Characterization Of Microwave Obtained Zno Thin Films By RF Magnetron Sputtering

Roger Ondo-Ndong, Hugues Martial Omanda, Honore Gnanga, Brice Sorli, Alain Foucaran

Abstract: We have grown ZnO thin films on glass and Si (001) substrates by r.f magnetron sputtering using metallic zinc target. The crystalline property of the films were observed to vary with the structural properties used. X-ray diffraction (XRD) measurement showed that the substrate temperature ZnO films exhibited preferred c-axis oriented (002). A study has been made of the influence parameters prepared on the film refractive index. They exhibited the refractive index of 1.97, a c-axis orientation of below 0.32° FWHM of X-ray rocking curves and an energy gap of 3.3 eV at room temperature. It was found that a RF power of 50 W, target to substrate distance 70 mm, very low gas pressures of 3.35×10^{-3} Torr in argon and oxygen mixed gas atmosphere giving to ZnO thin films a good homogeneity and a high crystallinity. The network analyzer shows losses are -5dB at a $k_{33} = 0.26$ experimental.

Index Terms: Zinc oxide; thin films, X-ray diffraction, crystalline property, refractive index, Electromechanic coupling coefficient.

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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 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. 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 crystalline 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 [7-9] this energy enhances the surface migration effect and surface bonding state. In this work, we investigated the electromechanical coupling of the parameters deposited on the piezoelectric properties of zno films. It has been found that the piezoelectric properties of zno films depend very much the structural and optical properties. Indeed, a zno hexagonal wurtzite structure and properties are determined by the orientation of the crystallites on the substrate. Fwhm of the (002) x-ray rocking curve must be less than 0.32 for an effective electromechanical coupling [10].

2 EXPERIMENTAL

Zinc oxide films were deposited by r.f magnetron sputtering using a zinc target (99, 99%) with diameter of 51 mm and 6 mm thick. Substrate is p-type silicon with (100) orientation. The substrates were thoroughly cleaned with organic. Magnetron sputtering was carried out in oxygen and argon mixed gas atmosphere by supplying r.f power at a frequency of 13.56 MHz. The RF power was about 50 W. The flow rates of both the argon and oxygen were controlled by using flow meter (ASM, AF 2600). The sputtering pressure was maintained at $3.35.10^{-3}$ torr controlling by a Pirani gauge. Before deposition, the pressure of the sputtering system was under 4.10^{-6} torr for more than 12 h and were controlled by using an ion gauge controller (IGC – 16 F). The presputtering occurred for 30 min to clean the target surface. Deposition rates covered the range from 0.35 to 0.53 µm/h. All films were annealed in helium ambient at 650°C for 15mn. 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. Measurements of transmittance in the range from 300 nm to 900 nm are made using a UV-Visible CARY spectrometer. The rough surface materials with in homogeneities or imply low volume detected signal. Thus, we must make an adjustment, before any measurement: The 100% for power transmission Pyrex substrate as a reference. Piloting, digital capture and processing of data is performed by a microcomputer. To characterize the films, we use a HP 8752 A Network Analyzer whose bandwidth ranges from 300 KHz to 1.3 GHz. This type of device is one of instruments to define with precision the characteristics of an electrical circuit

3 RESULTS AND DISCUSSION

3.1 Crystallographycs

For papers accepted for publication, it is essential that the electronic version of the manuscript and artwork match the hardcopy exactly! The quality and accuracy of the content of the electronic material submitted is crucial since the content is not recreated, but rather converted into the final published version. ZnO films deposited by r.f. magnetron sputtering have a smooth surface and a good adherence with the substrate. The Fig.1shows that the intensity of the crystal orientation of the zinc oxide film varies depending on the parameters deposited. Indeed, if we look at the diagram of ZnO given in Fig.1a and we compare the diffracted intensities on the ASTM file, we note that the peaks do not have the expected intensity

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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.

