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ScienceDirect
Thin Solid Films 516 (2008) 6210–6214
thin solid films
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Pre-heating temperature dependence of the *c*-axis orientation of ZnO thin films☆

A.M.P. Santos, Edval J.P. Santos *

Laboratory for Devices and Nanostructures, Department of Electronics and Systems, Universidade Federal de Pernambuco, C.P. 7800, 50670-000, Recife-PE, Brazil

Received 29 June 2006; received in revised form 26 October 2007; accepted 23 November 2007
Available online 3 December 2007

Abstract

Highly *c*-axis oriented zinc oxide, ZnO, thin film has been obtained at a very low pre-heating temperature, 120 °C. After depositing all layers, the film is annealed at 350 °C, for 5 h. The deposition process is designed to be compatible with silicon/silicon-dioxide substrates, to make piezoelectric coatings for integrated smart sensors. The films are synthesized by the sol–gel method and deposited onto a glass substrate. The deposition solution is prepared by dissolving zinc-acetate 2-hydrate in methanol. To optimize the film quality with respect to c-axis orientation, and surface uniformity, the selected parameters are: pre-heating temperature, spin-coating speed and number of coating layers. The effect of the deposition conditions is studied by applying experimental design and response surface techniques on the characteristic (002) peak, obtained by X-ray diffraction analysis. Surface uniformity and grain size are observed by scanning electron microscopy.

Keywords: Zinc oxide; Sol–gel method; Thin films; Oriented films; Experimental design

1. Introduction

Zinc oxide thin films have found widespread technological applications, as it exhibits a variety of properties such as: semiconducting (II–VI), photoconducting, piezoelectric, birefrigence, acousto-optical, transparency in the infrared region, and opto-electric properties [1,2]. This makes this material very interesting for theoretical and experimental studies. In particular, its wide bandgap (3.37 eV) can be useful for the manufacturing of optoelectronic devices in the deep blue or ultraviolet spectral region, and (optical) integrated circuits. Some of the applications include: photovoltaic devices, energy efficient windows, liquid crystal displays, laser diodes, sensors, spintronic devices, and immobilization of biomolecules. More recently, it has also been used as a material to produce nanostructures, such as: nanoparticles, and nanorods. Quality of the film is typically determined with regard to transparency, conductivity, crystalline orientation, and surface uniformity. ZnO films can be produced in various phases, such as: wurtzite (hcp), zincblende (fcc), rocksalt (fcc), cesium chloride (sc). Under ambient conditions ZnO crystallizes in the wurtzite structure, a tetrahedrally coordinated structure with hexagonal lattice. In this orientation the film displays piezoelectric properties, which is useful for surface acoustic wave devices and sensors [3–15].

Due to its low cost, and capability to coat large surface areas, sol–gel is the technique selected for our study. In this technique, the substrate is coated a number of layers with a ZnO-based gel; after each coating, the substrate is pre-heated; after finishing the deposition process, the substrate is annealed. Sol–gel synthesis also allows to control the grain size. Several studies have shown that the optical and electrical properties could be considerably improved by optimized deposition conditions [13,16–18].

Ohyama et al. [19] studied the crystallization of dip-coated sol–gel deposited films to produce piezoelectric ZnO films for surface acoustic wave, SAW, applications. They varied the pre-heating temperature from 200 °C up to 500 °C, and annealing temperature from 500 °C up to 800 °C. They have observed that the pre-heating temperature of dip-coating produced films have

☆ This work has been supported by FINEP/CTPETRO, PETROBRAS/CTPETRO, CNPq/Millenium Institute, and CNPq/FACEPE.
* Corresponding author.
E-mail address: edval@ee.ufpe.br (E.J.P. Santos).

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doi:10.1016/j.tsf.2007.11.111

a strong effect on the crystal orientation. Their best films are achieved with a pre-heating temperature of 300 °C, which is quite high, for the pre-heating step.

