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X-RAY ANALYSIS OF THE INFLUENCE OF SUBSTRATE TEMPERATURE ON THE CRYSTALLINE STRUCTURE OF ZnO THIN FILMS GROW BY RF MAGNETRON SPUTTERING

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ABSTRACT

ZnO thin films were prepared on Si (100) substrates by RF sputtering. The crystalline property of the films were observed to vary with the substrate temperature used. X-ray diffraction (XRD) measurement showed that the substrate temperature ZnO films exhibited preferred c-axis oriented (002) of below 0.32° full width at half maximum of X-ray rocking curves, an extremely high resistivity of 10^{10} Ω.cm and an energy gap of 3.3 eV at room temperature. It was found that a substrate temperature of 100°C and target/substrate distance about 50 mm, very low gas pressures of $3.35\text{x}10^{-3}$ Torr in argon and oxygen mixed gas atmosphere giving to ZnO thin films a good homogeneity and a high crystallinity.

Keywords: Z*inc oxide, Thin films X-ray diffraction, crystalline property*

1. INTRODUCTION

Zinc oxide is one of the most interesting II–IV compound semiconductors with a wide direct band gap of 3.3 eV [1–6]. It has been investigated extensively because of its interesting electrical, optical and piezoelectric properties making suitable for many applications such as transparent conductive films, solar cell window and MEMS waves devices [4]. The full-width at half-maximum (FWHM) of the (0 0 2) X-ray rocking curve is known to be suppressed below about 0.5° for obtaining effective electromechanical coupling [2]. The thermal stresses were determined by using a bending-beam Thorton method [3] while thermally cycling films. ZnO has hexagonal Wurtzite structure and some properties are determined by the crystallite orientation on the substrate. For example, for piezoelectric applications, the crystallite should have the c-axis perpendicular to the substrate. Many techniques, such as metal-organic chemical vapour deposition [7], spray pyrolysis [8] and sputtering [9–12], have been developed and employed to deposit ZnO thin films onto different substrates.

According to the literature, the reactive sputtering technique has received a great interest because of its advantages for film growth, such as easy control for the preferred cryst alline orientation, epitaxial growth at relatively low temperature, good interfacial adhesion to the substrate and the high packing density of the grown film. These properties are mainly caused by the kinetic energy of the clusters given by electric field. This energy enhances the surface migration effect and surface bonding state.

In this paper, the effects of substrate temperature on the crystalline property of ZnO films were particularly studied.

2. EXPERIMENTAL PROCEDURE

Zinc oxide films were deposited by RF magnetron sputtering using a zinc target (99.99%) with diameter of 51 and 6mm thick. Substrate is p-type silicon with (1 0 0) orientation. The substrates were thoroughly cleaned with organic. Magnetron sputtering was carried out in an oxygen and argon mixed gas atmosphere by supplying RF power at a frequency of 13.56 MHz. The distance between target and substrate was about 50 mm. The flow rates of both the argon and oxygen were controlled by using flow meter (ASM, AF 2600). The sputtering pressure was maintained at 3.35x10_3 Torr controlling by a Pirani gauge. Before deposition, the pressure of the sputtering system was under $4\text{x}10^{-6}$ Torr for more than 12 h and were controlled by using an ion gauge controller (IGC—16F). Thin films were deposited on silicon, sapphire and glass substrates under conditions listed in Table 1. These deposition conditions were fixed in order to obtain the well-orientation zinc oxide films.

The presputtering occurred for 30 min to clean the target surface. Deposition rates covered the range from 0.35 to 0.53 mm h^{-1}.

In order to investigate the crystallographic properties of the ZnO films, we carried out an X-ray diffraction (XRD) analysis using CuKα (λ=0.154054 nm) radiation.

Tableau 1: Parameters of sputtering deposition of ZnO

Samples	Substrate Temperature	Mixture gas Ar +O_2	Sputtering pressure	Power RF	Target-substrate distance	Sputtering time
ZnOT1	50°C	20-80%	3,35x10^{-3} Torr	50 W	7 cm	6h
ZnOT2	100°C					
ZnOT3	150°C					
ZnOT4	200°C					
ZnOT5	250C°					

3. RESULTS AND DISCUSSIONS

ZnO films deposited by r.f. magnetron sputtering have a smooth surface and a good adherence with the substrate.

We find that the intensity of the crystal orientation of the zinc oxide film varies depending on the substrate temperature. Indeed, if we look at the diagram of ZnO given in Fig.1 and we compare the diffracted intensities on the ASTM file, we note that the peaks do not have the expected intensity or do not appear. Therefore, we can give the preferential orientation of ZnO films by the intensity of the highest peak. The use of the peak relative to the (002) plane as reference peak is necessary because of its high reflectivity of these plans. This is in effect, the last to be present on the diagram when the preferred orientation increases. Thus, in Fig.2, we can say that the intensity of the diffraction peak increases with temperature up to 100 ° C where it reaches a maximum and then decreases for the intensity above 100 ° C temperatures.