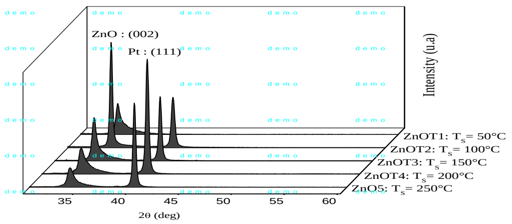

Fig. 1. a

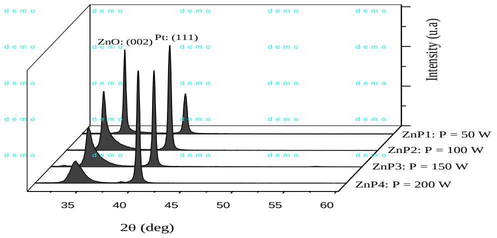

Fig. 1. b

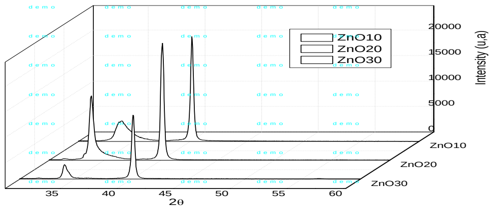

Fig. 1. c

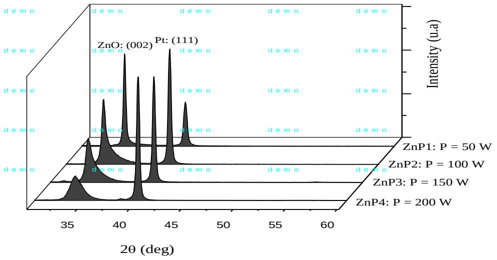

Fig. 1.d

Fig.1: *XRD diagram from ZnO samples deposited on silicon at different parameters: a) different substrate temperature ; b) different power RF ; different ratio Ar/O$_2$; d) different target-substrate distance*

The Fig.1.b shows the X-ray diffraction patterns at different power RF. These curves show a progressive decrease in the intensity of the diffraction peak as the injected power is increased, up to 200W. 50W, very little energy ions and the crystallization is much higher and resembles thermal deposition processes. The Fig.1c shows the spectra obtained for the three samples. We find that all samples exhibit a diffraction peak corresponding to the orientation (002) plane.

We can also derive the change in the intensity of the diffraction peaks. It is observed that the intensity of the various diffraction peaks increases with the level of oxygen in the gas mixture up to 20%. Then, the intensity decreases for the sample prepared at 30% oxygen. The Fig.1d shows a comparison of X-ray diffraction pattern for all the samples prepared at different target-substrate distances. It shows individual peaks of the existence of ZnO when the deposits are made to target-substrate distance of less than 7 cm. Beyond that, there is only the peak (002) of the ZnO is present but with a poor crystallization to 9 cm. We can say that the layers formed at a distance of less than 7 cm target-substrate are polycrystalline, although the preferential orientation of these layers are the (002) plane.

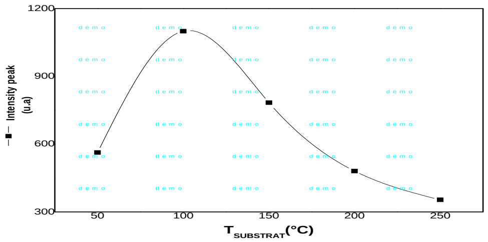

Fig. 2.a

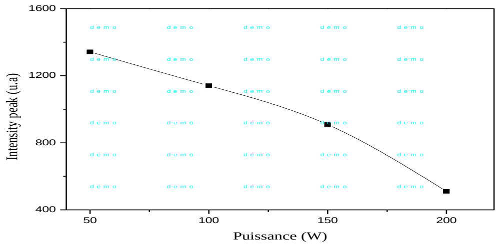

Fig. 2.b

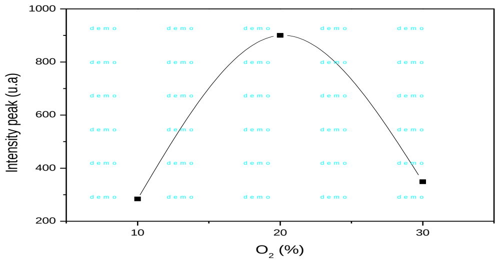

Fig. 2.c

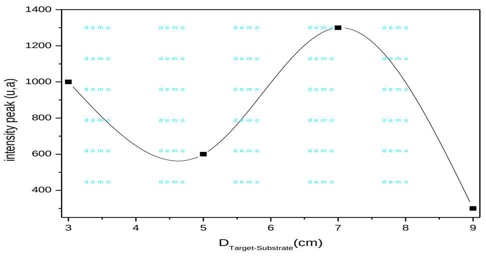

Fig. 2.d

Fig.2: *Intensity peak (002) at different parameters: a) different substrate temperature; b) different power RF; c) different ratio Ar/O$_2$; different target-substrate distance*

