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High quality *c*-axis oriented thin ZnO film obtained at very low pre-heating temperature ☆

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Abstract

Highly oriented ZnO thin film has been obtained at a very low pre-heating temperature, with the spin-coating sol–gel technique. The dependence of the *c*-axis orientation on the pre-heating temperature has been studied with experimental design and response surface techniques to optimize the deposition process with respect to *c*-axis orientation, and surface uniformity. The optimization variables selected for this study are: pre-heating temperature, spin-coating speed and number of coating layers. The films are probed with X-ray diffraction and electron microscopy.

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

1. Introduction

Zinc oxide thin films exhibit a variety of properties such as: semiconducting (II–VI), photoconducting, piezoelectricity, birefrigence, acousto-optical, transparency in the infrared region, and opto-electrical properties. This makes this material very interesting for theoretical and experimental studies [1,2]. ZnO films can be produced in various phases, such as: wurtzite (hcp), zincblende (fcc), rocksalt (fcc), cesium chloride (sc) [3]. Under ambient conditions ZnO crystallizes in the wurtzite structure, a tetrahedrally coordinated structure with hexagonal lattice. ZnO films can crystallize in different orientations as a function of the deposition technology, annealing temperature, substrate, etc. The most common orientation is (002) (hexagonal wurtzite), which presents the densest atomic packing and minimum surface energy [4–9]. Quality of the film is typically determined with regard to transparency, conductivity, crystalline orientation, and surface uniformity. Crystalline orientation is key to achieve ZnO thin film with piezoelectric properties.

Due to its low cost, and capability to coat large surface areas [16], sol–gel is the technique selected for this study. One possible difficulty with sol–gel is the purity of the film, which can affect the electrical and optical properties of the film, due to the high density of carrier traps and potential barriers at grain boundaries [7]. However, several studies have shown that the optical and electrical properties could be considerably improved by optimized deposition conditions [10–14].

Many researchers have prepared zinc oxide thin films with the sol–gel technique. Ohyama et al. [15] studied the crystallization of dip-coated sol–gel deposited films to produce piezoelectric films for 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-coated produced films has a strong effect on the crystal orientation. Their best result is achieved with a pre-heating temperature of 300 °C. Bao et al. [6] also used sol–gel deposited films and studied the orientation by varying the annealing temperature from 400 °C up to 600 °C, which is a very high temperature for our application. In the work of Castanedo-Pérez et al. [17], Z_n $(CH_3COO)_2$ is used as precursor, they have studied the effect of the annealing temperature from 200 °C to 450 °C (pre-heating at 100 °C) on the formation of ZnO. The film obtained is not highly

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oriented, as they were concerned with the optical transmission properties of the film. Jiwei et al. [18] deposited ZnO films on SiO_2/Si also with sol–gel with pre-heating at 200 °C, annealing from 300 °C up to 600 °C, the resulting films displayed good orientation. Paul et al. [9] used a two-step heat treatment, 50 °C in air, followed by 550 °C in furnace, repeating the cycle many times. The annealing was carried out in high vacuum at 400 °C, with good results. Alam and Cameron [19] 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 [20] studied the dependence of the crystallization on the relative concentration of zinc actetate dihydrate to monoethanolamine. The films were pre-heated at 300 °C and after finishing the coating cycles, they were annealed at 550 °C to get (002) oriented films. Chakrabarti et al. [8] varied annealing temperature from 500 °C up to 700 °C. But their films have not shown good orientation on the various substrates used. Aslan et al. [5] achieved good quality films by varying the annealing temperature from 450 °C up to 550 °C. Li et al. [7] varied the pre-heating temperature from 100 °C up to 500 °C, but their results were reasonable above 200 °C, annealed at 600 °C. Zhang et al. [4] have achieved very high quality films by starting the deposition process with a seed layer deposited by PLD. In their work the pre-heating temperature varied from 300 °C up to 600 °C, and annealed at 600 °C. Just recently, the work of Wang et al. [16] came to our attention, 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. It is almost the same range as in the work of Ohyama et al. [15], but did not get good results.

Most authors have focused their attention on the effect of the annealing temperature on the crystallization and have considered high temperatures for the pre-heating cycle.

Our objective is to apply experimental design and response surface techniques to produce highly oriented films, with the lowest thermal budget possible. The process 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 study are: pre-heating temperature, spin speed and number of coating layers. 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 dihydrate, Zn $(CH_3COO)_2$ (99.5%, Merck), in methanol (99.9%, 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. After coating the required number of layers, the ZnO thin film is annealed at 350 °C for 5 h. This procedure was performed on glass substrates and on silicon wafers with a silicon-dioxide layer.

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 [14]. 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. Relative peak intensity ($I_{(002)}/I_{(002)}+I_{(001)}+I_{(101)}$ [19]) is the dependent variable.

