ON THE KINETICS OF SOL GEL Al:ZnO THIN FILMS CRYSTALLIZATION ON SILICON SUBSTRATE

Viorica MUŞAT[1], Joao CANEJO[2]
Catalina ITICESCU[1]
[1]"Dunarea de Jos "University of Galati
[2] Faculty of Science and Technology, CENIMAT, New University of Lisbon
email: Viorica.Musat@ugal.ro

ABSTRACT

Recently, there is a growing interest in applying ZnO thin films on silicon buffer substrates for p-n junction devices, optical wave guide, etc.

A sol gel process is very attractive technique for obtaining oxide thin films, due to easy control of film composition, easy fabrication of large area thin films with low cost and the ability to coat-specific shapes substrates.

This paper presents a kinetic investigation of the crystallization (550-650°C) of high preferential c-axis oriented ZnO thin films on p-type (100) silicon wafer substrate, from XRD data.

KEYWORDS: Al-doped ZnO, thin films, sol-gel, X-ray diffraction, atomic force microscopy, kinetic curves

1. Introduction

Zinc oxide (ZnO) based thin films are inexpensive n-type, wide band gap (3,2eV) semiconductor materials with high transmittance in VIS-NIR region and electrical (resistive or conductive) properties depending on the doping element(s) and microstructure. Transparent and conductive Al:ZnO thin films on glass substrate with high c-axis orientated crystalline structure along (002) plane are extensively studied for various applications including transparent conducting electrode for different electronic devices such as solar cells and electroluminescence displays [1-5]. Recently, there is a growing interest in applying n-type conductive doped-ZnO thin films on p-type silicon buffer substrate for p-n junction devices [6], optical wave guide [7] and ultraviolet (UV) photoconductive detector [8]. Between the most important applications of UV detection are missile warning system, air quality monitoring, accurate measurement of radiation for the treatment of UV irradiated skin, etc [9-10] With the use of wide band-gap semiconductors such as ZnO (UV) photoconductive detector, the need for costly filters to attenuate unwanted and IR radiation would be eliminated [11]. As transparent conductive oxide (TCO), doped ZnO films are very promising alternative materials to tin oxide and indium tin oxide because of their superior abundance in nature, nontoxicity and the excellent stability in hydrogen plasma which is an unavoidable processing ambient in silicon-related fields [12].

A sol gel process is very attractive technique for obtaining oxide thin films, because the advantages of easy control of film composition, easy fabrication of large area thin films with low cost and the ability to coat-specific shapes substrates.

Only few quantitative kinetic studies concerning the crystallization of oxide thin films are presented in the literature. The kinetic parameters of the crystallization of $Sr_{0.7}Bi_{2.3}Ta_2O_9$ (SBT) [13-14], $Sr_{0.7}Bi_{2.3}Ta_2O_9$-$BiTiTaO_9$ (SBT-BTT) [13], $Pb_{0.53}Zr_{0.47}Ti$ (PZT) [15-16] and TiO_2 [17] thin films were evaluated. To date, no papers about the kinetic parameters of sol-gel Al:ZnO thin films crystallization have been found.

This paper presents, based on XRD data, qualitative kinetic study (variation of XRD curves parameters of annealed films as a function of the annealing time) of the crystallization (550-650°C) of Al(2wt%):ZnO thin films deposed on silicon substrate by sol-gel method.

2. Experimental

The thin films used as samples for the kinetic study were prepared via a non-alkoxide route and a spin-coating technique at 1500 rpm (rotation per minute) on p-type (100) silicon wafer substrate.

The thin films deposition was performed using a sol prepared with $Zn(CH_3COO)_2 \cdot 2H_2O$ 99.5%, $AlCl_3 \cdot 6H_2O$ 98% as cation sources and ethanol as solvent. The concentration of metal ions in the solution was 0.50 mol l^{-1}. In order to study the kinetics of crystallization, the as-deposed thin films samples were stabilized by preheated in air for 5 min at 400ºC. In order to study the kinetics of crystallization, different pieces of stabilized thin films were annealed for different times (10, 20, 30, 40, 50, 60, 90 and 120 minutes) at 550, 600 or 650°C; three series of eight samples corresponding to the three values of the crystallization temperature have been obtained .