The Fig.2shows that the intensity peak (002) of the zinc oxide film varies depending on the parameters deposited. Thus, in Fig.2a, 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. 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 [11, 12]. The evolution of the intensity of the diffraction peak is shown in Fig.2b. This result can be explained by the facts that at low power, varying the temperature of the substrate after deposition is low since there is little energy zinc atoms impinge the substrate. Thus, the mobility of the atoms deposited on the substrate is low. This results in a better crystal orientation. However, at high power, the change in temperature of the substrate after deposition is consistent. As a result, the mobility of atoms of zinc deposited on the substrate is increased and consequently, a crystal disorientation. [13] We can tell from these observations that zinc oxide produced 50W has better crystal orientation relative to the samples prepared at 100, 150, 200W under the experimental conditions. Looking at the evolution of the peak intensity as a function of oxygen in Fig.2c rate, we can conclude that the best crystal orientation is obtained for an oxygen level of 20% in the gas mixture Ar/O_2. From these results, we can say that our zinc oxide samples crystallize better at low oxygen levels, and especially for an oxygen level of 20%. This dependence of the crystal orientation of the ZnO thin films with the oxygen in the gas mixture O2-Ar rate was studied in previous work. It has been shown that the crystal orientation in the (002) c-axis perpendicular to the substrate surface is obtained of 15-40% oxygen level [14-16] by spraying a metal target pure zinc. This confirms our results. To reflect this change in the intensity of the diffraction peak and the width at half maximum of the latter, we have plotted different distances target substrate. The curves are shown in Fig.2d. These results confirm that the sample prepared at the target-substrate distance equal to 7 cm has the best diffraction peak and width to the finest mid-height.

3.2 Refractive index

The Fig.3shows that the refractive index of the zinc oxide film varies depending on the parameters deposited. The Fig.3a shows that a given wavelength, the refractive index increases from 1.87 to 1.97 when the substrate temperature ranges from 50°C to 100°C. Above 100°C, the value of the refractive index decreases as the substrate temperature increases to 1.63. Comparing these results with those obtained by X-ray diffraction where we observed a better preferential orientation of the (002) plane for the sample prepared at 100 ° C. This shows that the variation of refractive index with temperature of the substrate can be accompanied by a change in the grain size in the growth direction. Bachari obtained the corresponding refractive indices ranging from 1.8 to 2.1 [17]. They also observed a decrease in the refractive index of ZnO films at high temperatures. The Fig.3b shows the variation of the refractive index as a function of different powers for a given wavelength. We see that the index decreases with power. It varies from 1.97 to 1.6 in from 50 to 200 W at 600 nm. The same behavior of the index in terms of power was observed by JF Chang et al. [11]. To highlight these observations, we have shown in Fig.3c changes in the refractive index as a function of oxygen concentration in the gas mixture at a given wavelength ($\lambda = 600$ nm). We find that the influence of the gas mixture on the refractive index is significant only when we have an oxygen level of 20%. In addition, we note a decrease in the index with increasing oxygen content in the gas mixture. We attribute this phenomenon, compared with the X-ray crystallographic misorientation of the structure. Indeed, the structural study showed that the optimum oxygen level, to develop well-crystallized films of ZnO was 20%. The Fig.3d shows that the target distance of 7 cm substrate is ideal for obtaining zinc oxide layers of good quality. Indeed, at this distance, the thermalization of the structure is efficient. The discharge (plasma) is maintained with a minimum of particle collision and the efficiency of sputtering is effective.

