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Study of ZnO sol-gel films: Effect of annealing

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Abstract

Thin films of zinc oxide were deposited by spin coating method on different substrates. The obtained samples were thermally treated at temperatures from 400 °C up to 850 °C. The structural study was performed by XRD and FПR techniques in order to observe the effect of the annealing temperatures. The sol-gel ZnO films showed polycrystalline hexagonal structure. The optical transmittance reached 91% and it diminished with increasing annealing temperatures.

Keywords: Sol-gel, ZnO, Thin films structure

1. INTRODUCTION

The importance of zinc oxide (ZnO), among other metal oxides, is increasing due to many applications. Thin films of zinc oxide combine interesting properties such as non-toxicity, good electrical properties, high luminous transmittance, excellent substrate adherence, hardness, optical and piezoelectric behaviour and its low price [1]. One of the topics in solar cell manufacturing is to obtain transparent anti-reflective surface coating of good conductivity with deposition techniques of low installation cost and minimum ambient impact [2]. On the other hand, this oxide has been applied in light emitting diodes [3], photodetectors [4], piezoelectric cantilever [5], gas sensors [6], buffer layer in C1GS solar cells [7], and dye sensitized solar cells (DSSC) [8]. ZnO has relatively high physical and chemical stabilities, and hence it has many high temperature applications, such as buffer for HI—V nitrides [9]. Furthermore, ZnO is a promising material for short wavelength light emitting devices and daylight-blind UV detectors [10].

Therefore, it is not surprising that it has been under intensive investigation and many methods have been employed for preparation of such a significant material in thin film form. Among them, chemical bath methods are low cost processes and the deposited films are found to be of comparable quality to those obtained by more sophisticated and expensive deposition process [11]. ZnO films have been prepared by a wide variety of techniques, including sputtering [1], spray-pyrolysis [12] and electrodeposition [13].

Sol-gel method is chosen due its relatively simplicity and has a general advantage of large area deposition and uniformity of the films thickness. The sol-gel process offers many advantages for thin film deposition including excellent control of the stoichiometry, easy modification of film composition, and relatively low annealing temperatures. Sol-gel derived ZnO films might be promising for low cost optoelectronic devices [14,15].

In this work, we present preliminary results of spin coating ZnO films in respect to their structural and optical properties. Especially, the influence of thermal treatment has been studied.

2. EXPERIMENTAL

The zinc precursor solution was prepared by dissolving zinc acetate dehydrate in an absolute ethanol to obtain 0.2 M concentration. In this route, triethanolamine (TEA) was used as a complexing agent in order to keep metal ions in the homogeneous solution without undergoing precipitation. The molar ratio TEA/Zn was fixed to 1. The solution was mixed at 50 °C/1 h by stirring on magnetic stirrer at atmospheric pressure and then ultrasonically treated at 40 °C/30 min.

The obtained sol was transparent and stable for two months.

The thin films were spin coated on Si and glass substrates at 4000 rpm and have undergone five layer depositions. The firing was performed at 400 °C/30 min after each layer processing. Finally, the samples were annealed at temperatures of 400, 500, 600 and 750 °C in air for 1 h for the case of Si substrates.

XRD spectra of sol-gel thin films were recorded by means of XRD diffractometer Bruker D8, at the grazing angle 2° and step time 8 s and step 0.1°.

FΠR measurements were performed in the spectral region 350-1600 cm^{-1} by Shimadzu FΠR Spectrophotometer IRPrestige-21.

Optical measurements were performed for samples deposited on glass substrates by using UV-3600 Shimadzu spectrophotometer. The samples for optical characterization were annealed at temperatures of 400, 500 and 600 °C.

3. RESULTS AND DISCUSSIONS

The recorded XRD spectra clearly indicate that the sol-gel ZnO films start to crystallize even at the low temperature annealing at 400 °C. The high degree of crystallization is manifested as the main five peaks (appeared in all spectra as seen from Fig. 1). significantly enhance their intensity with increasing annealing temperature. Only for XRD spectrum of 600 °C treated film is detected a new maximum at 54.08 (small intensity) that can be probably assigned to cubic zinc peroxide (ZnO_2) phase. The other XRD maxima correspond to wurtzite structure. There is no preferential growth orientation observed. This indicates that sol-gel derived ZnO films are polycrys-talline with a hexagonal structure. The average crystallite dimension is estimated from XRD pattern according to Scherrer's formula and the result is presented in Table 1. It is seen that the crystallite size is sensitive to annealing temperature as the values are increasing with the temperatures from 22 nm (400 °C annealing) to 40 nm after high temperature treatment at 750 °C.

