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Temperature annealing effect on structural and optical properties of ZnO thin films prepared by sol-gel method

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Abstract. ZnO thin films have been synthesized by sol-gel method. The effect of the annealing temperature on the morphological, structural and optical properties of the ZnO thin films was investigated. A good crystllinity and good transmittance in the visible spectrum was obtained at the annealing temperature of 400°C.

1. INTRODUCTION

In recent years, the growth and characterization of zinc oxide (ZnO) materials have been widely studied, mainly for application in developing short-wavelength optoelectronics devices. ZnO is an important n-type semiconductor material with wide band gap (direct band gap energy of 3.5 eV), good chemical stability, good electrical conductivity and high transmittance with the UV-visible region [1–3]. These characteristics are required in various applications dealing with transparent heating elements for photovoltaic devices, transparent electrodes used on electroluminescence devices and gas sensors [4–7]. Many papers report on the physical properties of ZnO obtained by various deposition techniques such as reactive RF and DC sputtering [8], chemical vapor deposition [9], spray pyrolysis [10], electrode position [11] and sol–gel technique [12]. Particularly,the attractive deposition technique among these mentioned is the sol-gel one for being successfully used for transparent semiconducting film. This technique is simple, cheap, and allows large depositionarea. Although some papers dealing with the physical properties of ZnO obtained by sol-gel have been published [13–15], the investigation of their precursor remains very limited. The properties of sol-gel ZnO films are strongly dependent on the preparation conditions [12,16,17]. A careful control of the substrate temperature, precursor and the films thickness, is necessary to obtain the desired properties of coating for energy efficient windows.

In this paper, we optimize the effect of different annealing temperatures on the structural and optical properties of the sample with a precursor $ZnCl_2$. It is also shown that sol-gel is an adapted technique to obtain ZnO films with a quality comparable with that of transparent conducting oxide thin films prepared by other techniques [10,11].

2. EXPERIMENTAL

The ZnO thin films studied were synthesized by sol-gel method, deposited on glass substrate previously cleaned and annealed at various temperatures for one hour.

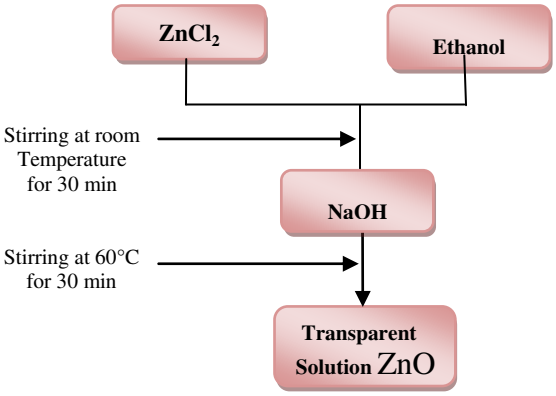

Figure 1. Procedure used preparing ZnO thin films.

Table 1. Time and temperature annealing of studied samples.

Samples	Annealing temperature (°C)	Annealing time (min)
ZnCl1	200	60
ZnCl2	300	60
ZnCl3	400	60
ZnCl4	500	60

The starting solution is prepared from the dissolution of 10^{-3} mol of $ZnCl_2$ in 50 ml of ethanol at room temperature and using monoethanolamine (MEA) as stabilizer. NaOH concentration of 16.10^{-3} mol/l obtained by dissolving 0.032 g NaOH in 50 ml of ethanol was added. The resulting mixture was stirred at 60 °C for 1h. The resulting solution is the total volume of 100 ml; the zinc chloride concentration is from 0.1 mol/l. Figure 1 shows the procedure used.

