Available online at www.sciencedirect.com
SCIENCE DIRECT®
Catalysis Today 89 (2004) 331–335
CATALYSIS TODAY
www.elsevier.com/locate/cattod

Characterization of ZnO films prepared by reactive sputtering at different oxygen pressures

B. Amrani*, S. Hamzaoui

Scanning Electron Microscope and Material Sciences Laboratory, University of Sciences and Technology of Oran (USTO), P.O. Box 1505 El-M'Naouar, Oran, Algeria

Abstract

The piezoelectric qualities of ZnO films are characterized by their high resistivity and polycrystalline structure which is preferentially textured in perpendicular to the substrate, both of them were studied as a function of sputtering parameters. This paper deals with the formation of ZnO thin films successfully deposited onto glass substrate by sputtering. The films feature plane (0 0 2) preferential orientation. The effects of the sputtering pressure, sputtering power and sputtering in an O_2 + Ar gas mixture on the preferential orientation of the ZnO films are studied. The results show that a lower sputtering pressure is conducive to the formation of the (0 0 2) plane.
© 2003 Elsevier B.V. All rights reserved.

Keywords: ZnO; Sputtering; Preferential orientation

1. Introduction

ZnO is a II–VI compound semiconductor with a hexagonal wurtzite crystal lattice structure and characteristic piezoelectric properties [1,2]. The high ultrasonic velocity and the fairly large piezoelectric coupling constant of ZnO films make them very suitable for device applications, particularly for the generation and detection of surface and bulk acoustic waves [3].

When applying ZnO film to surface acoustic wave (SAW) devices, the structure is required to have a polycrystalline preferential orientation, a homogeneous composition, high resistivity and low surface roughness.

A variety of deposition techniques, including the sol–gel method [4,5], spray pyrolysis [6], chemical vapor deposition [7], pulsed laser deposition [8], reactive evaporation [9], and sputtering [10] have been employed for the growth of the ZnO. In this paper, the preparation of ZnO film by reactive radio-frequency (rf) sputtering is studied.

We have succeeded in preparing ZnO films with a (0 0 2) preferential orientation onto glass substrate. In particular, the ZnO (1 0 0) plane is difficult to prepare with physical vapor deposition (PVD) methods.

2. Experimental details

ZnO thin films are deposited on glass substrate measuring 12 mm × 8 mm by radio-frequency sputtering. The target was a sintered oxide ceramic disk of ZnO (purity 99.5%), 80 mm in diameter. The target–substrate distance was 5.5 cm. A thermocouple was positioned on the reverse side of the substrate holder to control the substrate temperature during the film growth, the sputtering gases were O_2 and Ar, which were combined in the sputtering chamber. Fig. 1 shows the geometries of the deposition zone of the sputtering system used in this work.

The substrates were carefully cleaned just prior to the deposition, to improve the deposited adhesion to the substrates. Finally, the substrates were exposed to dry N_2 flow and spin dried. Before each deposition, the sputtering chamber was pumped down to below 3×10^{-3} Torr. The target was pre-sputtered in O_2 for 15 min, in combination with a shutter, ensuring stabilized sputtering conditions. Several parameters—total sputtering pressure, sputtering mixture ratio and rf power—were changed for the different deposition runs of ZnO.

Observation of the crystallinity and microstructure of ZnO films were accomplished using X-ray diffraction (XRD) and scanning electron microscopy (SEM), and the resistivity of the ZnO films was measured by a two-point probe system.

* Corresponding author.
E-mail address: abouhalouane@yahoo.fr (B. Amrani).

0920-5861/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2003.12.014

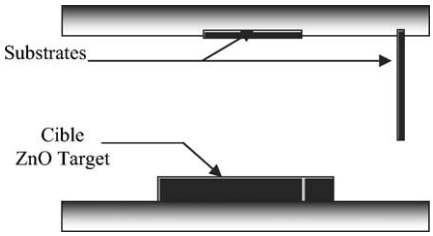


Fig. 1. Schematic representation of the target–substrates geometric configuration.

