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FUNCTIONAL ZnO THIN FILMS OBTAINED BY RADIOFREQUENCY BEAM ASSISTED PULSED LASER DEPOSITION

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Abstract. Piezoelectric and *p* type semiconductor ZnO thin films were deposited by radiofrequency beam assisted pulsed laser deposition. Optical, electrical and structural properties were found to depend on both deposition parameters and radiofrequency beam characteristics.

Key words: type semiconductor, ZnO, thin films, radio frequency beams, pulsed laser, deposition optical.

1. INTRODUCTION

ZnO become recently a very fashionable material due to its applications generated by the particular properties. It is a wide band-gap semiconductor transparent in the visible range (optical band-gap of 3.4 eV), has high piezoelectric coefficient and electromechanical coupling factor. The control of the background conductivity increases its potential application in ultrasonic transducers, SAW devices and sensors, resonators, filters, gas sensors, etc. [1–4]. In films ZnO shows a strong tendency to grow with its *c*-axis perpendicular to the substrate surface even if the substrate is amorphous. Good quality, highly oriented ZnO thin films are needed for the SAW applications to reduce the propagation loss and to increase the electro-mechanical coupling coefficient. Moreover, for operating surface wave devices in liquids it is necessary to generate surface shear displacements, where the wave displacement is perpendicular to the direction of the wave propagation and in the plane of the crystal surface. In special conditions (oxygen lack [5] or doped with Al [6]) it became conductor and can be used as transparent conductive oxide. The high exciton binding energy and band gap energy of ZnO thin films open the prospect of fabricating semiconductor lasers in the ultraviolet spectral range. A prerequisite for laser diode fabrication is highly *p*-doped ZnO which is a challenging task, with very few and non reproducible results. Several techniques were used for ZnO thin films growth [7, 8]. Among them Pulsed Laser Deposition (PLD) demonstrated to be one of the most attractive [7, 8]. In this paper we report on the piezoelectric and *p*-type semiconductor thin films obtaining by radiofrequency beam assisted pulsed laser deposition, a complex PLD based technique, starting from a pure Zn target in oxygen reactive atmosphere. The morphological, compositional, structural and electrical properties were investigated by AFM, TEM, XRD, Hall effect, piezoelectric measurements.

2. EXPERIMENTAL

The set-up is presented in Fig. 1a. A laser beam delivered by a Nd:YAG laser (τ_{FWHM} = 5 ns, wavelength of 265 nm, 355 nm or 1064 nm) is focused on a high purity Zn metallic target. During the process the target is rotated and translated for avoiding drilling or crater formation. In the interaction area the material is ablated. The laser plasma is ignited in front of the target and develops perpendicular to it. The substrate is placed parallel or tilted in respect to the target, at a distance in the range of (3–8) cm. Separately, a gas discharge is generated by an RF generator (13.56 MHz). The developed radiofrequency double chamber discharge geometry allows the generation of a “beam” of excited and ionized species (Fig. 1b) which is directed onto the substrate (with different angles), where the target atoms generated by laser ablation also arrive. In this way the reactivity increases in comparison to the simple ablation in a reactive atmosphere and also a preferential orientation of the film is expected to be obtained [For details see 9, 10]. For *p* type doping a mixture of N_2/O_2 was used in the discharge. Influence of the deposition parameters and of the rf beam addition on the ZnO layers has been investigated by techniques as Atomic Force Microscopy (AFM), X-ray diffraction (XRD), Transmission Electron Microscopy (TEM), Hall effect and piezoelectric measurements.

3. RESULTS AND DISCUSSIONS

3.1 PIEZOELECTRIC THIN FILMS DEPOSITION; *c*-AXIS *VERSUS a* AXIS GROWTH

Pt coated silicon, r-cut Sapphire and MgO were used as substrates, the laser fluence varied between 2 and 20 J/cm^2 and the oxygen pressure in the range of

5×10^{-2}–10^{-1} mbar. The substrate temperature was varied between room temperature and 500°C. The radiofrequency beam was directed towards the substrate surface under different incident angles. Two *c*-axis growth directions were emphasised: perpendicular on film surface and in plane, parallel with one substrate axis orientation (*a*–axis).