The first experimental design is a linear model 2^3 factorial central composite design, with three central points. This leads to eleven experiments, which includes 8 factorial points and 3 central points.

After the analysis of the variable effects in the first experimental design, another experimental design was prepared to further optimize the process. The second experiment is a quadratic model 2^3-full-factorial central composite design, with three central points. This leads to 17 experiments, including 6 star points factorial. Statistical significance of the regression coefficients was determined with the *F*-test analysis of variance (ANOVA), which revealed that the regression is statistically significant at 95% of confidence level ($p<0.05$).

3. Results and discussion

The results of Ohyama et al. [15] 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, this work was also performed on spin-coating produced films by Wang et al. [16]. Both studies used the same temperature range.

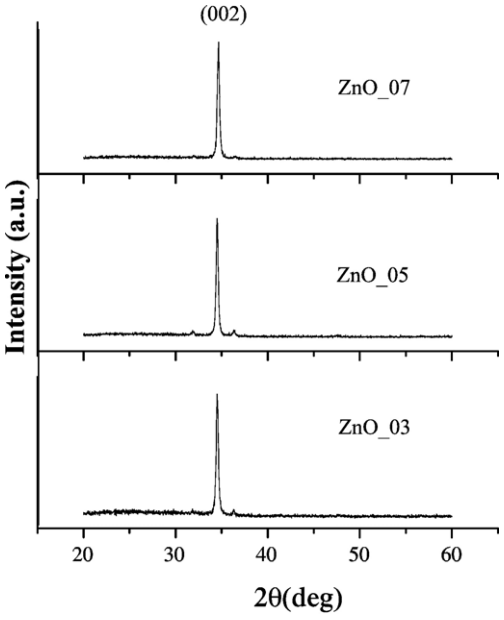

Fig. 1. The XRD patterns of thin films annealed at 350 °C. ZnO_03 T_{pre} = 120 °C, 5190 rpm, 12 layers, ZnO_05 T_{pre}120 °C, 2810 rpm, 18 layers, ZnO_07 T_{pre}120 °C, 5190 rpm, 18 layers.

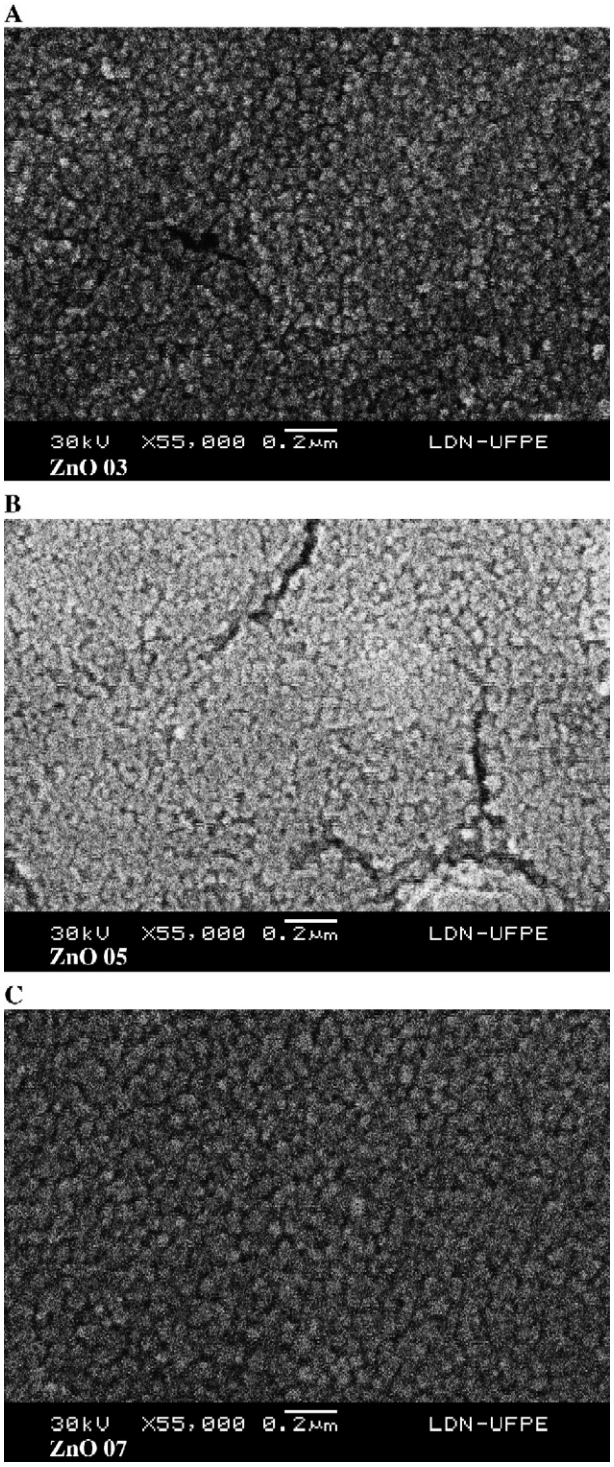

Fig. 2. Film surface observed with the SEM at 55,000 magnification (bar 0.2 μm), for conditions ZnO_03 T_{pre}=120 °C, 5190 rpm, 12 layers, ZnO_05 T_{pre}120 °C, 2810 rpm, 18 layers, ZnO_07 T_{pre}120 °C, 5190 rpm, 18 layers.