The sputtering was carried out at a working gas pressure in the (1.5–9) $\times 10^{-2}$ Torr range and with a rf power in the range 50–150 W.

3. Results and discussion

3.1. Deposition rate

Fig. 2 shows the deposition rate of the ZnO films as a function of the sputtering mixture ratio for two different rf power (50 and 150 W). The deposition rate was calculated by dividing the film thickness by the sputtering time for each run. The deposition rate of the films, grown at a total sputtering pressure of 1.5×10^{-2} Torr, was in the range 3.2–2.1 nm min^{-1} for an rf power of 50 W, and was in the range 4.8–6 nm min^{-1} for an rf power of 150 W when the O_2/Ar gas flow ratio changed between 50 and 100%. At a given rf power, the deposition rate gradually decreased with the decreasing of the Ar percentage in the sputtering mixture.

These results can be explained by considering the greater sputtering yield of Ar atoms, which have an atomic mass higher than that of O_2 molecules. Furthermore, at a given mixture ratio, the deposition rate was higher for the films grown with a higher rf power, as can be expected.

3.2. Structural analysis

Fig. 3 shows the XRD patterns of ZnO thin films deposited at different sputtering pressures with a rf power of 100 W and a oxygen concentration of 50%. When the sputtering pressure was 1.5×10^{-2} Torr, only the (0 0 2) diffraction peaks with 2θ of 34.54° appeared in the XRD patterns. With a sputtering pressure between 40 and 6×10^{-2} Torr, the preferential orientation of the films was not distinct. When the sputtering pressure increased to 9×10^{-2} Torr, the (0 0 2) peaks disappeared.

These results can be explained by the reduced energy loss of atoms which impinge on the growing film. In fact, at low pressures, the collision frequency of atoms with the plasma neutrals is lower than that a higher pressures; therefore, the atoms have more energy to rearrange according to the hexagonal wurtzite crystalline structure at the substrate surface.

The lattice spacing d_{002}, calculated by substituting the experimental 2θ value into the Bragg's equation, were 2.5946 Å. The lattice constants c were calculated using the relationship $d_{002} = c/2$ to be 5.1891 Å.

The amount of uniform strain in the ZnO films was calculated from the relationship $[c(\text{film}) - c(\text{powder})]/c(\text{powder})$ and varied $\sim -0.3\%$. Such results indicate that the films were in a state of tensile stress. The main contributions to the film strain can be attributed to the lattice mismatch and to the difference between the thermal expansion coefficients of the ZnO and glass substrates [10] (Figs. 4 and 5).

