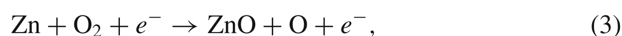
and they are non-existant in the ZnO film prepared at this same TSD but at 0·4 mbar of oxygen pressure.

The annealing performed to films grown with same parameters as of figure 2(d) produced a deterioration of optical quality as can be observed by the presence of small yellow–green band (see figure 2(e)).

Performed plasma analysis revealed that for any of the two used oxygen pressures, the established shock wave was decelerated to kinetic energies lower than 1 eV after 20 mm of expansion. Inside the plasma plume, the plasma temperature was calculated to be of the order of 0·2–0·5 eV. Furthermore, over this distance, the ionization ratio of the produced plasma was very low. All these results rule out or reduce, to lower the probabilities of ZnO formation during the plasma expansion through one of the following reactions:

$$Zn^{+} + O_2 \rightarrow ZnO^{+} + O, \quad (1)$$

$$Zn^{*} + O_2 \rightarrow ZnO + O, \quad (2)$$



$$Zn + O_2 + e^{-} \rightarrow ZnO + O + e^{-}, \quad (3)$$

after accounting their energy thresholds.

Reaction (1) has been reported (Fisher *et al* 1990) to have a threshold of about 3 eV and a maximum cross-section at 6 eV. Although no data was found for the energy requirement of reaction (2), it can be expected that the excitation of the atomic zinc should, at least, equal the dissociation energy of the oxygen molecule (5·12 eV) (Itikawa *et al* 1989). Similar energy requirement should be seen in the electron participating in reaction (3). It should be noticed that reactions with atomic oxygen can take place with the participation of a third body and that reaction (3) could be obtained as well with an energetic atom instead of an electron. In any case, energy requirements for participating atom or electron will be similar to the above mentioned reactions. The low probability of ZnO formation during the plasma phase was pointed out by other authors, which suggested that Zn nuclei oxidize on the substrate to form the final compound (Im *et al* 2000).

One possibility for such process to take place is assuming that a Zn thin film is deposited and then oxidized by oxygen atmosphere. For zinc oxidation at temperature between 370 and 415 °C, the weight gain per area (l) in g/cm^2 of the forming oxide will follow a parabolic law as a function of time (t) (Tuck *et al* 1981). It is defined as:

$$\iota^2 = \kappa_p t, \quad (4)$$

where κ_p is the parabolic constant. For the temperature and pressures used in our experiments, $\kappa_p \approx 1{\cdot}9 \times 10^{-15}$ $g^2\ cm^{-4}\ s^{-1}$ (Tuck *et al* 1981). Calculation of (4) for 100 ms, time between laser pulses and for 0·25 cm^2 substrate area gives a weight gain of $3{\cdot}5 \times 10^{-9}$ g. Using the