The observation that the pre-heating temperature is an important parameter affecting the orientation of the film was not further investigated by other researchers. Most researchers explored the effect of the annealing on the crystallization.

Bao et al. [20] also used sol–gel deposited films and studied the orientation by varying the annealing temperature from 400 °C up to 600 °C, but they have not achieved good results. In the work of Castanedo-Pérez et al [21], $Zn(CH_3COO)$ is used as precursor, they have studied the effect of the annealing temperature from 100 °C to 450 °C (pre-heating at 100 °C) on the formation of ZnO. The film obtained is not highly oriented, as they were concerned with the optical transmission properties of the film. Jiwei et al. [22] deposited ZnO films on SiO_2/Si also with sol–gel with pre-heating at 200 °C, annealing from 400 °C up to 650 °C, the resulting films displayed good orientation, as measured from X-rays difraction, XRD. Natsume et al [23] produced the film by spin-coating, pre-heating at 80 °C, annealing from 500 °C up to 575 °C, the resulting films displayed very good orientation, but required very high annealing temperatures. Alam et al [24] used dipping solution, pre-heating 260 °C and annealing from 300 °C up to 700 °C, but did not achieve a good orientation of the films. Znaidi [25] studied the dependence of the crystallization on the relative concentration of zinc actetate dihydrate to monoethanolamine. They have used two procedures, one set of films were pre-heated at 300 °C, and annealed at 550 °C, another group of films were pre-heated at 100 °C, and annealed at 135 °C, and 450 °C, to get (002) oriented films. In this second procedure, they did not get uniform films. Lee et al [26] pre-heated at 350 °C and annealed at 600 °C, followed for another annealing at 500 °C, in nitrogen with 5% hydrogen. Aslan et al. [27] achieved good quality films by varying the annealing temperature from 450 °C up to 550 °C. Li et al [28] varied the pre-heating temperature from 100 °C up to 500 °C, but their results were reasonable above 200 °C, annealed at 600 °C. In a later work, Li et al [29] has set the pre-heating temperature at 300 °C, and used three different temperatures for annealing (400 °C, 500 °C, and 600 °C). They observed that by increasing the annealing temperature, the films orientation is improved, as expected. Zhang et al [30] has achieved very high quality films by starting the deposition process with a seed layer deposited by pulsed laser deposition. In their work the pre-heating temperature varied from 300 °C up to 600 °C, and annealed at 600 °C. Just recently, came to our attention the work of Wang et al. [16], which also uses the sol–gel method, with pre-heating temperature from 300 °C up to 450 °C, and annealing temperature from 550 °C up to 800 °C. Almost the same range as in the work of Ohyama et al. [19], but did not get good results.

Our objective is to apply experimental design and response surface techniques to produce piezoelectric films with the lowest thermal bugget possible (combining pre-heating and annealing). The optimized film should be compatible with silicon/silicon-dioxide substrates. Such films can be useful to make piezoelectric coatings for integrated smart sensors. The parameters selected for this study are: pre-heating temperature, spin speed and number of coating layers. This investigation has been carried out with the aim of optimizing the film with respect to the (002)-orientation. The paper is divided into four sections, this introduction being the first, next the experimental procedure is described. In the third section, the results and analysis, and finally the conclusions.

2. Experimental procedure

2.1. Materials preparation

Our films were prepared by dissolving zinc acetate dyhidrate, 8% (Merck), in methanol (Carlo Erba) under stirring at 60 °C, until a transparent and homogeneous solution is obtained. The microscope glass substrates are cleaned with neutral cleaning agent in ultrasonic bath for 20 min, washed in deionized water, acetone (5 min), deionized water on ultrasonic bath (5 min), isopropanol (5 min) and dry nitrogen and preserved in desiccator. The solution is then spun-on onto the substrate, and the substrate is pre-heated at a selected temperature for 10 min. After coating the required number of layers, the ZnO thin film is annealed. Considering the literature, to get oriented films, the annealing temperature is above 400 °C. Experiments with annealing temperature below 400 °C did not get oriented films [24]. For this work, we selected 350 °C for the annealing temperature. The film is annealed for 5 h. The flowchart of the preparation of the ZnO thin film is presented in Fig. 1. This procedure was also performed on silicon wafers with a silicon dioxide layer, and on alumina.