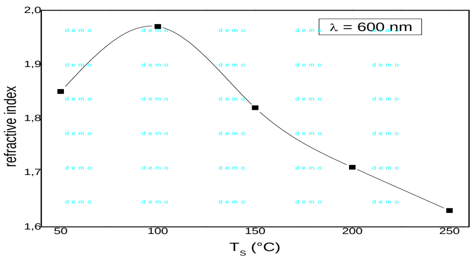

Fig. 3.a

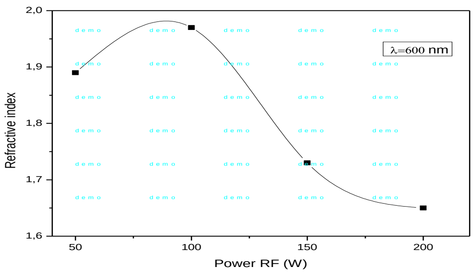

Fig. 3.b

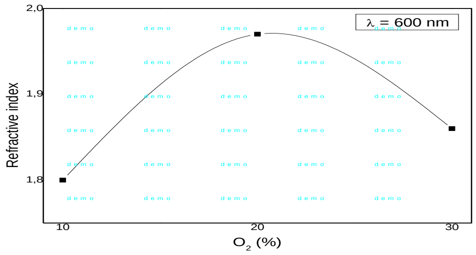

Fig. 3.c

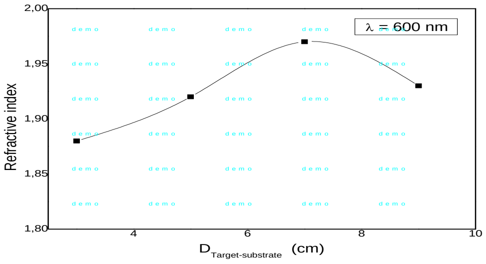

Fig. 3.d

Fig.3: Refractive index at different parameters: a) different substrate temperature; b) different power RF; c) different ratio Ar/O$_2$; d) different target-substrate distance.

3.3 Electromechanical coupling coefficient

In a piezoelectric solid, the propagation of an elastic wave with wave vector is governed by an eigen value equation called Christoffel equation [18]:

$$\Gamma_{ik} u_k = \rho V^2 u_i \quad (1)$$

Dans un solide piézoélectrique, la propagation d'une onde élastique de vecteur d'onde n est régie par une équation aux valeurs propres appelée équation de Christoffel : Which u_i are the components of the displacement, ρ is the density of the solid and Γ_{ik} the tensor Christoffel

$$\Gamma_{ik} = \left(C^E_{ijkl} + \frac{e_{uij} e_{vkl} n_u n_v}{\varepsilon^S_{rs} n_r n_s} \right) n_j n_l \quad (2)$$

The resolution of the Christoffel equation leads to three real and positive eigen values corresponding to propagation speeds of three waves. They are obtained by solving:

$$\left| \Gamma_{ik} - \rho V^2 \delta_{ik} \right| = 0 \quad (3)$$

The wave propagates along the z direction. The Christoffel tensor in the case of a piezoelectric material:

$$\Gamma = \begin{vmatrix} C_{44} & 0 & 0 \\ 0 & C_{44} & 0 \\ 0 & 0 & C_{33} + \dfrac{e_{33}^2}{\varepsilon_{33}} \end{vmatrix} \quad (4)$$

We therefore obtain an active piezoelectric longitudinal wave speed

$$V_3 = \sqrt{\frac{C_{33} + \dfrac{e_{33}^2}{\varepsilon_{33}}}{\rho}} \quad (5)$$

This wave propagates along the c- axis ZnO thin films. Speed of longitudinal waves of the order of 6330 m/s. The electromechanical coupling coefficient is defined as:

$$k_{33} = \frac{e_{33}}{\sqrt{\varepsilon_{33} C_{33} + e_{33}^2}} .$$

This allows us to calculate and find $k_{33} = 0.3$ We conducted a microwave characterization of ZnO layers developed for the measurement of electromechanical coupling coefficient and operation of the piezoelectric activity. Indeed, the network analyzer generates wave trains, such instantaneous electromotive force generator $e = E_0 \cos(\omega t)$ and frequency f. we worked in reflection. This technique is used to evaluate the efficiency with which the transducer converts electrical activity in mechanical activity and vice versa.

