Effect of the microwave-assisted thermal annealing on structural and optical properties of the sol–gel-derived ZnO thin films

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Abstract

ZnO thin films were prepared by sol–gel spin coating technique, and the effect of microwave-assisted thermal annealing on structural and optical properties was investigated. Structural features, microstructural morphology and optoelectronic properties were studied using XRD, FE-SEM, UV–visible spectrophotometry and four-point probes measurement system. During microwave-assisted annealing, rapid volumetric heating preserved nanostructure along with pore-free dense morphology. Also, this annealing technique induced larger tensile strain and increased preferential orientation along (002). Power consumption for sintering was reduced as obvious from the decreased annealing time. An increase in optical band gap with a decrease in electric resistivity by one order of magnitude can be attributed to its nanostructured pore-free structure, and the induced strain resulted from microwave-assisted annealing.

Keywords Zinc oxide · Sol–gel · Microwave · Texture coefficient · Band gap · Resistivity

1 Introduction

Transparent conducting oxides (TCO), which are optically transparent and electrically conductive, have become promising components these days in a large number of modern devices including flexible electronics, optical devices, transparent heaters, touch screens and solar cells [1, 2]. Many binary oxide systems such as SnO_2 , In_2O_3 , ZnO, CdO, Ga_2O_3 , Ti_2O_3 and PbO_2 are primarily formed from p-block heavy metals and show good transparent conducting properties [3, 4]. Out of this wide exhibit, In-doped SnO_2 (ITO) and F-doped SnO_2 (FTO) are the mostly utilized TCOs in current enterprises due to having dominant electrical and optical properties [1, 5]. Nonetheless, the relative shortage and staggering expenses associated with indium are noteworthy disadvantages for ITO, while FTO is unquestionably financially savvy and it requires higher statement temperature, which confines its viable usage in adaptable gadgets [6, 7]. Owing to low cost, high chemical

stability and being non-toxic ZnO is an excellent option to the ordinarily utilized ITO [8]. The II–IV group semiconductor material ZnO usually adopts a hexagonal wurtzite crystal structure with $a = 3.25 \text{ \AA}$ and $c = 5.12 \text{ \AA}$ [9]. It has a large excitonic binding energy $\sim 60 \text{ meV}$ and a direct wide band gap ($\sim 3.37 \text{ eV}$ at room temperature) [10]. By changing the annealing condition and varying dopants, it is possible to adjust the resistivity values of ZnO between $10^{-3} \Omega\text{cm}$ and $10^{12} \Omega\text{cm}$ [11, 12]. Combinations of properties such as wide band gap along with its piezoelectric and optical properties make ZnO unique and crucial for the present and future device applications such as solar cells, optical detectors, biosensors and photoinduced nonlinear optical materials [13]. And thus, they have attracted huge academic and industrial interest with a large number of papers on ZnO being published every year.

Several techniques have been established to deposit ZnO thin films, such as chemical vapour deposition, sputtering, sol–gel, spray pyrolysis, electrodeposition, atomic

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layer deposition, and RF magnetron sputtering [14–19]. Out of this wide exhibit, sol–gel technique is the most attractive one to fabricate ZnO thin films due to its versatility in controlling chemical composition, good film quality and low cost [20]. Microwave-assisted annealing is emerging as a novel and innovative technology due to being advantageous over other conventional radiant annealing. It is a volumetric heating method that increases the atomic rotation of a sample with direct absorption of electromagnetic radiation, a potential approach to enhance energy efficiency and has advantages of thermal uniformity, rapid heating process and low thermal budget [21]. Such benefits also include reduced power consumption, preservation of nanostructures, improved properties and better product performance [22]. In comparison with furnace annealing (FA), microwave annealing (MWA) holds promise in low thermal budget applications due to the unique interaction mechanisms between microwaves and materials being thermally treated [23]. Conventional radiant annealing results in surface heating, whereas microwave-assisted annealing results in volumetric heating. Volumetric heating is much rapid and energy efficient process. In volumetric heating, unlike conventional radiant annealing, heat is dissipated from thin film surface and the resulting temperature profile is inverted. Such heating is effective to retain nanostructure with larger apparent surface area.

In this study, ZnO thin films were prepared by sol–gel spin coating technique. The influence of microwave-assisted annealing on structural, optical and electrical properties has been systematically studied and reported. High loss tangent of ZnO along with its moderate dielectric constant results in increased effective heat generation during microwave-assisted annealing process.