2.2. Optimization of ZnO thin film

In order to optimize the preparation of c-axis oriented ZnO thin films, experimental design and response surface method are used. Ko et al [31] used neural network and analysis of variance, ANOVA, to optimize pulsed laser deposited ZnO-films.

Response surface methodology (RSM) is a collection of mathematical and statistical techniques widely used to determine the effects of variables in order to achieve the optimal process conditions [32]. Factorial design of limited set of variables is advantageous compared to the conventional method. This methodology allows the verification of the effects of the variables individually and their interactions. Empirical models and statistical analysis are extremely important to elucidate basic mechanisms in complex situations, thus proving better process control and understanding. The main objective of RSM is to determine the optimum operational conditions for the system or to determine a region that satisfies the operating specifications [32]. For this study, two experimental designs have been carried out. The independent variables are: pre-heating temperature, spin-coating speed, and number of coating layers. The relative peak intensity ($I_{(002)}/(I_{(002)}+I_{(001)}+I_{(001)})$ [24]) is the dependent variable.

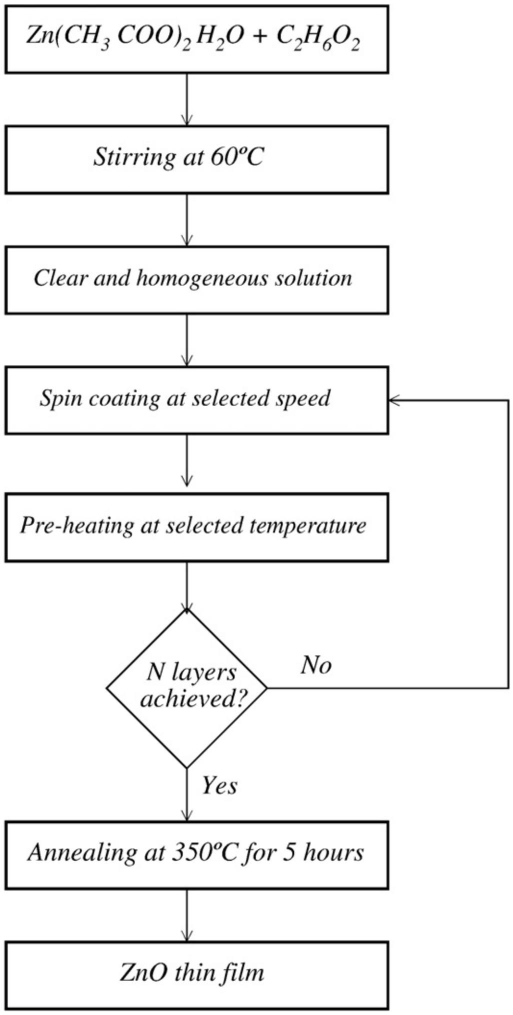

Fig. 1. Flowchart presenting the procedure for preparation ZnO thin films by sol–gel and spin-on coating.

2.2.1. First experimental design

The first experimental design is a 2^3 factorial central composite design, linear model, with three central points. This leads to eleven experiments, which includes 8 factorial points and 3 central points. In Table 1, the range and levels for the three variables are presented.

2.2.2. Second experimental design

After analysis of the variable effects in the first experimental design, another experimental design was prepared to further optimize the process. The second experiment was a 2^3 full factorial central composite design quadratic model, with three central points. This leads to 17 experiments, including 6 star points factorial (Table 2). Statistical significance of the regression coefficients was determined by the *F*-test ANOVA, which revealed that the regression is statistically significant ($p<0.05$) at 95% of confidence level. The parameter α is the distance of the axial points from the central point. This parameter is calculated from the number of variables. In this experiment $n=3$, which yields $\alpha=(2^n)^{1/4}=1.68$.