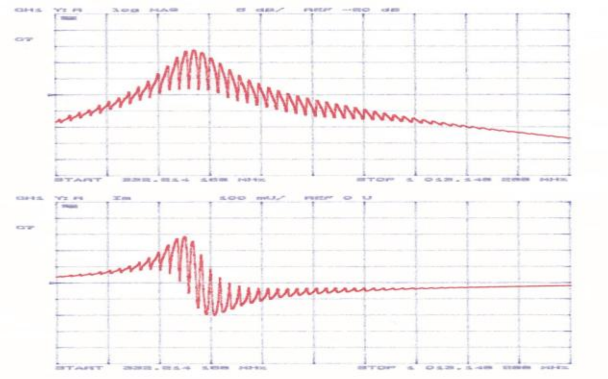

Fig. 4: *Electrical admittance of ZnO resonator with losses.*

The Fig.4 shows the variation of real and imaginary parts of the electric admittance of the frequency depending on the sample obtained. We observe a change in the electrical input admittance of the resonator and the appearance of the produced oscillations superimposed on the general envelope. These oscillations are due to the propagation medium. They reflect changes in real and imaginary parts of the electrical admittance measured. This means that the system reacts to the electrical load with a lag effect. Indeed, the shape of the curves shows that there is interference of waves propagating in the propagation medium which is the silicon substrate.

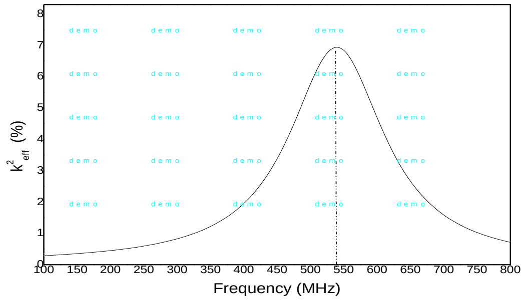

Fig. 5: k^2_{eff} *distribution coefficient as a function of the frequency.*

To determine the coupling coefficient of structure, placed the fundamental resonance of the resonator, ie at frequencies where the real part of the admittance is maximum and the minimum susceptance. Observed that the Fig.5 value of the coupling coefficient reaches a maximum when the number of the propagation mode in the substrate thickness increases. The manner in which this maximum is observed is the fundamental mode of propagation of ZnO. By 0.4% loss in the substrate and 0.4% loss in the piezoelectric layer, since the speed of the materials used are complex. We obtain a coupling coefficient k$_{eff}$ = 0.26. This value is of the order of 92% of the theoretical value. Fig.6 shows the evolution of the coupling coefficient of ZnO thin films for the various deposition parameters. These curves follow the same variation of the intensities of the peaks (002) as a function also of the various deposition parameters. We get the order 0.26, which corresponds to 92% of the theoretical value. This result is substantially equal to that obtained by the network analyzer.

