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The effects of the deposition parameters of ZnO thins films on their structural properties

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Abstract

Structural properties of thin zinc oxide (ZnO) films reactively sputtered on Si substrates using radio frequency (rf) magnetron have been studied in this work as a function of the substrate temperature (30 to 760°C) during deposition and the concentration of oxygen (10 to 90%) in the Ar-O_2 gas mixture.
The X-ray diffraction (XRD) have shown that the ZnO films grown at the ambient temperature are most weakly crystallized and the film crystalline quality stabilises above 200°C. However, the best crystalline quality is obtained for the (002) orientation at the ambient temperature with an Ar/O_2 gas mixture of 10% of oxygen. Also, the film growth rate varies with the substrate temperature and the amount of oxygen. The increasing of oxygen in the gas mixture induces a decreasing of the (002) peak intensity, and increases slightly those of the (100) et (101) orientations.
The film stoichiometry is near Zn_1O_1 as observed from Energy dispersive X-ray spectroscopy (EDXS). The scanning electron microscopy (SEM) has shown a columnar structure of the ZnO films.

I. Introduction

ZnO is an attractive material for large variety of applications as microelectronic, piezozlctric, optoelectronic and photovoltaic devices. It is a wide-bandgap oxide semiconductor with a direct energy gap of about 3.37 eV. A goal of this study is to obtain suitable films for shear wave transduction. The zinc oxide has emerged as one of the most promising materials, due to its optical and electrical properties associated with the high chemical and mechanical stability, which makes it a lower cost material, when compared to the most currently used transparent conductive oxide materials ITO (indium tin oxide) and SnO_2 (tin oxide).
During the last years, several deposition techniques for thins films have been developed and studied, such as, ion-beam-assisted deposition [1], chemical vapour deposition CVD [2], pulsed-enhanced chemical vapour deposition PECVD [3], spray pyrolysis [4,5], molecular beam epitaxy (MBE) [6], pulse Laser deposition (PLD) [7,8], sol-gel processing [9,10], reactive DC sputtering [11,12] and AC. magnetron sputtering technique which is one of the most widely used to its reproducibility and efficiency [13-16]. The growth methods of ZnO films are compatible with a wide range of substrates (pyrex, quartz, silicon, sapphire…).
Consequently, many potential applications, such as transparent electrode in solar cells [17,18], transparent conductors, piezoelectric transducers and surface acoustic wave devices [19,20] could be archived.
Radio frequency magnetron sputtering exhibits interesting advantages: the low substrate temperature, the good adhesion of the films on the substrates, and a high deposition rate. The

physical properties of the films depend on the sputtering parameters, such as the substrate temperature, the oxygen partial pressure and the sputtering power [21]. Therefore, it is meaningful to report in this paper, the effects of the deposition parameters on ZnO thins films structural properties using r.f. magnetron sputtering.

II. Experimental approach

Zinc oxide films elaborated by r.f. magnetron sputtering are very sensitive to the deposition parameters, these should therefore be optimised in order to obtain highly orientated ZnO films.
The fig. 1 shows the apparatus of r.f. magnetron sputtering. It consists of a cylindrical plasma chamber.
The ZnO films were deposited by r.f. magnetron system on silicon Si(100) substrates. The Zinc target (purity 99.99%) diameter was 100 mm (4 inch) and 6.35 mm thick. The distance between the cathode and the substrate holder was 70 mm. The deposition chamber was pumped down to a base pressure of 5.10^{-7}mbar by a turbomolecular pump prior to the introduction of the argon-oxygen gas mixture for ZnO thin film production. The pressure was fixed at 2.10^{-2}mbar and the time deposition was 3000s.