Table 1
Real values and coded levels used in the first experimental design

Variables	Level -1	Level 0	Level 1
Pre-heating temperature (°C)	150	200	250
Spin-coating speed (rpm)	2800	4000	5200
Coating layers (*N*)	12	15	18

Table 2
Real values and coded levels used in the second experimental design

Variables	Level −1.68	Level −1	Level 0	Level 1	Level 1.68
Pre-heating temperature (°C)	100	120	150	180	200
Spin-coating speed (rpm)	2000	2810	4000	5190	6000
Coating layers (*N*)	10	12	15	18	20

$\alpha=(2^n)^{1/4}=1.68$ [32]; where *n* is the number of variables

2.3. Characterization the crystal structure and surface

The crystal orientation has been determined by XRD with CuKα ($\lambda=0.15418$ nm) radiation source. The measurements have been carried out in the range 20°–50°. The film surface uniformity and grain size were observed with electron microscopy, JEOL-6460.

3. Results and discussion

The results of Ohyama et al. [19] suggest that the pre-heating temperature of dip-coating produced films have a strong effect on the crystal orientation. Recently, we have found out that, these results were also studied on spin-on coating produced films by Wang et al. [16]. They have used the same temperature range

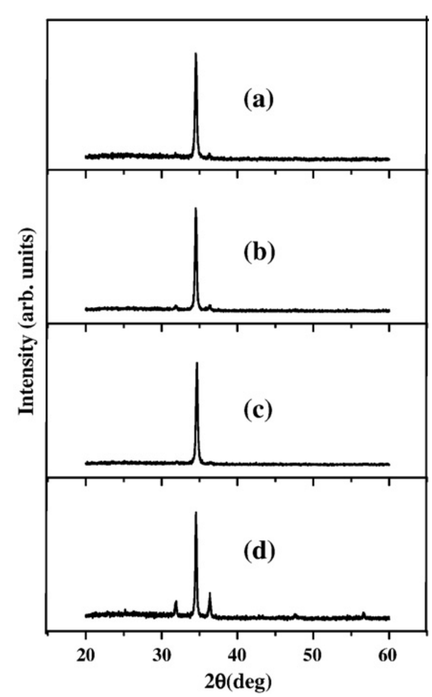

Fig. 2. The XRD patterns of ZnO thin films annealed at 350 °C at (a) $T_{pre}=120$ °C, 5190 rpm, 12 layers, (b) $T_{pre}=120$ °C, 2810 rpm, 18 layers, (c) $T_{pre}=120$ °C, 5190 rpm, 18 layers, (d) $T_{pre}=100$ °C, 4000 rpm, 15 layers.

Table 3
Relative (002)-peak intensity, and FWHM for the best results

Run assay	Relative peak intensity (002)	FWHM (deg)	Grain size (nm (Std. Dev.))
ZnO_03	0.862	0.25	46.31 (7)
ZnO_05	0.887	0.26	58.03 (8)
ZnO_07	0.938	0.28	63.07 (10)
ZnO_09	0.737	0.28	39.63 (6)

as in the Ohyama et al. [19] paper. Considering that the rate of solvent desorption and drying could have an importante effect on the crystallization, we have decided to investigate this effect. We were also interested in using lower temperatures for annealing and pre-heating. Besides, we are interested in depositing very high quality ZnO films onto silicon chips to make surface acoustic wave and multilayer bulk acoustic wave devices and integrated sensors, this demands the lowest temperature treatment possible. To reduce the number of experiments, we have made use of statistical optimization techniques.

The experiment has been carried out with two designs, as mentioned before. The first design was exploratory, and the second was made to find the optimimum conditions. The resulting films were primarily observed by X-rays. The best films were further observed with scanning electron microscopy, SEM.