The lattice parameters calculated from XRD data are in good agreement with those reported in JCPDS 01-07-8070. Dislocations are an imperfection in a crystal associated with misregistry of the lattice in one part of the crystal with respect to another part. Unlike vacancies and interstitial atoms, dislocations are not equilibrium imperfections. In fact, growth mechanism involving dislocation is a matter of importance [16]. The dislocation density of the films is given by the Williamson and Smallman's relation:

$$\delta = n / d^2$$

where *n* is a factor, which equals unity giving minimum dislocation density and *d* is the grain size [17]. Dislocation densities exhibit a decrease with increasing annealing temperatures, which indicates lower concentration of lattice imperfections.

The Zn-O bond length in the wurtzite structure can be estimated from the expression given in ref. [17]. The corresponding values are 1.9507, 1.9524, 1.9498 and 1.9512 for the films treated at 400, 500, 600 and 750 °C, respectively. The film crystallinity has been improved with annealing.

The vibrational properties of ZnO films have been studied by FTIR spectroscopy. The FTIR spectra are shown at Fig. 2. The band positions and numbers of absorption peaks are depending on crystalline structure, chemical composition and also on film morphology [18]. The main absorption band of sol-gel ZnO films treated at 400, 500 and 600 °C is located near 395 cm^{-1} as after highest temperature annealing it is slightly shifted towards 403 cm^{-1}. This band is corresponding to Zn-O bonds [18]. The peak at 1020 cm^{-1} is attributed to Si-O-Si bonds due to the silicon wafer. The other weaker bands at 425,470 cm^{-1} are assigned to the stretching vibrations of Zn-O. The absorption band appeared at 515 cm^{-1} only in the spectrum of highest annealed film is one of the 1R active modes (408 and 513 cm^{-1}) that are theoretically confirmed [19] and it corresponds to wurtzite ZnO.

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Table 1 *XRD data (lattice parameters and grain size values) determined for sol-gel ZnO thin films.*

Sample	T_{ann} (°C)	*a*	c	Grain size (nm)	Dislocation density 6×10^{-4}(l/nm^2)
ZnO	400	3.249	5.202	22	20.66
ZnO	500	3.252	5.206	29	11.89
ZnO	600	3.248	5.197	35	8.16
ZnO	750	3.249	5.209	40	6.25
JCPDS 01-07-8070		3.2489	5.2049		

Fig. 1. *XRD spectra of sol-gel ZnO films thermally treated at different temperatures.*

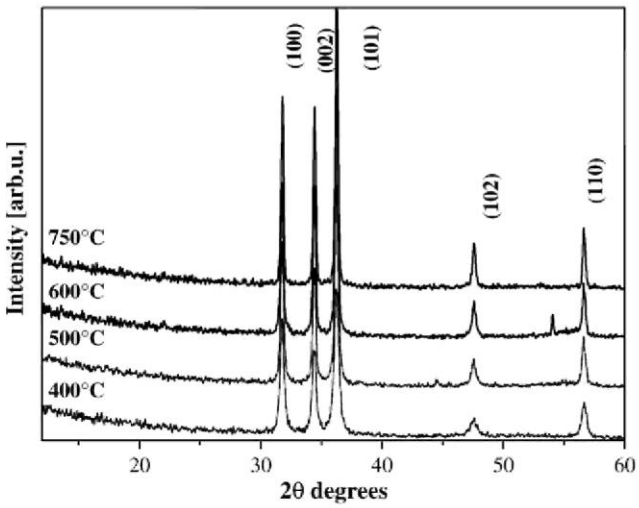
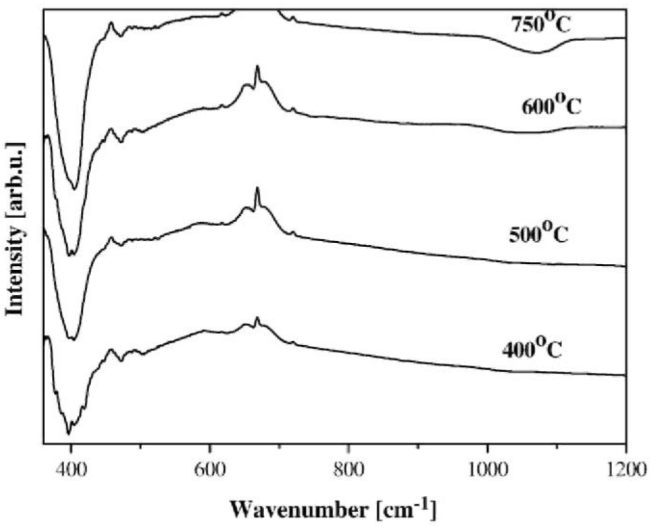