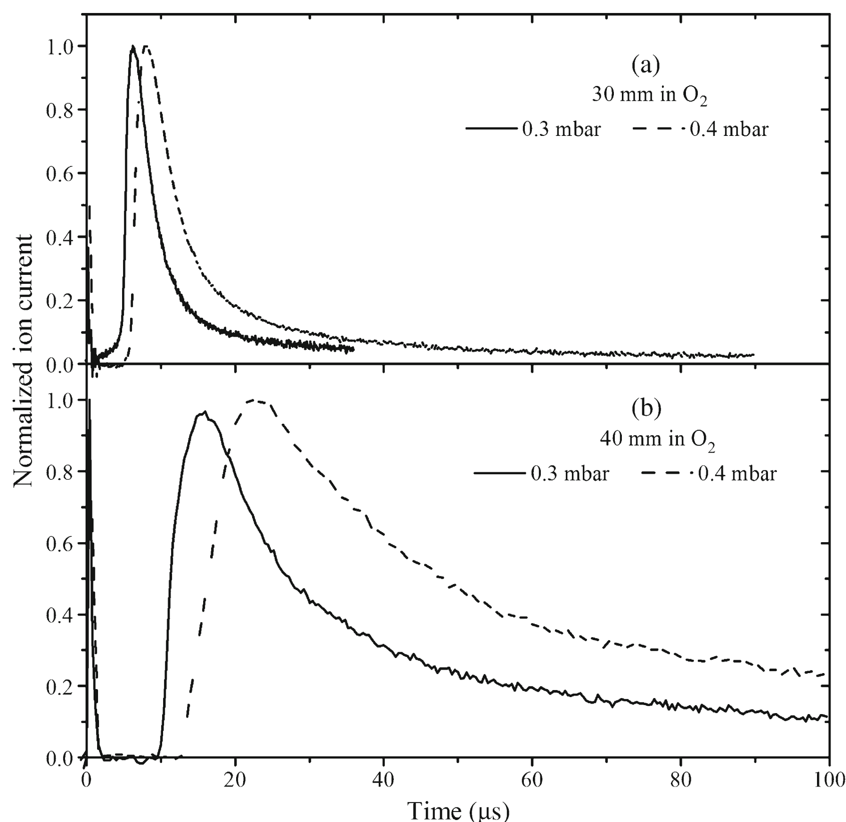


Figure 3. Ion currents measured using a planar Langmuir probe placed at same positions of substrates, (**a**) 30 mm and (**b**) 40 mm. FWHM are (**a**) 4 and 6 µs and (**b**) 16 and 31 µs for 0·3 and 0·4 mbar of O_2, respectively.

obtained average deposition rate, the substrate area and the ZnO bulk density (5·6 g/cm^3), the mass of oxide formed is $4{\cdot}2 \times 10^{-9}$ g/pulse, which suggest that the above mentioned oxidation process may take place. Although, if this is so, the stoichiometry would be the same for all grown films.

Another possibility is that the oxide forms during plasma residence time. An estimate of this time can be obtained from the ion currents measured with the Langmuir probe, shown in figure 3. It can be observed that the plasma residence times, taken as the full width at half maximum of the curves, at a TSD of 40 mm are 4–5 times greater than those measured at a TSD of 30 mm. This implies a reduction in the rate of arrival material, it is the amount of material that is deposited on the substrate over a period of time after one laser pulse. The lower the rate of arrival material, the greater the time and area the adatoms have for their surface diffusion. This of course increases the probability for both reaching sites of minimum energy and the collision of oxygen and zinc adatoms to form the oxide. All this will be translated into a growth with better stoichiometric properties and the formation of greater grains, which agree with the experimental results in this work.

A higher probability for oxide formation during de-material arrival can be expected as well due to the presence of atomic oxygen formed during the target ablation. Atomic oxygen is a key element to allow the formation of ZnO. The dissociation of molecular oxygen leads as well to atomic oxygen, but this is a slow process which furthermore involves the adsorption of the oxygen molecule to the surface of the film. The probability of such adsorption is known to be very low (Carley *et al* 2002).

Once the plasma plume moved away from the substrate position, the oxidation can take place as well but, the oxygen incorporation will be mainly due to the diffusion into the formed ZnO (Robin *et al* 1973). This is a process which involves interaction with defects and hole migration. The diffusion coefficient has been measured to vary from $4{\cdot}9 \times 10^{-16}$ to $3{\cdot}2 \times 10^{-15}$ cm^2/s as temperature varies from 940 to 1141 °C at 700 torr of oxygen (Robin *et al* 1973). Diffusion data for lower pressures and temperatures are not available, but it is to be expected that there will be a decrease in the coefficient values. In general, depth of the diffusion will at most be of the order of Ångströms, which is only noticeable at earlier times of the growth when the film thickness is of this order.

4. Conclusions

In conclusion, low probability for ZnO formation during the plasma phase of PLD process is shown. It had been demonstrated that such formation takes place through the oxidation of Zn species on the substrate surface while the ablated material is being deposited. An important aspect is that to select a suitable combination of growth parameters as to maximize the time of residence of the plasma over the growing film. This reduces the rate of material arrival increasing the surface diffusion of adatoms and their interaction.

Acknowledgements

The authors thank CONACYT–Mexico, SIP–Instituto Politécnico Nacional–Mexico, EU Competitive and Sustainable Growth Program and Enterprise Ireland.

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