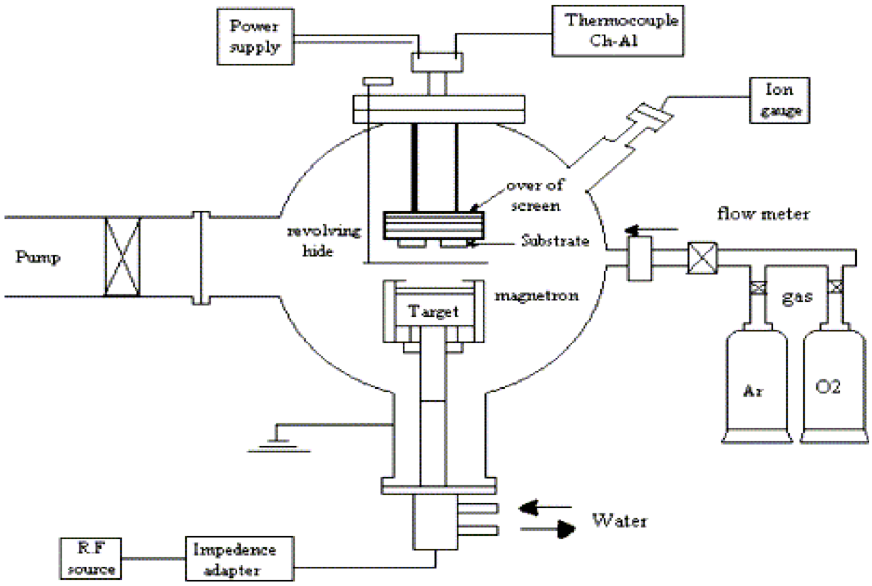


Fig.1 Radio frequency magnetron sputtering system.

The RF power delivered by the RF generator was varied between 20 and 100 watts. The substrate holder temperature was varied from the room temperature to 760°C and the oxygen percentage in Ar/O_2 gas mixture was varied from 10 to 90%.
All these conditions were summarized in the table I.

TABLE I. DEPOSITION CONDITIONS OF ZnO BY R.F MAGNETRON SPUTTERING

R.F Power	20W and 100W
Pressure	2.10^{-2} mbar
O_2 in Ar/O_2	10% to 90%
Gas flow	25sccm
Target	ZnO (purity 99,99%)
Temperature	ambiant to 760°C
Deposition time	3000s

The crystallographic properties of films were analysed by X-ray Diffraction (XRD) using the Cu Kα (with λ = 1.5405 A°) radiation. The morphology of the films is obtained by using scanning electron microscopy (SEM). The atomic compositions and the stoechiometry of the ZnO films were determined by Energy Dispersive X-ray Spectroscopy (EDXS).

III. Results and discussion

III.1 Structural and morphologic properties

Fig. 2 shows the XRD pattern for samples deposited at several temperature (ranging from 31 to 760°C, $p=2.10^{-2}$mbar, P=100W, $Ar-O_2$ at 50-50%). We observe only one strong peak at 2θ~34.4°, which can be attributed to the (002) line of the hexagonal ZnO würtzite phase

[22,23]. All the sputtered ZnO films are highly textured, with the c-axis perpendicular to the substrate surface.
The intensity of the (002) peak increases as a function of the substrate temperature showing an improvement of the films crystallinity. Moreover the peak intensity increases while its full width at half maximum (FWHM) decreases. Further increasing of substrate temperature leads to a slightly decreasing of the peak intensity for films prepared at 760°C. It indicates a saturation of films crystallinity.

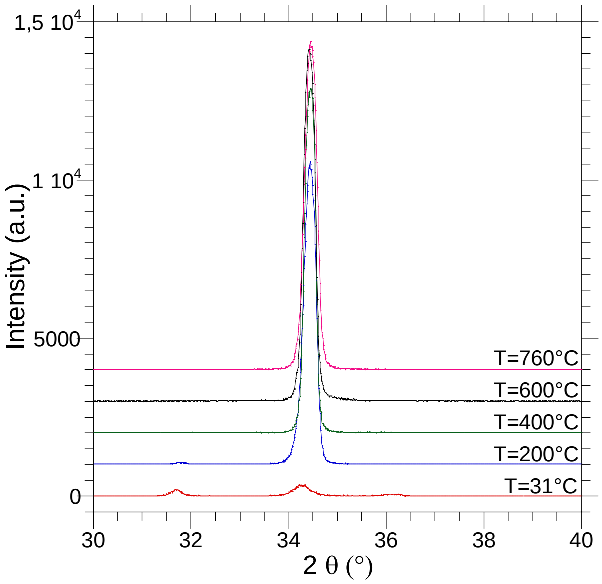


Fig.2 X-ray spectra of ZnO thin film as a function of substrate temperature.

Fig.3 shows the XRD spetra obtained for samples deposited at several oxygen percentage varied from 10 to 90%, room-temperature, P=100W and a pressure of 2.10^{-2}mbar. The XRD diffraction spectra also reveals the existence of ZnO single phase with hexagonal würtzite structure with a preferential orientation in the (002) direction. The increase of oxygen percentage from 10 to 90% in the gas mixture decrease the (002) peak intensity, while increases slightly those of the (100) and (101) orientations.