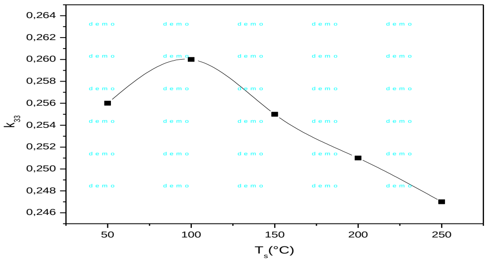

Fig. 6.a

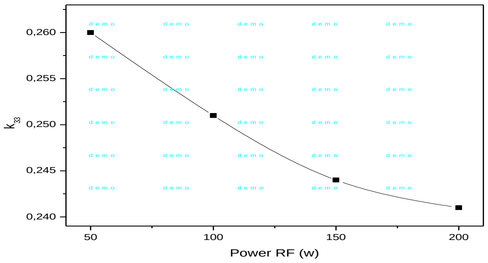

Fig. 6.b

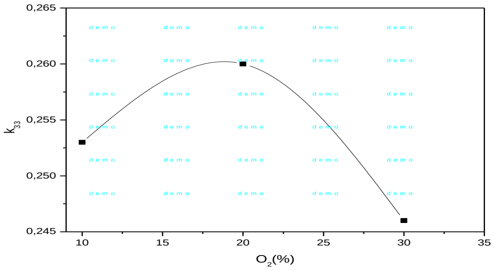

Fig. 6.c

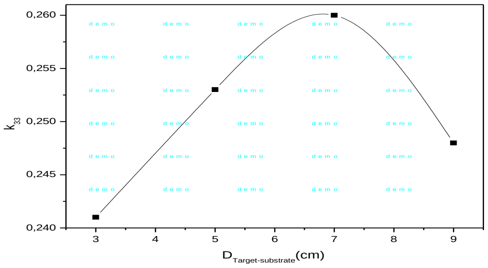

Fig. 6.d

Fig.6: *Electromechanical coupling coefficient at different parameters: a) different substrate temperature; b) different power RF; different ration Ar/O_2; different target-substrate distance.*

4 CONCLUSION

In this study, intrinsic zinc oxide (ZnO) films have been deposited on the glass and 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. . We performed several sets of samples we characterized optically. This systematic study led us to an area of very specific definition of manufacturing parameters for obtaining ZnO films of good quality. The evolution of the electromechanical coupling coefficient of ZnO thin films for the various deposition parameters. These curves follow the same variation of the intensities of the peaks (002) as a function also of the various deposition parameters. We get the order 0.26, which corresponds to 92% of the theoretical value.

REFERENCES

[1] L.-J. Meng, M.P. Dos Santos, *Thin Solid Films* 250, pp.26-32, 1994.

[2] T. Inukai, M. Matsuoka, K. Ono, *Thin Solid Films* 257, pp.22-27, 1995.

[3] M.-Y. Han, J.-H. Jou, *Thin Solid Films* 260, pp. 58-64, 1995. V. Craciun, J. Elders, J.G.E. Gardeniers, J. Geretovsky, I.W. Boyd, *Thin Solid Films* 259, pp. 1-4, 1995.

[4] T.K. Subramanyam, B. Srinivasulu Naidu, S. Uthanna, *Crystal Res. Technol.* 8 (34), pp. 981-988, 1999.

[5] A. Sanchez-Juarez, A. Tiburcio-Silver, A. Ortiz, E.P. Zironi, J. Rickards, *Thin Solid Films* 333, pp. 196-202, 1998. J. Molarius, J. Kaitila, T. Pensala, M. Ylilammi, *Journal of Materials Science: Materials in Electronics* 14, pp. 431-435, 2003.

[6] Y.C. Lin, C.R. Hong, H.A. Chuang, *Applied Surface Science*, volume 254 issue 13, pp. 3780-3786, 2008.

[7] Y.J. Kim, Y.T. Kim, H.J. Yan, J.C. Park, J.I. Han, Y.E. Lee, H.J. Kim, *J. Vac. Sci. Technol.* A 15, pp. 1103-1107, 1997.

[8] R. Ondo-Ndong, G. Ferblantier, M. Al Kalfioui, A. Boyer, A. Foucaran, *Journal of Crystal Growth* 255, pp 130-135, 2003.

[9] R. Ondo-Ndong, F. Pascal-Delannoy, A. Boyer, A. Giani, A. Foucaran, *Mat. Sci. Eng*., B 97, pp. 68-73, 2003. W-J. Jeong, G-C. Park, *Solar Energy Mat. And Solar Cells*, 65, pp. 37-45, 2001

[10] P. Martin, R. Nettefield, T. Kinder, A. Bendavid, *Applied Optics*, 31 pp. 6734-6740, 1992.

[11] S. J. Chang, Y. K. Su, Y. P. Shei, *J. Vac. Sci. Technol.*, A13 (2), pp. 381-384, 1995.

[12] K. B. Sundaram, A. Khan, *Thin Solid Films*, 295, pp. 87-91, 1997. K. H. Yoon, J-W. Choi, D-H. Lee, *Thin Solid Films*, 302, pp. 116-121, 1997.

[13] J. F. Chang, H. L. Wang, M. H. Hon, *J. Cryst. Growth*, 211, pp. 93-97, 2000.

[14] D. Royer, E. Dieulesaint, *Ondes élastiques dans les solides*, Tome 2, ed. Masson 1996.