To eliminate organic species present in the starting solution and to densify the material, the sample was annealed at temperature ranging from 200 °C to 500 °C for one hour. Table 1 summarizes the experimental conditions for preparing samples. X-ray diffractograms were recorded at room temperature using the apparatus "Philips X'pert MPD" operating at 40 KV, 30 mA and equipped with a Cu anode (λ=1.5406 Å) in the range

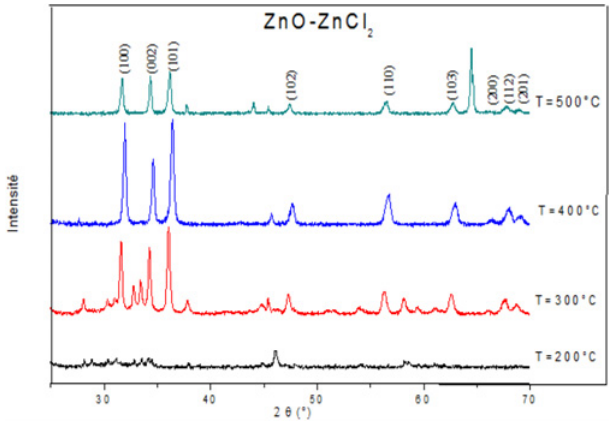

Figure 2. X-ray pattern of ZnO films prepared at various annealing temperatures.

of 2θ between 25° and 70°. The morphological study of layers was done using a scanning electron microscope JEOL JSM type-5500. Optical characterization was carried out at room temperature using SHIMADZU UV-VIS 3101 spectrophotometer.

3. RESULTS AND DISCUSSIONS

3.1. Structural and morphological characterization

The X-ray diffraction patterns of ZnO films as a function of the different annealing temperatures are shown on Figure 2.

All the diffraction peaks were identified as being from ZnO. The indicated peaks shown in the Figure 2 were identified as being polycrystalline ZnO with a hexagonal wurtzite phase from temperature higher than 400 °C. Note that, for the low substrates temperatures (200 °C), one obtains an amorphous structure and from 300 °C, the crystallization begins with the appearance of additional peaks to those of ZnO. Other peaks [(102), (110), (200), (103), (112), (201)] are also observed, but their intensity is very small compared to that of the (100) or (002) peaks (JCPDS: 76-0704). Nevertheless, their presence indicates that other orientations are possible on the films and that these orientations do not disappear with increasing temperature. To conclude, the films deposited at $T_s = 400$ °C are polycrystalline with maximum intensities for(100), (002) and (101) peaks but without any preferential orientation. The lattice constants of hexagonal ZnO film are reported in JCPDS standard data a = 3.2530 Å and c = 5.2130 Å. The lattice constant a and c for all the films are shown in Table 2. These values are agreement with JCPDS data (Table 2) and that seems not being affected by the temperature.

For all the films, relative percentage error (d% error) (by using equation ($d\% = |d_h - d|/d*100$) [18]) data calculated are given in Table 2. The experimental d_h and JPCDS d-values are in relatively good agreement and show hexagonal structure.

The grain size of crystallites was calculated using a well-know Scherrer's formula [19]. The values found for the grain size are in the range 30–70 nm which agrees with the values reported in the literature. It can be seen that as long as the temperature annealing increase the grain size of the films increases.

Table 2. a, c, d% error and grain size for the films.

(hkl)	Temperature annealing 400 °C				Temperature annealing 500 °C			
	a(Å)	c(Å)	d% error	Grain size (nm)	a(Å)	c(Å)	d% error	Grain size (nm)
(100)	3.24	5.20	0.35	59.97	3.25	5.21	0.13	46.63
(002)			0.59	46.99			0.15	70.41
(101)			0.43	30.36			0.24	42.47