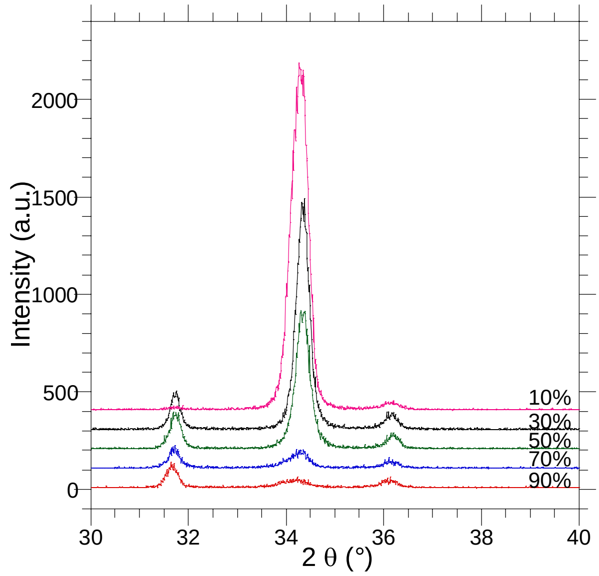


Fig.3 X-ray spectra of ZnO thin film as a function of oxygen percentage in the gas mixture

TABLE II. THICHNESS AND GRAINS SIZE FOR DIFERENT PERCENTAGE OF OXYGEN IN THE GAS MIXTURE.

Perc. O_2 (%)	Max size (nm)	Min size (nm)	Mean size (nm)	σ nm^2	Ecart Type nm
30	78	61	70	3.080	1.755
50	59	55	57	0.446	0.668
70	52	47	50	1.734	1.317
90	30	24	27	1.297	1.139

For each sample, we have chosen ten measurements of the grains size on the SEM analysis. When the percentage of oxygen in the gas mixture increases, the mean size of the grains decrease, which explains the poor crystalline quality at high O_2 concentration. The variance and the standard deviation are small, which reveals the good homogeneity of the ZnO films in grain size. A typical SEM image shows the columnar structure of the ZnO films Fig.4. The column size is summarised in the table II.

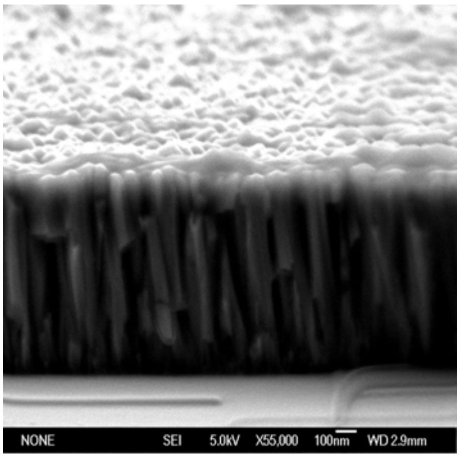


Fig.4 Cross section SEM micrograph of ZnO films at 30% of oxygen percentage in gas mixture