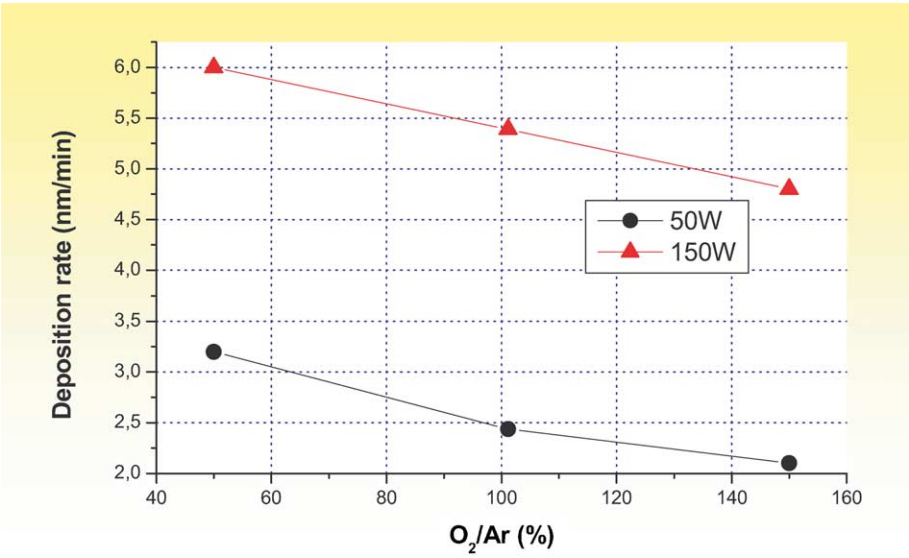
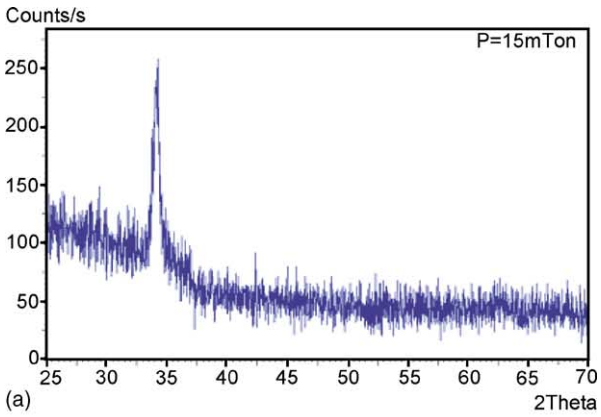
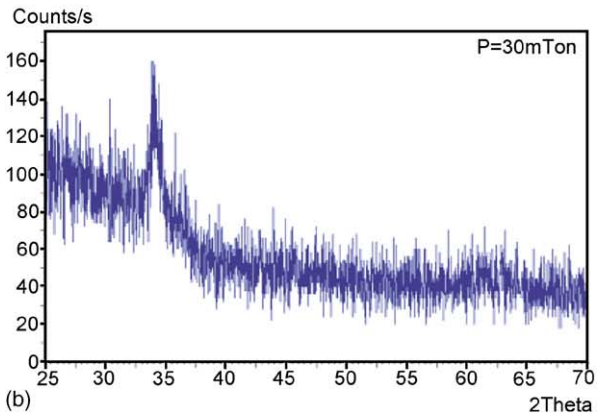
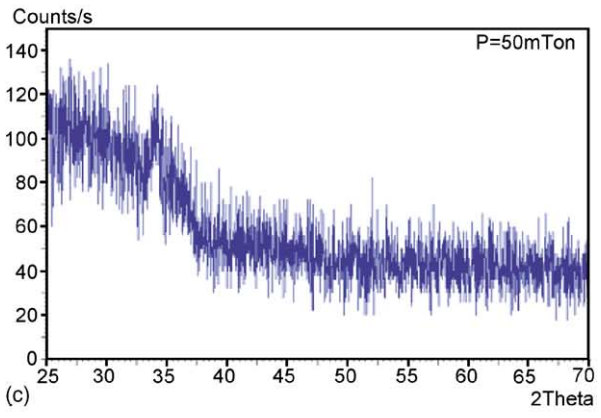


Fig. 2. Deposition rate of ZnO films, the sputtering gas mixture ratio for films grown at T_{sub} = RT, with a sputtering pressure of 15 mTorr and deposition time of 3 h.







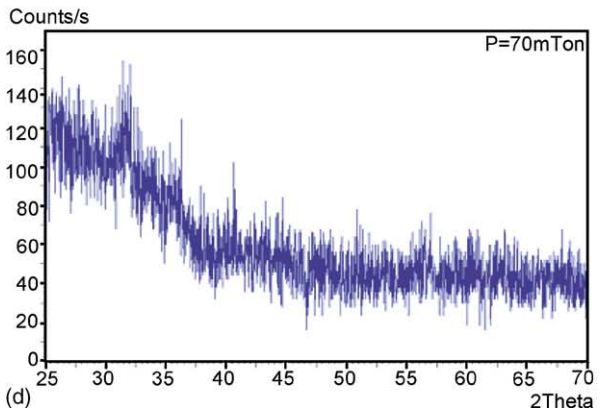


Fig. 3. XRD spectra of ZnO films deposited at T_{sub} = RT, with rf power of 150 W, O_2/Ar gas ratio 50% and deposition of 3 h, at different sputtering pressure: (a) 15 mTorr, (b) 30 mTorr, (c) 50 mTorr, (d) 70 mTorr, (e) 90 mTorr.