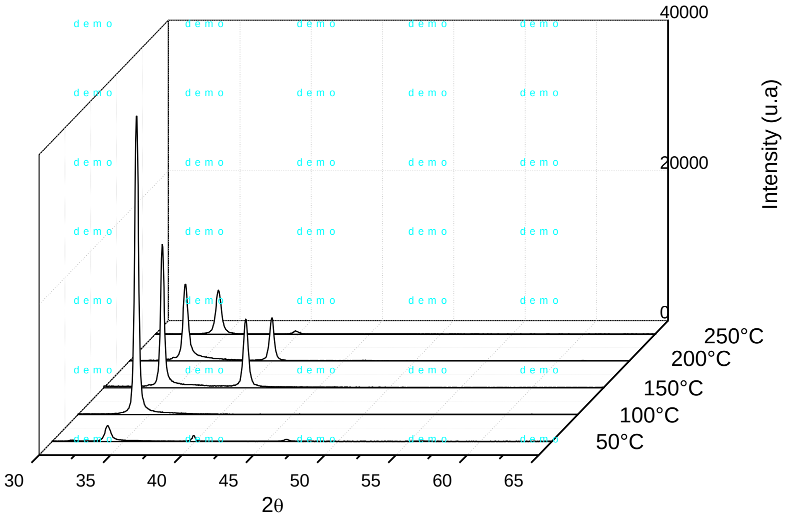

Fig. 1: XRD diagram from ZnO samples deposited on silicon substrate at different substrate temperature

This change can be interpreted by the fact that the increase of the substrate temperature improves crystallization grains of ZnO films. However, at high temperatures and low pressure, the effect of the temperature leads to the formation of defects in the layer and may also lead to degradation of the structural quality of the film [13, 14].

Thus, the temperature 100 ° C seems to be the optimum temperature for growth of ZnO films our experimental conditions referred to in Table 1.

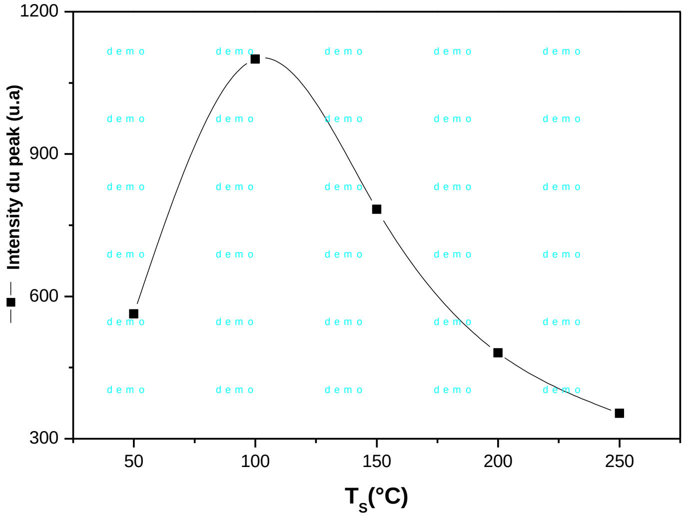

Fig. 2: Evolution du pic de diffraction en fonction de la température du substrat.

Fig.3 shows the change of the 2θ position depending on the temperature substrate. When the temperature varies, constant movement of the 2θ position of either side of the observed massive ZnO (34.42 °) value. This tells us that all the layers are in a state of compression parallel to the direction of the layer growth. Therefore, we can assume that this change in stress really comes from the difference in thermal expansion coefficients between the sprayed material and the substrate.

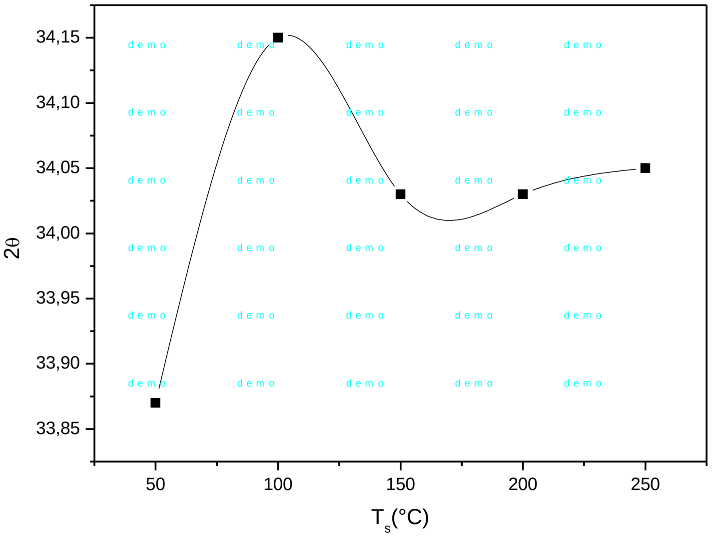

Fig.3: 2θ depending on the substrate temperature.

Assuming a homogeneous strain across the films, the crystallite size may be estimated from the full-width at half maximum (FWHM) of (002) diffraction peak using Schere's formula [14]:

$$D = \frac{0.9\lambda}{\delta \cos\theta} \qquad (1)$$

Where λ, θ and δ are the X-ray wavelength, Bragg diffraction angle and FWHM of the ZnO (002) diffraction peak, respectively [15].
Fig.4 represent the evolution of the diffraction peak on the (002) plane of ZnO thin films synthesized under these experimental conditions.