Considering the effect of the three selected variables (pre-heating temperature, spin-coating speed, and number of coating layers) on the crystallinization of the film. After the first experimental design, it was already clear that the pre-heating temperature was the only statistically significant, ($p \leq 0.05$), variable effect. The (002) peak intensity is higher as the values of pre-heating temperature decrease from level +1 to level −1. In this experiment, the best condition is achieved with pre-heating temperature at 150 °C, spin coating speed of 5200 rpm and 18 coating layers.

With these results, the second experimental design was prepared. In this second experimental design, we have confirmed that the pre-heating temperature is the only variable that displays statistically significant ($p \leq 0.05$) effects on ZnO thin film *c*-axis orientation. Considering the relative peak intensity, the best results for the *c*-axis orientation are obtained for ZnO_03 (pre-heating = 120 °C, spin speed = 5190 rpm and coating layers = 12), ZnO_05 (pre-heating = 120 °C, spin speed = 5190 rpm and coating layers = 18), and ZnO_07 (pre-heating = 120 °C, spin speed = 5190 rpm and coating layers = 18). The largest relative intensity has occurred at conditions ZnO_07.

In Fig. 2a–d, the XRD spectra of the best ZnO thin films are presented. In all deposited films, it is observed a strong *c*-axis

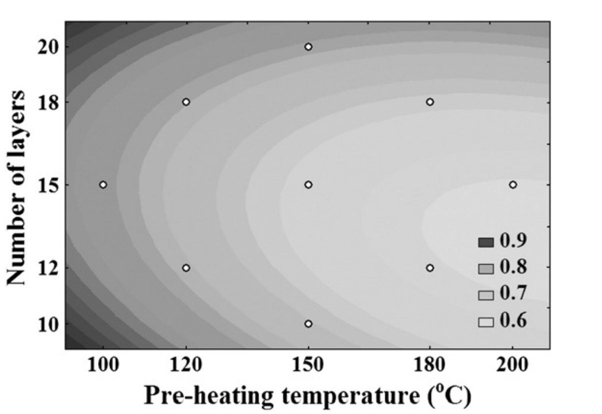

Fig. 3. Response surface of the relative peak intensity (0.6–0.9) as a function of coating layers and pre-heating temperature. The circles represent the experimental-design parameter levels.