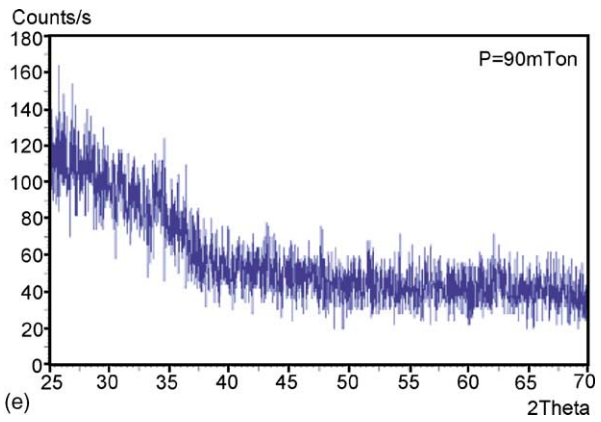
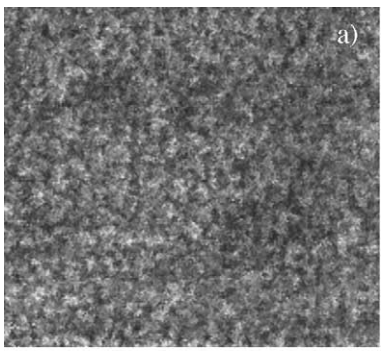
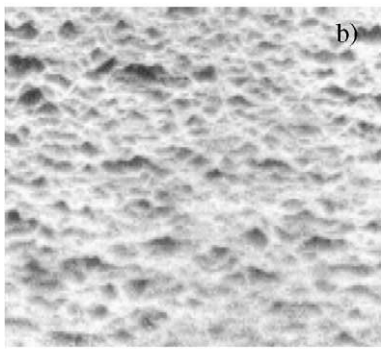


Fig. 3. (*Continued*).





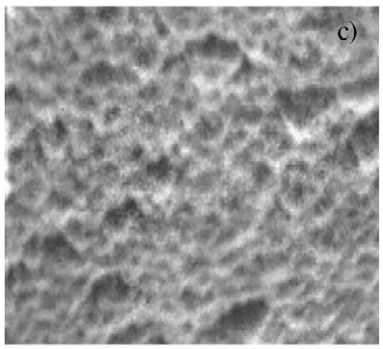


Fig. 4. Scanning electron micrographs of the ZnO films, deposited under an ratio of 50/50 at room temperature, as a function of total pressure (a) 15, (b) 50, (c) 90 mTorr.

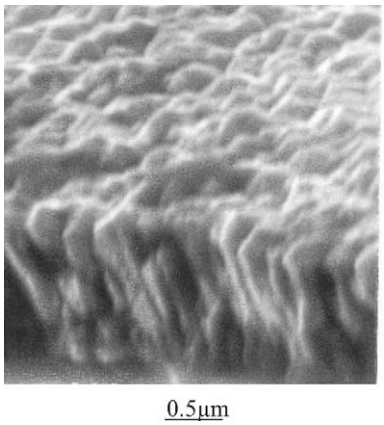


Fig. 5. *c*(0 0 2)-axis oriented ZnO films used to estimate the thickness.

3.3. Morphologic analysis

The surfaces of the thick ZnO films were observed by SEM. The structure inside each island was formed from 100 to 500 nm (Figs. 4 and 5). The comparison of the crystallite size obtained by XRD and the grain size by SEM suggests that columns are formed by many staked crystallites.