2 Experimental procedure

ZnO thin films were prepared by sol–gel spin coating technique using zinc acetate di-hydrate (ZAD) precursor. ZAD was first dissolved in the solvent 2-methoxy ethanol, and mono-ethanolamine (MEA) was added drop-wise as stabilizer maintaining ZAD to MEA ratio 1:1. Solution was then magnetically stirred at 80 °C for 1 h until it turned into a clear solution. After ageing for 24 h at room temperature, solution was ready to be served as the coating solution. Thin films were produced on glass substrates by dynamic spin coating. At first, glass substrates were cleaned properly in several steps. Following substrate preparation, solution was dropped onto the pre-heated substrates placed on spin coater. Once a layer was deposited, the film was dried at 180 °C for five minutes. Subsequent layers were deposited similarly to have thin films consisting of three layers. For conventional annealing, thin films were annealed at 500 °C

for 2 h. The other set of films were pre-annealed in a microwave oven operating at 2.65 GHz frequency with a maximum power input of 1.2 kW for 5 min and then annealed at 500 °C for 1 h. Structural, optical and electrical properties of the thin films were characterized for both conventional and microwave-assisted annealing.

Structural parameters including lattice parameters and texture coefficient were determined using X-ray diffraction (XRD) using monochromatic Cu-K α radiation ($\lambda = 0.154$ nm). Crystallite size was calculated using Debye–Scherrer formula. Surface morphology was observed using field emission scanning electron microscope (FE-SEM). Transmittance was measured using ultra violet-visible spectrophotometer (UV–Vis), and band gap was calculated from Tauc plot. Electric resistivity was measured using four-point probe measurement system.

3 Results and discussion

3.1 Structural parameters

Crystallization of ZnO for both conventional and microwave-assisted annealing processes was confirmed by XRD analysis (Fig. 1). Thickness of both the films was around 118 nm. XRD patterns were studied using standard data from Joint Committee of Powder Diffraction Standards (JCPDS 36-1451) [24]. Analysing the XRD patterns, structure–property relationship of the thin films was studied and effect of microwave-assisted annealing on the optoelectronic properties was investigated.

Microwave-assisted annealing shifted (002) peak in the XRD pattern towards right. Texture coefficient (TC) is the texture of a particular plane, which implies preferred orientation if deviates from unity. Texture coefficients for different planes are calculated using Eq. 1 [25, 26]:

$$TC_{hkl} = \frac{\frac{I}{I_0}}{\frac{1}{n} \sum \frac{I}{I_0}} \quad (1)$$

Fig. 1 XRD pattern of ZnO thin films prepared by conventional (left) and microwave-assisted annealing (right)

Table 1 Bragg angle and texture coefficients

Annealing type	Bragg angle (002) plane, $2\theta^\circ$	Texture coefficient (002)	Texture coefficient (100)	Texture coefficient (101)
Conventional	34.376	1.49	0.81	0.71
Microwave-assisted	34.402	1.62	0.77	0.59

Fig. 2 FE-SEM images of ZnO thin films prepared by (a, b) conventional and (c, d) microwave-assisted annealing

where TC_{hkl} is the texture coefficient of plane with indices hkl , I is the X-ray diffraction intensity, n is the number of diffraction peak considered, and I_0 is the intensity of reference diffraction pattern [JCPDS data card (36-1451)]. TC values calculated for different orientations, viz. (002), (100) and (101) planes, are listed in Table 1. Preferred orientation along (002) plane is evident from the highest value of TC for (002) plane for both type of annealing. Upswing along preferred orientation (002) exhibiting enhanced texture for microwave-assisted annealing compared to conventional annealing is obvious as TC value increased from 1.49 to 1.62 (Fig. 2).

Crystallite size was calculated from XRD data using Debye–Scherrer equation. Microwave-assisted

Table 2 Inter-planar spacing and crystallite size

Annealing type	Full width half maxima (FWHM), $2\theta^\circ$	Inter-planar spacing (d), Å	Crystallite size, nm
Conventional	0.44983	2.605	19.80
Microwave-assisted	0.46477	2.604	17.10

annealing resulted in decreased crystallite size as shown in Table 2. Preservation of this nanocrystallite structure is attributed to the rapid volumetric heating by microwave-assisted annealing [18].

3.2 Induced strain and residual stress

Induced strain and residual stress in the annealed thin films were calculated using XRD data (Table 3). Lattice parameters are calculated using Eq. 2 [27]. Induced strain along c-axis perpendicular to substrate surface is calculated using Eq. 3 [28]. Here, c is the lattice parameter of hexagonal wurtzite unit cell of the ZnO films, and $c_0 = 5.2066 \text{ \AA}$ is the unstrained lattice parameter for bulk ZnO [29]. Residual stress σ is determined using Eq. 4 [30]. C_{ij} is the elastic stiffness constants for ZnO single crystals: $c_{11} = 208.8 \text{ GPa}$, $c_{33} = 213.8 \text{ GPa}$, $c_{12} = 119.7 \text{ GPa}$, and $c_{13} = 104.2 \text{ GPa}$ [31].