Considering that the rate of solvent desorption and drying could have an important effect on the crystallization, we have decided to investigate this effect by using a lower temperature range for pre-heating. Besides, we are interested in depositing very high quality ZnO films onto silicon chips to make SAW and multilayer BAW devices and integrated sensors, this demands the lowest temperature treatment possible.

Table 1
(002)-peak intensity, relative peak intensity, and FWHM for the best results

Run assay	Relative peak intensity (002)	FWHM (degree)	Grain size (nm (standard deviation))
ZnO_03	0.862	0.25	46.31 (7)
ZnO_05	0.877	0.26	58.03 (8)
ZnO_07	0.938	0.28	63.07 (10)

Following the preparation sequence presented earlier, the resulting films were primarily observed by X-rays diffraction, with CuKα (λ=0.15418 nm) radiation source. The measurements were carried out in the range 20°–50°. The best films were further observed with SEM, JEOL-6460, to exam the surface uniformity and grain size. Considering the effect of the three selected variables (pre-heating temperature, spin-coating speed, and number of coating layers) on the crystallization of the film. After the first experimental design, it is already clear that the pre-heating temperature is the only statistically significant ($p \leq 0.05$) effect. This is also confirmed in the second experimental design.

In Fig. 1, the X-ray diffraction patterns of ZnO thin films are presented. For the X-rays the films are deposited on glass substrates, and annealed at 350 °C for 5 h, in hot plate. 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=2810 rpm and coating layers=18), and ZnO_07 (pre-heating=120 °C, spin speed=5190 rpm and coating layers=18). The largest intensity of the (002)-peak is observed at conditions ZnO_05, while the largest relative intensity has occurred at conditions ZnO_07. Under the SEM, ZnO_05 film has displayed cracks.

The films with the optimal conditions also displayed the best uniformity, as shown in Fig. 2. The grain size is of the order of 50 nm, which are compatible with the FWHM measurements, can be seen in Table 1. The FWHM is approximately 0.26 °C for all selected samples. Considering that for the X-rays used, λ=0.15418 nm and using Scherrer's relation $d=0.94\lambda/\mathrm{FWHM}_{rad}\cos\theta$), the expected grain size is about 40 nm, which is close to the observed value.

Considering the relative peak intensity, a response surface plot was prepared. The plot as a function of pre-heating temperature and number of coating layers is presented in Fig. 3. One can see that for a low pre-

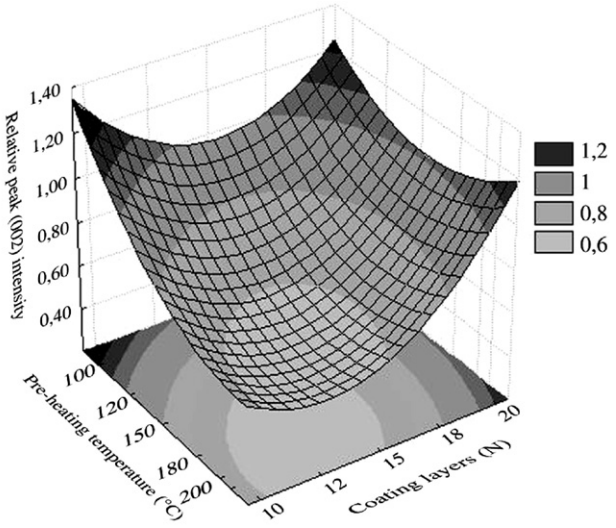

Fig. 3. Response surface (a) and contour diagrams (b) as function of pre-heating temperature and spin speed (rpm).

heating temperature, it is possible to get high quality film almost independent of film thickness.

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 = 120 °C, spin speed = 5190 rpm and coating layers = 18. With such conditions the highest (002) relative peak intensity is achieved. We have successfully deposited *c*-axis oriented zinc oxide thin films on glass substrate from zinc acetate by an inexpensive sol–gel process using low annealing temperature (350 °C). The process was also repeated on silicon dioxide. This result is very interesting for the integration of ZnO thin films for the construction of integrated smart sensors.

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