Atomic Force Microscopy studies reveal that the excited and ionized beam addition has results in the diminishing of both the roughness and the droplet's density on the film surface. In Fig. 2 AFM images of the surfaces of two samples deposited in the same experimental conditions except the radiofrequency beam addition are presented. It can be noticed a roughness with two orders of magnitude lower and a small droplets density for layers grown in the presence of rf beam. A similar tendency was observed irrespective of the substrate type: in Fig. 3 are presented three AFM images representing ZnO surfaces of layers deposited in the same experimental conditions except the substrate. For layers of several hundreds of nanometers until one micron, values of some nm of the roughness (rms) are noticed; the droplets density is also low. Scanning Electron Microscopy images in cross section show a columnar structure with columns perpendicular on the film surface, both when a simple ablation process or an assisted one was used, irrespective of the laser wavelength. A typical image is presented in Fig. 4. The radiofrequency addition slowly increases the columns dimensions and density. ZnO layers have the natural tendency to grow with *c*-axis perpendicular to the film surface. Several behaviors were noticed in our experiments, depending on the deposition conditions. Thus, in a normal configuration, with the substrate parallel to the target, the RF oxygen plasma beam assisted deposition results in obtaining of ZnO layers with (00l) texture. In Fig. 5 is presented a 2D X-ray diffraction spectrum

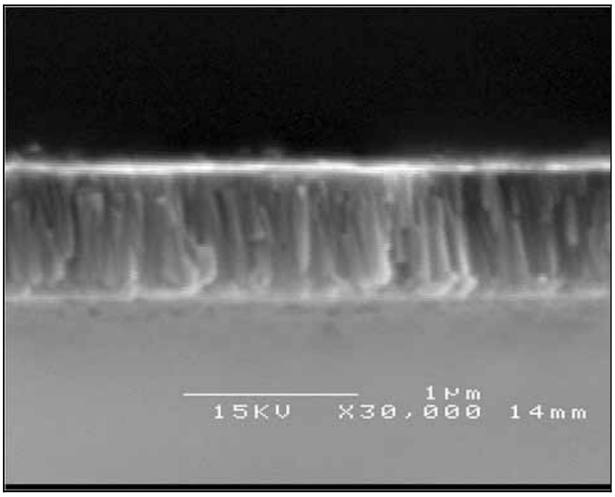

Fig. 4 – Scanning electron microscopy images in cross section of a layers prepared in the following experimental conditions: $\lambda = 1060$ nm, laser fluence 20 J/cm^2, oxygen pressure 0.05 mbar, substrate temperature 350°C, Pt coated Si substrate.

of a layer deposited in the presence of rf discharge beam on a Pt coated silicon substrate: it can be seen that the only ZnO peaks present are (00l), (001) and (002). The radiofrequency addition suppressed practically any other orientation. For these layers the c lattice parameter derived from (002) lines give a value of $c = 5.186$ Å, very close to standard 5.20661 Å. The films were highly transparent, with a band-gap of 3.23 eV.

The direction of the ZnO layer's *c*-axis was found to strongly depend on the synergy between the pulsed laser ablation parameters, substrate type and temperature and radiofrequency beam addition [8, 10, 11]. Two examples have been chosen to demonstrate how this happens.

The first example concerns the use of single crystal as substrate: r-cut Sapphire and MgO. Completely crystalline, one direction a-axis oriented ZnO layers have been obtained on r-cut Sapphire substrate kept at a temperature of 200°C during deposition (Fig. 6a). Radiofrequency power used in discharge was of 200 W and a direction of the beam tilted respect to substrate normal with an angle of 60 degree was set. A similar result was obtained using a MgO substrate at room temperature. The (100) and (101) orientation are evidenced: the edge or/and the faces of the hexagonal prism of the ZnO cell are parallel with the MgO cubic axis (Fig. 6b). A very sharp interface was noticed and an epitaxial growth was evidenced by HRTEM in cross section analyze (Fig. 7). The rf beam addition was found to almost fully suppress the (002) layers orientation, inducing in plane growth (Fig. 8 a and b).

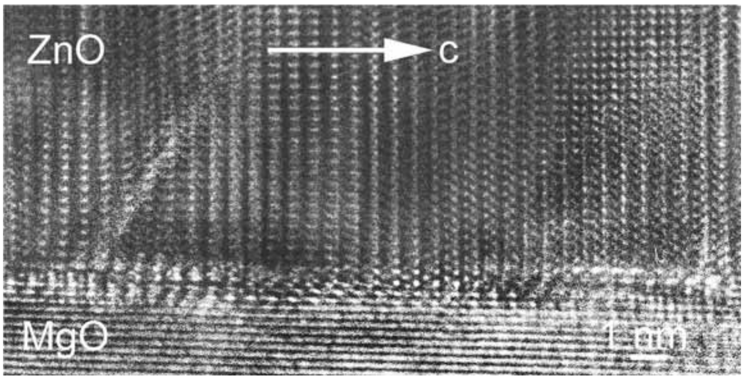

Fig. 7 – High resolution TEM in cross section of the interface between the a axis oriented ZnO layer grown on MgO single crystal.