After the annealing (crystallization) treatment, the X-ray patterns of the samples were recorded in 2θ = 30-37 degree range, at room temperature using a Rigaku diffractometer (model RAD IIA) with CuKα radiation.

The kinetic plots present the values of (002) peak intensity, net area and FWHM of the annealed samples that were normalized taking into consideration the ratio between its surface area and the surface area of the biggest sample.

The thickness of the crystallized thin films was measured using a Sloan Dektak 3D surface profilmeter. The final postheated films have a thickness of about 180 and 200 nm for samples annealed at 650 and 550 °C, respectively.

The morphology on the surface of the films was analyzed using an AFM microscope. Tapping mode AFM experiments were performed in a Nanoscope IIIa Multimode AFM microscope (Digital Instruments, Veeco). Commercial etched silicon tips with typical resonance frequency of ca. 300 Hz (RTESP, Veeco) have been used as AFM probes.

The electrical resistivity of the films was measured in dark, using a KEITHLEY 617 Model Programmable Electrometer.

3. Results and discussions

Figure 1 shows the XRD patterns of the films crystallized at 550, 600 and 650°C in air for different periods between 10 min and 120 min, and the normal random orientated ZnO pattern. The XRD patters of the crystallized films (Fig. 1) show a most important (002) peak, indicating a preferential c-axis orientated würtzite type, comparative to the normal random orientated wurtzite structure characterized by (101) most intense peak.

The film crystallized at 600°C show the highest preferential c-axis orientation. Characteristic to c-axis orientated crystalline structure are the grains uniformly perpendicular to the substrate surface.

The AFM micrographs (Fig. 2) confirm this orientation and show non-porous and cracks free films morphology with average grain size depending on the speed of film deposition. Higher speed deposition, higher grain size.

The surface roughness mean square (rms) of the films, estimated from AFM measurements, rises from ~12 nm to ~26 nm when the deposition speed increases from 1500 rpm to 3000 rpm, respectively.