$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \quad (2)$$

$$\varepsilon_{zz} = \left(\frac{C - C_0}{C_0} \right) 100\% \quad (3)$$

$$\sigma = \frac{2C_{13}^2 - C_{33}(C_{11} + C_{12})}{2C_{13}} \cdot \varepsilon_{zz} \quad (4)$$

Microwave-assisted annealing resulted in increased induced strain in the annealed thin films. This observation is also in accordance with the calculated decreased crystallite size for microwave-assisted annealing where finer crystallites induce strain in the thin films. Finer structure for microwave-assisted annealing was also evident from the FE-SEM micrographs analysed later.

3.3 Surface morphology

The effect of annealing process on the morphology of nanostructure was studied using FE-SEM. At lower magnification, observed ganglia-like pattern is the characteristic feature of ZnO thin films. Ganglia-like structure looks similar to the nerve cell structure in human body. This structure is found on the annealed ZnO thin films as a structural feature. The height and width of the ganglia hills, their branches and twisting appearance are related to the features like degree of annealing, doping concentration, induced strain, etc. The increased branches in ganglia-like pattern for microwave-assisted annealing are in close agreement with the observed induced tensile strain

earlier. Higher-magnification images show the spherical particles with size distribution in nanometre range. The structure is much finer for microwave-assisted annealing. Such preservation of nanostructure can be ascribed to the rapid volumetric annealing from which the dense structure was derived.

3.4 Optical property

Microwave-assisted annealing shifted the absorption peak towards lower wavelength, popularly known as blue-shift as shown in Fig. 3. Nevertheless, average transmittance was decreased after microwave-assisted annealing, and both techniques achieved an average transmittance above 85% which is quintessential for use in optoelectronic devices (Table 4).

Increased band gap for microwave-assisted annealing, as evident from the calculated band gap using Tauc plot (Fig. 4), substantiates the fact of blue-shift. The increased band gap can be imputed to the quantum confinement effect as microwave-assisted annealing resulted in decreased crystallite size from 19.80 to 17.10 nm. Increased band gap due to the quantum confinement effect also has been reported by others for the crystallite size range similar to that reported here, where effect can be varied from mild to significant depending on the size regime [32, 33]. For the nanoscale, quasi-continuous density of states in the valence and the conduction bands get split into discrete electronic levels. For crystallites in nanometre range, a decrease in crystallite size enhances

Fig. 3 Transmittance of ZnO thin films

Table 3 Lattice parameters, induced strain and residual stress

Annealing type	Lattice constant (c), Å	Lattice Constant (a), Å	Strain (ε_{zz})	Stress (σ), GPa
Conventional	5.2036	3.1346	-0.057%	0.133
Microwave-assisted	5.2075	3.1370	+0.017%	-0.039

Table 4 Optical and electrical properties

Annealing type	UV absorption peak, nm	Average transmittance in visible range, %	Band gap, eV	Resistivity, ohm-cm
Conventional	400	90	3.30	3.35×10^2
Microwave-assisted	380	86	3.75	4.78×10^1

Fig. 4 Band gap calculation from Tauc plot

the quantum confinement effect as energy spectrum becomes more and more discrete, which results in the widening of band gap [34]. An increase in optical band gap by microwave-assisted annealing has been reported by other studies as well where the magnitude of band gap increase can be varied depending on material type and annealing parameters. One study showed an increase in optical band gap by 0.1 eV only where other studies showed an increase by quite higher margin [35, 36].

3.5 Electrical properties

Resistivity of ZnO thin films was decreased by one order of magnitude for microwave-assisted annealing (Table 4). Reduced resistivity can be ascribed to a number of factors. Morphological study showed more dense and uniform films with less pores and inter-particle voids for microwave-assisted annealing. Pores and inter-particle voids cause discontinuities between nanoparticles inhibiting the mobility of charge carriers, resulting in relatively high electrical resistivity for conventional annealing [37]. During microwave-assisted annealing, rapid volumetric heating enhances densification and thus, resistivity is expected to decrease due to an increase in apparent surface area. Since this technique preserves nanostructures and the dimensions are matched with the minority charge carrier diffusion length, this enhances the probability that the charge carriers reach the interface before they recombine.

Increased preferential orientation along (002) plane, as evident from calculated tensile strain for microwave-assisted annealing, also contributes to the decreased electrical resistivity [38]. Such significant effect on resistivity by microwave-assisted annealing has also been reported by other researchers where the effect was found to be much more effective than not only for furnace annealing but also for rapid thermal annealing [39].

4 Conclusion

ZnO thin films were prepared by both conventional and microwave-assisted annealing to study the effect of microwave. Microwave-assisted annealing was found to preserve the nanostructures by rapid volumetric heating and resulted preferential orientation along (002) plane with induced tensile strain. The wide optical band gap with 86% average transmittance makes it quintessential for optoelectronic devices applications. Preserved nanostructure with less pores and voids, decreased crystallite size and induced tensile strain with preferential orientation along (002) plane resulted in lower electric resistivity for microwave-assisted annealing. Thus, the improved optoelectronic properties of ZnO thin films for microwave-assisted annealing with less power consumption would make it highly desirable for industrial scale up.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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