The rezistivity and the piezoelectric properties were tested. High values of resistivity have been measured for all films. Piezoelectric test for layers grown with *c*-axis perpendicular on the film surface have been performed. Values of 7–8.5 pC/N for d_{33} coefficient have been measured: the best results have been obtained for ZnO layers deposited in the presence of radiofrequency beam.

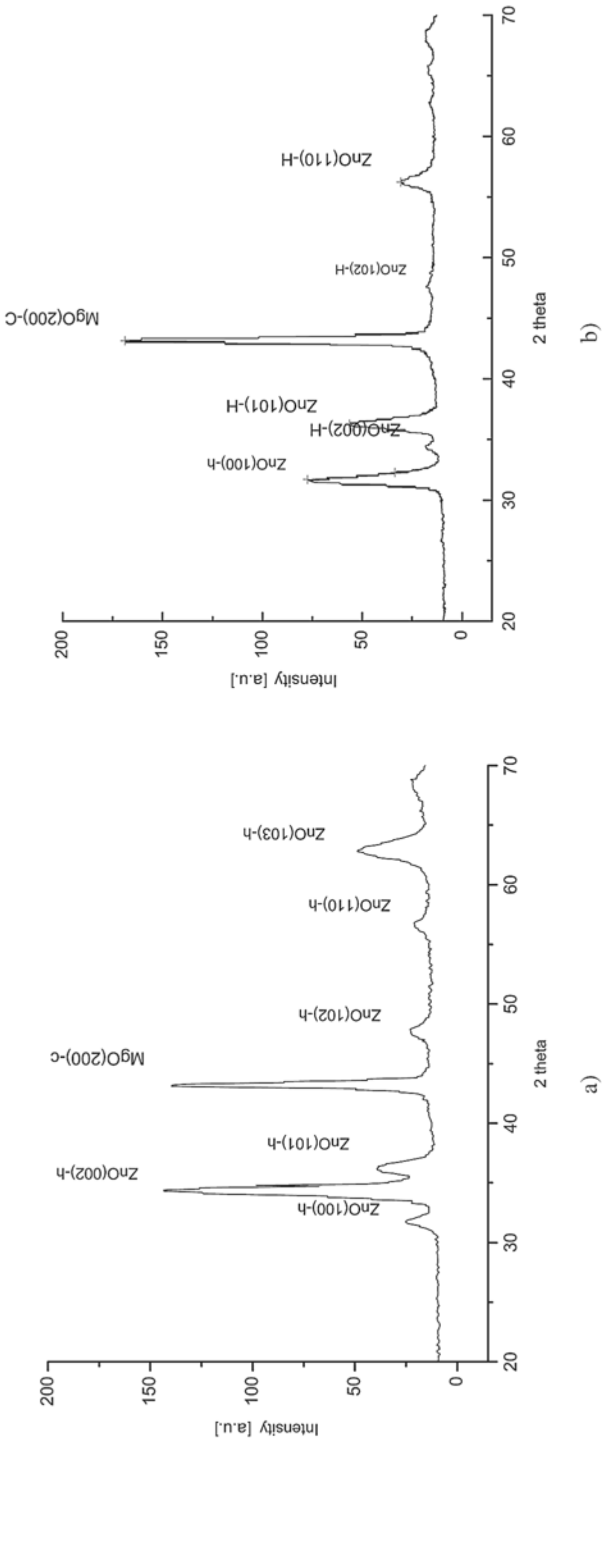

Fig. 8 – X-ray diffraction spectra of two ZnO layers deposited in the same experimental conditions without (a) and with rf beam addition (b).

3.2. *p*-TYPE ZnO THIN FILMS GROWTH

For obtaining *p*-type ZnO thin films the same experimental set-up was used. The samples were grown on Si and quartz substrate at 355 nm laser wavelength, 10 Hz repetition rate, laser fluence of 3 J/cm^2, 4 cm distance from the target at 400°C and a RF power of 100 W. The parameter varied in these experiments was the N_2/O_2 ratio. Maintaining the oxygen pressure at 0.05 mbar and for only one run at 0.09 mbar the nitrogen pressure was varied in order to obtain the following N_2/O_2 ratios: 0.15, 0.3, 0.5 and 1.