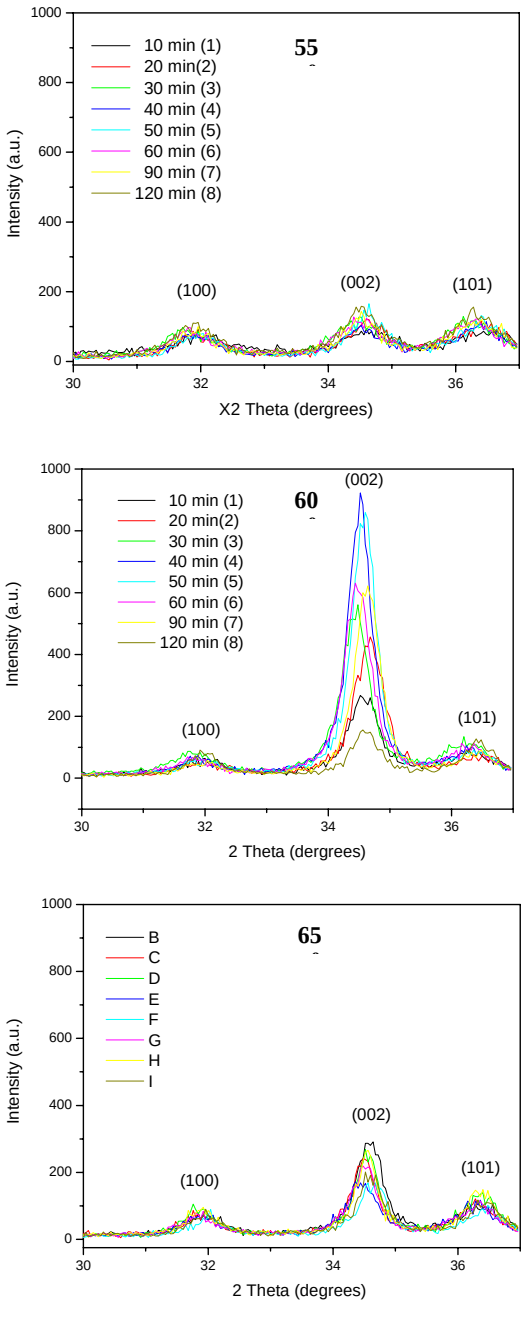

***Fig. 1**. XRD patterns of the thin films annealed in air at different temperature values.*

Figure 3 shows the variations, during annealing, of the net area, FWHM and inter-planes distance (*d*) related to the most intense (002) peak for samples annealed (crystallized) at 550, 600 and 650°C.

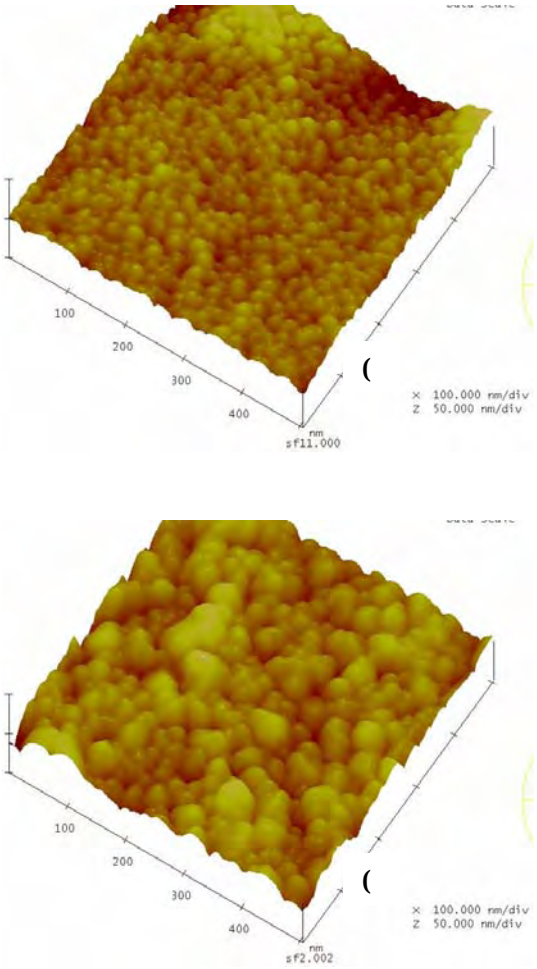

***Fig. 2**. AFM images, 3D surface topology, of thin films deposed at 1500rpm (a) and 3000rpm (b) after crystallization in air at 650C.*

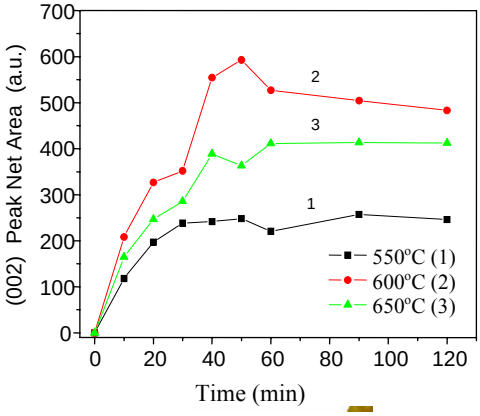

***Fig. 3**. The variation of the net area related to the most intense (002) peak, during the annealing at 550, 600 and 650°C.*

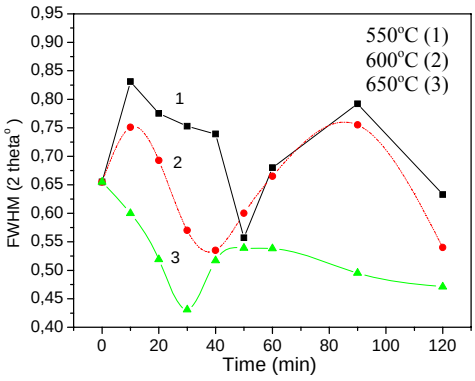

***Fig. 4**. The variation of the half width FWHM of the most intense (002) peak, during the annealing at 550, 600 and 650°C.*