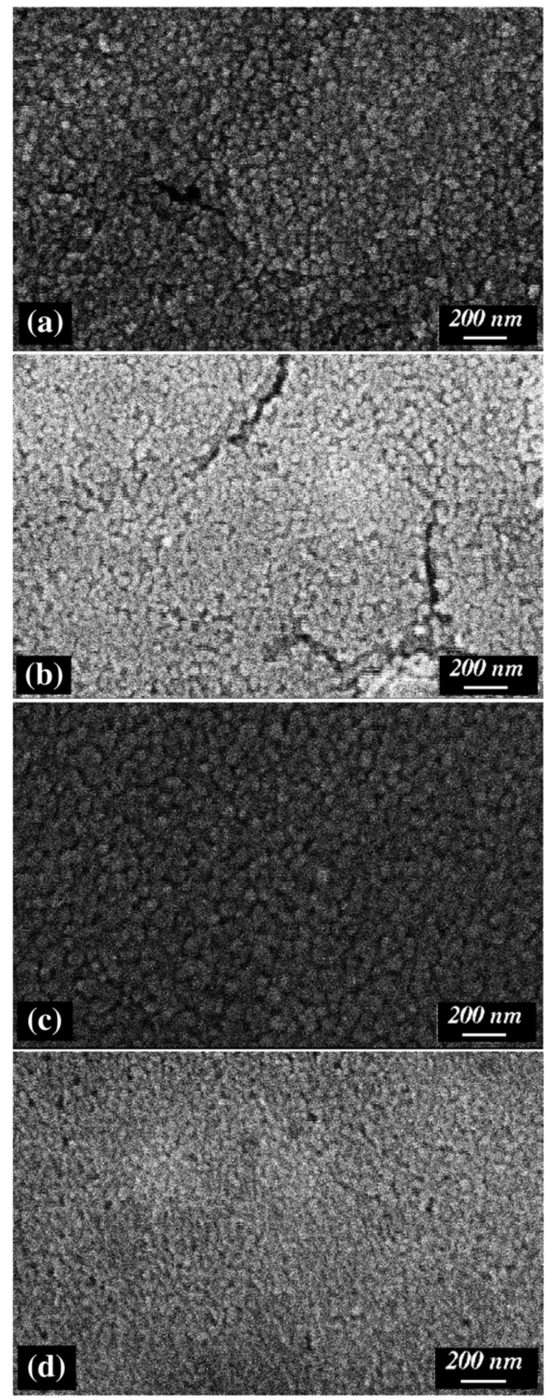

Fig. 4. Film surface observed with the SEM for conditions (a) ZnO_03: 120(−1), 5190(+1), 12(−1), (b) ZnO_05: 120(−1), 2810(−1), 18(+1), (c) ZnO_07: 120 (−1), 5190(+1), 18(+1), and (d) ZnO_09: 100, (−1.68), 4000(0), 15(0)). The bar measures 200 *nm*.

preferred orientation, and that this orientation has a strong dependence on the pre-heating temperature. As can be seen in the figure, the peak at 34.70° is much higher than the other two peaks. The full-width half maximum (FWHM) for each condition are listed in Table 3.

The response surface plot of the relative peak intensity as a function of number of coating layers and pre-heating temperature is presented in Fig. 3.

Our results show that there is a strong dependence of the pre-heating temperature on the crystallization. The optimal condition parameters are: pre-heating temperature 120 °C, spin speed 5190 rpm and coating layers 18. With such conditions the highest relative (002)-peak intensity is achieved. The films with the optimal conditions also displayed the best uniformity as shown in the Fig. 4. Some of the films are under high stress, as the film is cracked.

From the SEM pictures, one gets the average grain size (see Table 3). The FWHM is approximately 0.26° for all selected samples. Considering that for the X-rays used, $\lambda = 0.15418$ nm, and using Scherrer's relation.

$$d = 0.94\frac{\lambda}{(\mathrm{FWHM_{rad}}\cos\theta)} \quad (1)$$

the expected grain size is 40 nm, which is about the observed value. To get an estimate of the grain size from the SEM images, the magnification was set to 55,000.

4. Conclusions

The methodology of experimental design and response surface analysis is used to find the optimum process parameters for the preparation of the *c*-axis oriented ZnO thin films with sol–gel. In particular, it has been shown that the pre-heating temperature plays an important role in the preparation ZnO thin films with high *c*-axis orientation. Considering the range used the optimal condition parameters are: pre-heating temperature 120 °C, spin speed 5190 rpm and coating layers 18. With such conditions the highest (002) peak intensity is achieved. With this paper we have grown highly *c*-axis oriented zinc oxide thin films on glass substrate from zinc acetate by inexpensive sol–gel process using low temperature of pre-heating (120 °C), and of annealing (350 °C). The films were also deposited onto silicon dioxide and alumina. Our results suggest that there is a trade-off between the pre-heating temperature and the annealing temperature. Lower pre-heating temperature may require higher annealing temperatures and longer annealing times. This will be further analysed. Although, the annealing temperature used in our experiment is the lowest found in the literature, which still yields oriented films.

Although, we have used a higher pre-heating temperature (120 °C) then in Natsume et al. (80 °C) [23], we achieved very good orientation with a much lower anealing temperature.

This result is very important when one is considering the integration of ZnO thin films onto integrated circuits for the construction of integrated smart sensors, which requires the lowest thermal treatment possible.

Acknowledgments

The authors thank Prof. J. A. O. de Aguiar for the X-rays measurements. We also acknowledge the financial support of FINEP/CTPETRO, PETROBRAS/CTPETRO, CNPq/Millenium Institute, and CNPq/FACEPE. One of the authors (A.M.P. S.) also acknowledges the support of CNPq/FACEPE.

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