AFM images, not shown here, indicate smooth surfaces with crystallites of the order of tens of nanometers. The XRD patterns for all samples exhibit only (002) and (004) peaks indicating that the *c*-axis is always oriented normal to the substrate surface. The *c*-parameters (around 5.22 Å) derived from the (002) peak position are very close to the *c*-parameter of the bulk material (5.20661 Å in JCPDS file no. 36-1451) revealing that the films are displaying a low degree of homogeneous distortion due to the lattice mismatch between the film and the substrate. A typical XRD pattern of as-deposited thin films is presented in Fig. 9 a for a N_2/O_2 ratio of 0.3. Apparently N_2/O_2 ratio in the 0.3–0.5 range favored higher crystallinity and higher grain size while high amount of nitrogen or oxygen conducted to low crystallinity and smaller grain sizes (Fig. 9b).

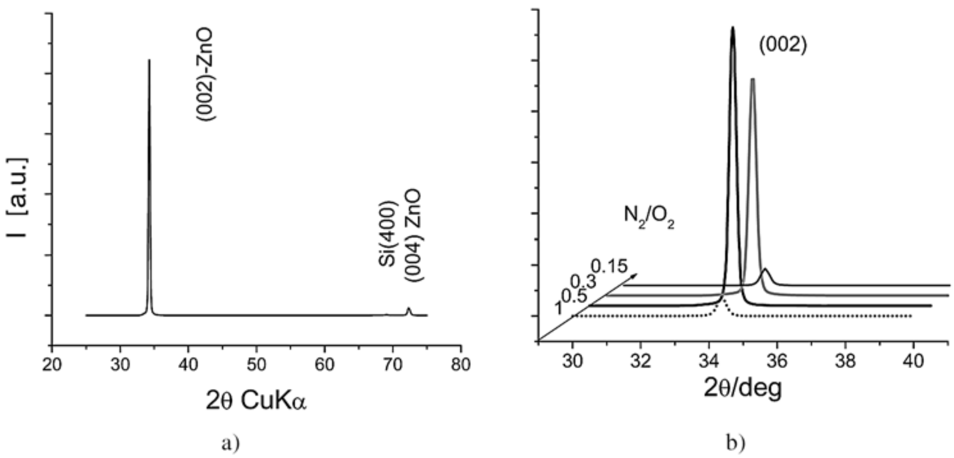

Fig. 9 – Representative XRD pattern of a nitrogen-doped ZnO film (N_2/O_2 = 0.3 in the gas mixture) (a) and (002) peak at various concentrations of nitrogen in the gas mixture (b).

Hall measurements gave for the carriers' mobility values of 12–16 Ωcm, the films having a high resistivity for a carrier concentration of 10^{16}–10^{17} cm^{-3}. Higher crystal orientation is thought to reduce resistivity (enhance mobility) because of the shorter carrier path length in a *c*-plane and the reduction in the scattering of the carriers at the grain boundaries and crystal defects. Additionally higher grain size should reduce the scattering of the carriers at the grain boundaries and therefore enhance the mobility. Better electrical properties are obtained for the 0.15 N_2/O_2 ratios; the resistivity is lower in this case and the mobility and carrier concentrations are comparable for all N_2/O_2 ratios. High resistivity and slightly *p*-type films are grown; the mechanism could be the incorporation of N, NO, N_2 and N_2O produced by the RF discharge as predicted by Yan and Zang [12] and previously reported by Joseph *et al.* [13] for ECR assisted PLD. These species are present in the plasma as shown by optical emission spectroscopy measurements performed at a few millimeters from the nozzle.

4. CONCLUSIONS

The addition of RF plasma beam results in very important achievements: i) almost droplet free films have been obtained; ii) the film roughness decreases several times; iii) the temperature for obtaining single phase *c*-axis oriented films decreases; iv) a-axis oriented layers can be obtained by an appropriate adjustment of the experimental conditions. Oxygen and Nitrogen simultaneous discharge assisting PLD allows the obtaining of *p*-type ZnO thin films, as it was demonstrated by Hall measurements. The films show a very good crystallinity, with (002) texture, a columnar growth and a smooth surface. The transmission in the visible range is 99.8% and the calculated optical band gap is 3.17 eV.

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