3.4. Electrical proprieties

Fig. 6 shows the effect of oxygen pressure on the resistivity. The electrical resistivity of the films formed at a low sputtering pressure of 1.5×10^{-2} Torr was $8.5 \times 10^{8}\ \Omega$ cm. As the sputtering pressure increased to 3×10^{-2} Torr electrical resistivity reached a minimum value of $5.0 \times 10^{8}\ \Omega$ cm; thereafter it increased to $9.2 \times 10^{8}\ \Omega$ cm at 9×10^{-2} Torr. At low sputtering pressures, the gas density is low and the sputtered zinc atoms can reach the substrate with less collisions resulting a slightly high zinc content in the films which leads to low electrical resistivity. In addition, the decrease of electrical resistivity in the sputtering pressure range 1.5×10^{-2}–3×10^{-2} Torr is caused by the reduction in the electron scattering from the grain boundaries due to improvement in the crystallinity of the films. At high sputtering pressures, the gas density is high and the sputtered zinc atoms can only reach the substrate with more collisions leading to the production of nearly stoichiometric zinc oxide films resulting in the increase of electrical resistivity. A remarkable fact of these results is that the reactive sputtering method allows the deposition of high resistive ZnO thin films.

4. Conclusion

This paper reports on the preparation of ZnO films with a reactive sputtering technique. It was found that the sputtering pressure is a very important factor for the crystalline preferential orientation of ZnO films. When the sputtering pressure is low, it is easy to form the (0 0 2) preferential orientation of ZnO films.

Acknowledgements

The authors would like to thank H. Bouziane for the SEM measurements. We also thank A. Hamou and Z. Harrache for useful discussions and for critically reading the manuscript.

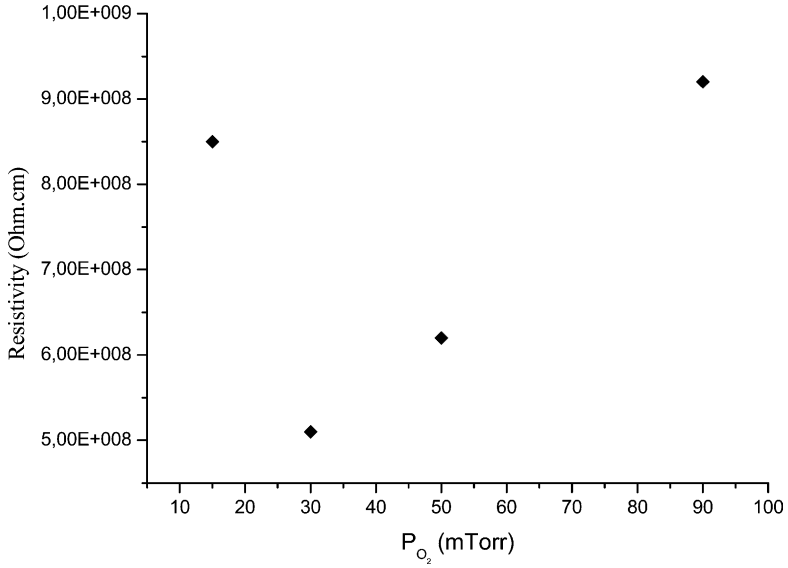


Fig. 6. Influence of the oxygen pressure on resistivity of ZnO films deposited by reactive sputtering.

References

[1] V. Srikant, D.R. Clarke, J. Appl. Phys. 83 (1998) 5447.
[2] T.L. Yang, D.H. Zhang, J. Ma, H.L. Ma, Y. Chen, Thin Solid Films 326 (1998) 60.
[3] P.M. Martin, M.S. Good, J. Johnston, L.J. Bond, S.L. Crawford, Thin Solid Films 379 (2000) 253.
[4] B.J. Lokhande, M.D. Uplane, Appl. Surf. Sci. 167 (2000) 243.
[5] W.W. Wenes, A. Yamada, K. Takahashi, M. Yoshino, M. Konagai, J. Appl. Phys. 70 (1991) 7119.
[6] Y. Natsume, H. Sakata, T. Hirayama, J. Appl. Phys. 72 (1992) 4203.
[7] S. Hayamizu, H. Tamaka, T. Kawai, J. Appl. Phys. 80 (1996) 787.
[8] K.L. Narasimhar, S.P. Pai, V.R. Palkar, P. Pinto, Thin Solid Films 255 (1997) 104.
[9] Y. Ohya, H. Saiki, T. Takahashi, J. Mater. Sci. 29 (1994) 4099.
[10] M.Y. Han, J.H. Jou, Thin Solid Films 260 (1994) 58.