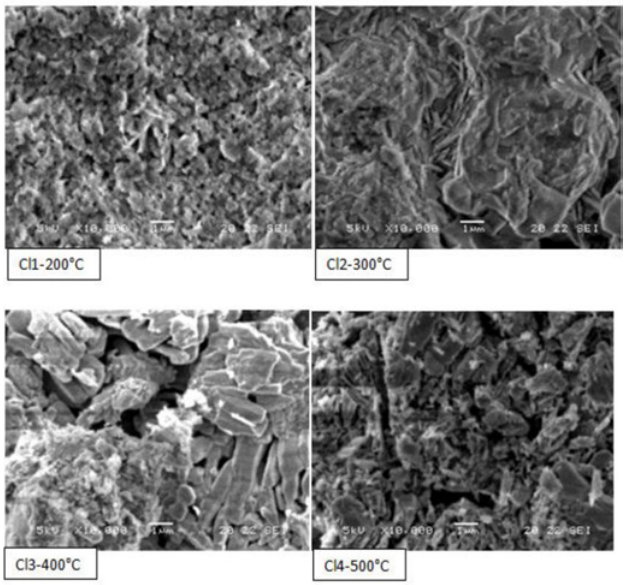

Figure 3. SEM images of ZnO films prepared at different annealing temperatures.

Typical SEM images of the surfaces of the ZnO films deposited at different annealing temperatures are shown on Figure 3.

Note that no cracks are observed on large scan area for all samples. The films are continuous and in fact consist of grains. The XRD results are therefore confirmed by SEM imaging: the crystallization of ZnO films increases with the annealing temperature. Figure 3 clearly shows that there is a change in the surface morphology of ZnO films due to change of the temperature. It is evident that the amorphous structure occurred throughout the films deposited at 200 °C All films deposited at T > 300 °C attain a microstructure with a close-packed morphology.

3.2. Optical characterization

Figure 4 shows the optical transmittance curves as function of the wavelength for the ZnO films deposited at various annealing temperatures.

The films deposited at 400 °C exhibit a high optical transmittance in the visible spectrum. The average optical

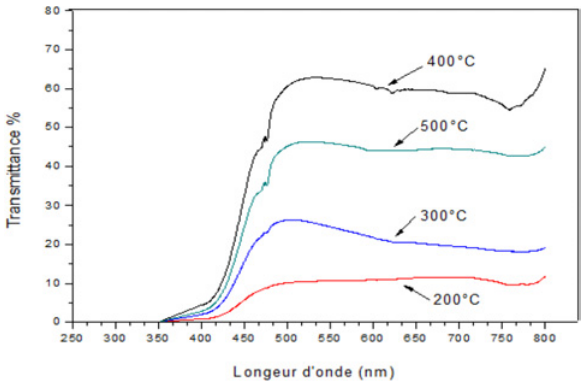

Figure 4. Optical transmission of ZnO films prepared at different annealing temperature.

Table 3. Band gap energy values calculated from optical transition measurements.

Precursor	Annealing temperature (°C)	E_g (eV)
$ZnCl_2$	200 °C	3.48
	300 °C	3.56
	400 °C	3.45
	500 °C	3.57

transmittance increases with the temperature and the maximum is obtained for 400 °C.

Furthermore, the absorption edge shifts towards shorter wavelength, suggesting a widening of the energy band-gap with increasing temperature. The shift in band gap is attributed to the variation in stoichiometry.The band gap energy was measured by extrapolating the plot of $(Ah\nu)^2$ versus $h\nu$ for different temperatures and is listed in Table 3.

A typical value of ZnO optical direct band gap is 3.4 eV as reported in the literature and is characteristic of the good crystallinity of ZnO films [20]. The widening of the band gap continues with increasing the temperature. This phenomenon is known as the Moss-Burstein shift [21]. According to the Moss-Burstein theory, the donor electrons occupy states at the bottom of the conduction band. Since the Pauli principle prevents states from being doubly occupied and optical transitions are vertical, the valence electrons require extra energy to be excited to higher energy states in the conduction band. These features suggest that ZnO films with enhanced optical properties can be produced by sol-gel at T = 400 °C.

4. CONCLUSION

The effect of the annealing temperature on the structural and optical properties of sol-gel ZnO thin films has been reported in this article. We have found that the optical transmittance depend strongly on the annealing temperature. The optimum value of temperature has been determined to get the best transmittance ZnO films.

The films deposited at 400 °C are polycrystalline and exhibit a higher transmittance. The best film in terms of transmittance consisted of close –packed grains.

These films may be useful for specific applications as transparent n-type windows in solar cells or for sensors devices where large surface areas are needed and may also be an important candidate for UV diode lasers applications.

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