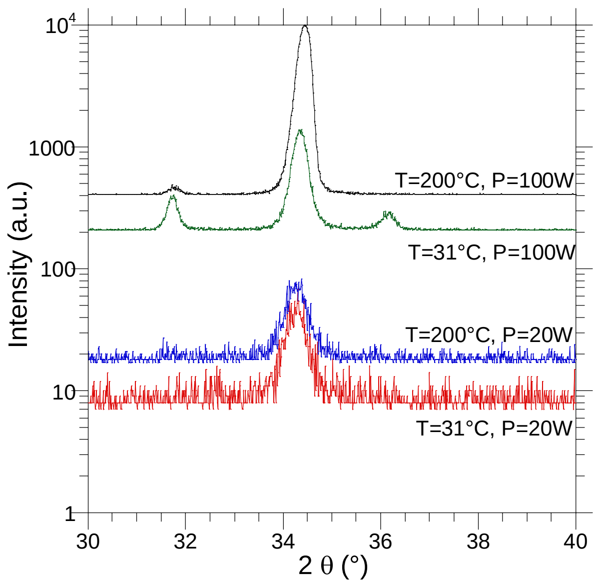
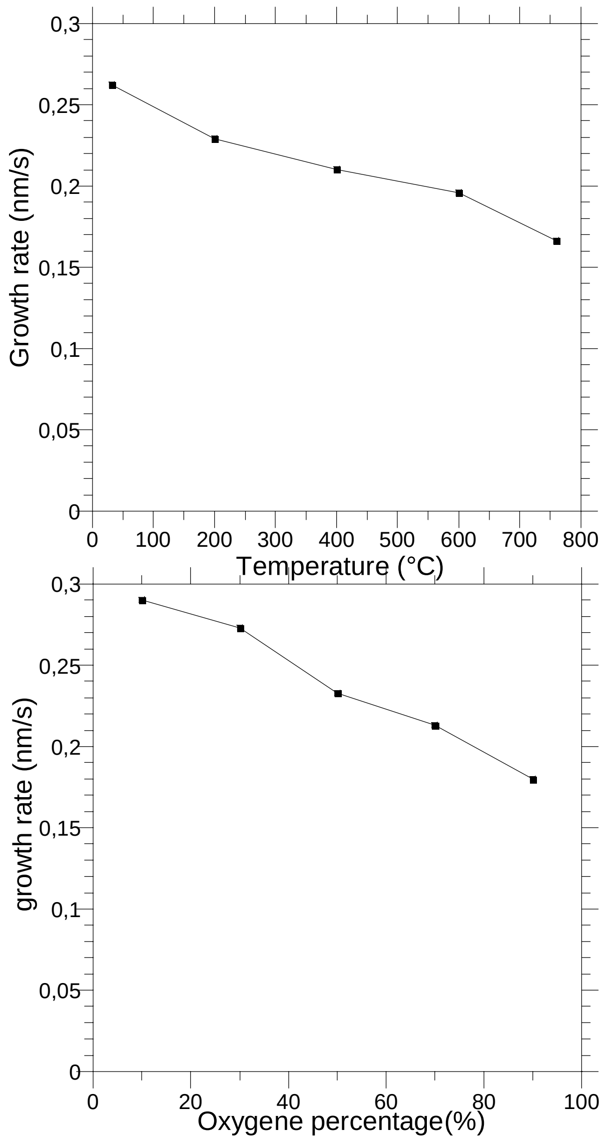


Fig.5 X-ray diffractograms of ZnO thin films as function of r.f. power, (a) at T=31°C, (b) at T=200°C.

For the same thickness (60 nm) for two films at P=20w, T=31 and 200°C, Ar-O_2 at 50-50%. Phrase incomplete et donc pas Claire.

Also, for the 700 nm films thick (P=100W, T=31 and 200°C, Ar-O_2 at 50-50%, the XRD spectrum shows a better crystalline quality for the 200°C and 100W film, fig5 .

III.2 Deposition rate and composition structure



(a)
(b)

Fig.6 ZnO growth rate as function of the substrate temperature (a) and oxygen percentage in Ar/O_2 gas mixture (b).

Fig.6 shows the variation of the deposition rate versus substrate temperature (a) and oxygen percentage in Ar/O_2 gas mixture (b). The increasing of the temperature and the oxygen percentage induces a decreasing of the rate deposition due to a decreasing of sticking coefficient.

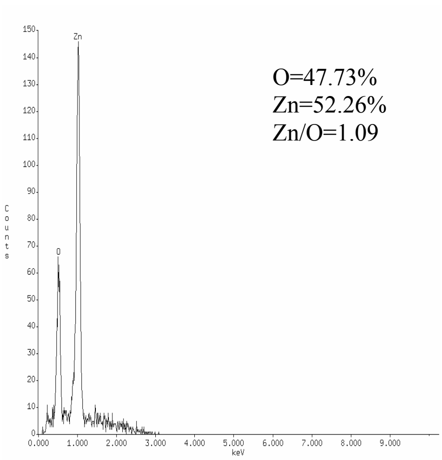


Fig.7 Atomic composition by EDXS characterisation

The results obtained by Energy Dispersive X-ray Spectroscopy (EDXS) are shown in Fig.7. We have used a standard sample ZnO results and we have compared with our results. The characterisation have revealed that all the films were stoïchiometric and there atomic compositions are Zn_1O_1.

IV. Conclusion

Zinc oxide thin films have been deposited by r.f. magnetron sputtering, using a ZnO target. The temperature substrate has been varied between 31°C to 760°C and the oxygen percentage in Ar/O_2 gas mixture varied between 10% to 90%. We have mainly observed the presence of the ZnO hexagonal phase of würtzite type and a preferential orientation of the film growth along the c-axis. The ZnO films formed at the ambient temperature are most weakly crystallized and the film crystalline quality stabilises above 200°C. Furthermore, the best crystalline quality is obtained for the (002) orientation at 400°C temperature in the presence of 50% of oxygen amount. At room-temperature, the highest quality is obtained at 10% of O_2 in the gas mixture.

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