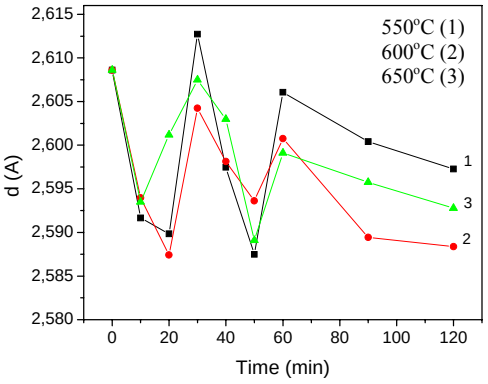

***Fig. 5**. The variation of the interplanar distance, d, related to the most intense (002) peak, during the annealing at 550, 600 and 650°C.*

From figure 3 one can see that during the first period of annealing (0-40 min), the net area of (002) peak continuously increase. The increase is the most important for the sample annealed at 600°C, smallest for the sample annealed at 550°C. The increase of (002) net area during annealing is an indication that the films crystallized at 600°C consist of a significantly larger amount of volume of crystalline phase, crystalline phase that is oriented perpendicular to the surface. Between 50-60 min annealing, the net area of the peaks decreases and after that, no significant variation occurs.

Generally, the decrease in FWHM of (002) peak confirms the improvement in the texture and quality (grain size) of c-axis orientated crystalline structure of the film. Figure 4 shows FWHM variation curves with minimum values and a shift of these minimum values depending on the crystallization/annealing temperature. Higher the annealing temperature, lower the minimum FWHM values (higher crystallite size) reached at shorter annealing time.

The variation of the interplanar distance according to (002) peak as a function of annealing time is presented in figure 5. This variation differs from the variation of the others parameters, each curve is characterized by two minimum and two maximum values situated at the same time values, for all the three series of samples annealed at 550-600 and 650°C. This variation shows that the mechanism of crystallization is complex and the rate determining step changes several times during annealing. The decrease of d during the first 20 minutes can be attributed to the total release of the organics from the stabilized films.

The film annealed in air at 600°C show the highest degree of crystallization and the highest preferential c-axis orientated crystalline structure. These results are in agreement with the literature data that recommend one hour annealing at 600°C in air for the crystallization of ZnO thin films deposed on silicon substrate [7-12].

The electrical measurements on the crystallized films showed very resistive films. A resistivity of 3.9×10^6, $8,7\times10^6$ and 3.9×10^7 Ωcm were obtained for the films crystallized at 550, 600 and 650°C, respectively.

The thickness of the thin films ranges between 250-300 nm and 200-250 nm for samples postheated at 450 and 500ºC respectively.

4. Conclusions

A qualitative kinetic study of isothermal crystallization, in the temperature range 550-650°C, of ZnO:Al (2wt%) thin films deposed on p-type (100) silicon wafer substrate was performed, based on X-ray diffraction patterns recorded at room temperature.

The crystallized films show a preferential c-axis orientated würtzite type structure with dominating (002) peak.

The variation of the net area, FWHM and inter-planes distance (d) related to the most intense (002) peak imply that the mechanism of films crystallization is complex and the rate determining step changes during annealing.

The film annealed in air at 600°C shows the highest degree of crystallization and the highest preferential c-axis orientated crystalline structure, in good agreement with the literature data that recommend one hour at 600°C annealing for the crystallization of ZnO thin films deposed on silicon substrate.

The crystallized films in air are resistive. Resistivity values of 3.9×10^6, $8,7\times10^6$ and 3.9×10^7 Ωcm were obtained for the films crystallized at 550, 600 and 650°C, respectively. After annealing in reducing atmosphere, the films turn in conductive.

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