The Fig.5 shows changes in the grain size of the ZnO layers and the width at mid-height as a function of substrate temperature.
We are seeing a rapid increase in grain size between 50 ° C and 100 ° C, and then a gradual decrease in temperature when we ride. This development is inversely proportional to changes in the full-width at half maximum of the diffraction peak. Indeed, we notice that the evolution of the width at half-height as a function of the substrate temperature is at a minimum. And this minimum is observed at 100 °C. Therefore, we can say that the sample made at 100°C is characterized by a large grain size means that a better crystallization of the thin films.

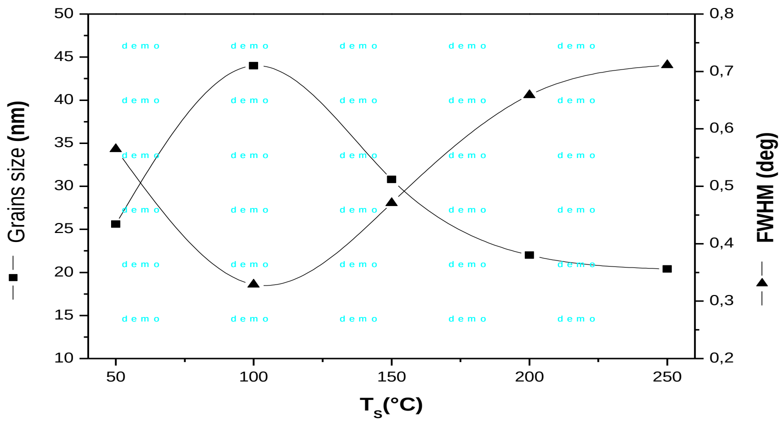

Fig.4 : Evolution de la taille des grains et de la largeur à mi-hauteur en fonction de la température du substrat.

Many imperfections are found in layers deposited by sputtering. The accumulation of these crystallographic defects in the film is the cause of micro-stress or intrinsic stress.
The inherent constraints of zinc oxide films were made calculated from relationship:

$$\Delta\sigma - = -\frac{E_c}{\nu_c}\left(\frac{2\theta_{ref} - 2\theta}{2\theta}\right) \qquad (2)$$

Where E_c and ν_c are the Young modulus and Poison ration of ZnO respectivrly.
Fig.5 shows the development of intrinsic stresses in the ZnO samples have almost identical thicknesses. All these samples exhibit compressive stresses from - to $9{,}365.10^{13}$ - $4{,}5.10^{13}$ $N.cm^{-2}$.
These stresses are due to the presence of nanograins of which the crystal lattice has interstitial defects [16, 17]. Moreover, the evolution of these constraints is the function of the substrate temperature. They are less than 100 ° C compared to the other samples. This shows that these intrinsic stresses are related to the dynamics of coalescence of the grains. A material with small grain offers many grain boundaries and supports the development of micro-constraints themselves caused by defects and disorientation between grains. We may think that these intrinsic stresses are due mainly to the phenomenon of relaxation after deposition.

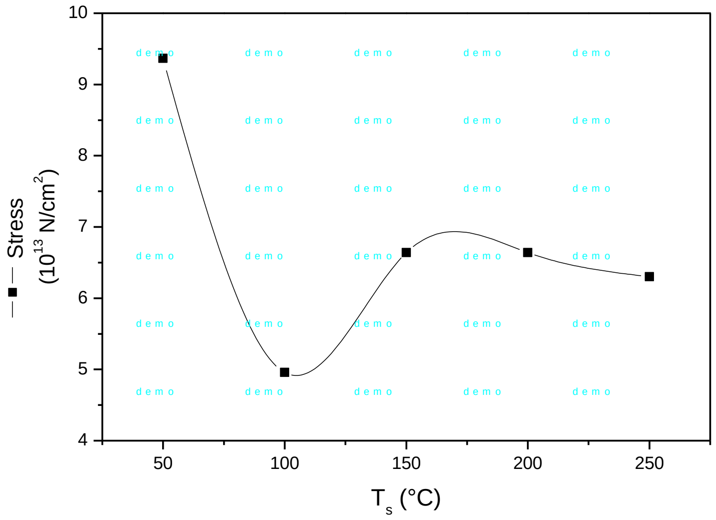

Fig.5: the variation of stress with respect to substrate temperature of ZnO films.

4. CONCLUSIONS

In this study, intrinsic zinc oxide (ZnO) films have been deposited on the silicon substrate by Rf magnetron sputtering technique. The best quality ZnO films in terms of crystalline structure have been grown at substrate temperature around 100°C. XRD shows that the films are well oriented where the c-axis grows normal to the substrate plane. A typical FWHM of about 0.32° for the (002) X-ray rocking curve was easily obtained for thin films deposited at substrate temperature of 100°C. All the samples deposited by RF magnetron sputtering have compressive stress. The FWHM correlated with a grains size and intensity peak of 34.27°. Consequently, well oriented zinc oxide thin films with crystalline structure could be successfully deposited by RF magnetron sputtering.

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