Fig. 2. *FTIR spectra of sol-gel ZnO films annealed at different temperatures.*



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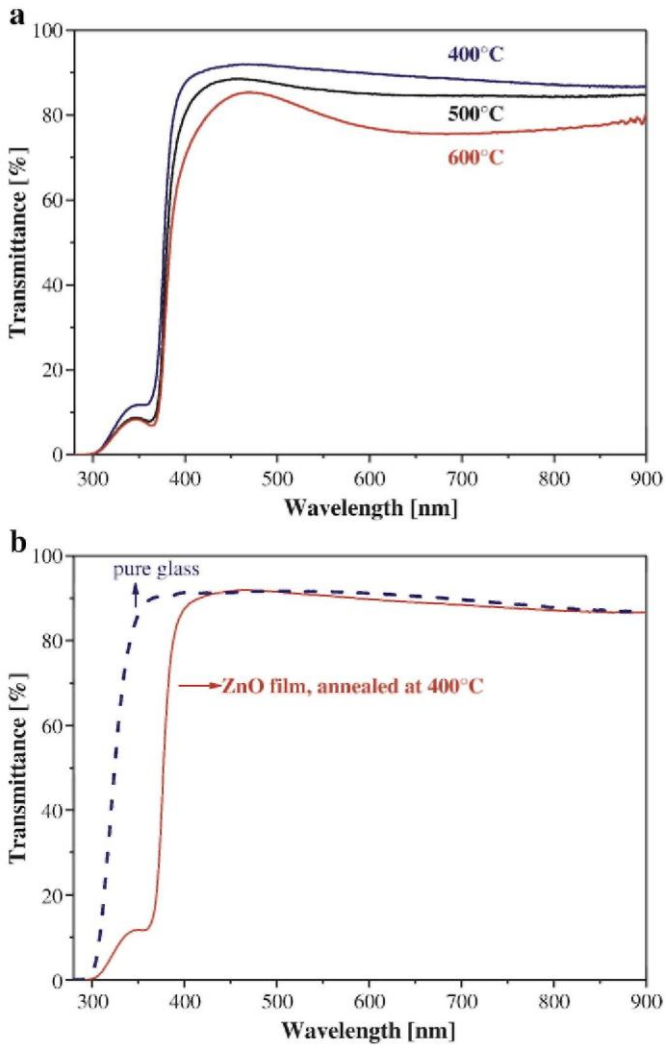
Optical properties are determined by spectrophotometric measurements for sol-gel ZnO films deposited on glass substrates and annealed at temperatures of 400, 500 and 600 °C (see Fig. 3).

The ZnO film, annealed at the lowest temperature is so transparent that its transparency is only limited by the substrate used as can been observed from Fig. 3b. The high temperature annealing leads to decrease of the transmittance in the visible range. The ZnO film treated at 400 °C shows transparency 91% at wavelength 550 nm and in the same time, the films annealed at 500 and 600 °C reveal transmittance values 87 and 80% (λ = 550nm), respectively. The same tendency of decreasing of the film transmittance with annealing temperatures is reported by other authors for zinc oxide films [20].

Small shoulders at-322, 321 and 320 nm (for films, treated at 400, 500, 600 °C, respectively) have been observed in the transmittance spectra revealing the excitonic absorption feature of the films. However, these shoulders show a substantial blue shift relative to that of bulk ZnO (-373 nm), which could be attributed to the confinement effects in thin films [21].

From transmittance measurements can be estimated by the optical band gap considering a direct gap semiconductor. The optical gap values of ZnO films, determined by second derivative spectrum [22], are 3.29 eV (400 °C annealed sample) and 3.28 and 3.27 eV for films, treated at 500 °C and 600 °C, respectively. There is no considerable effect of annealing procedures. The estimated optical band gaps coincide with those reported in literature and are slightly different from the bulk zinc oxide of 3.37 eV.

Fig. 3. *UV-VIS spectra of ZnO films obtained on glass substrate and treated at temperatures of 400, 500 and 600 °C (a), and (b) represents the comparison with bare substrate.*



4. CONCLUSIONS

Low cost sol-gel method has been shown to be suitable to obtain ZnO thin films with optical and structural qualities suitable for optoelectronic applications. The ZnO films grow in wurtzite hexagonal polycrystalline structure with high optical transmittance. The crystallite sizes increase with increasing annealing temperature and for samples annealed at 750 °C the value is closed to 40 nm. There is almost no effect of the thermal treatment on the values of the optical band gaps.

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