Research Paper

Effect of Post-Heat Treatment on the Properties of Sol-Gel Derived ZnO Thin Films for Transparent Electronics

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Abstract

Highly transparent and conducting sol-gel derived ZnO thin films were deposited using spin coating method onto a glass substrate. The deposited films were post-heated at different temperatures between 250°C and 550°C. The influence of post-heating temperatures on the optoelectronic properties were investigated. Experimental results showed the polycrystalline nature of the films with a hexagonal wurtzite structure, preferably oriented along c-axis. The crystallinity of the ZnO thin films improved after post-heat treatment. The average optical transmittance of the films increases from 67% to 89% as the post-heating temperature is increased from 250°C to 450°C. The Photoluminescence (PL) spectra shows a dominant UV emission peak around 378 nm due to free exciton emission and a broad peak at $\sim$ 522 nm is due to non-stoichiometric intrinsic defects. The electrical resistivity decreased after post-heat treatment. A minimum resistivity of 4.92 $\times 10^{-2}$ Ω cm was obtained after the film was heated at a temperature of 450°C. The results show that the post-heating treatment is a significant parameter which influences the properties of sol-gel derived ZnO thin films making it suitable for transparent electronics.

1   Introduction

ZnO is a multifunctional n-type semiconductor material due to its unique optical and electrical properties. It is a promising alternative TCO material for a high-cost ITO thin film and possess novel properties such as large exciton binding energy (60meV), wide and a direct band gap (3.37eV), high refractive index and excellent chemical and thermal stability [1-3]. Thin films of ZnO are widely used in the optoelectronic device applications such as organic light-emitting diodes(LED), liquid crystal displays (LCD), antireflection coating in the solar cell industry and transparent thin-film transistors, etc. [4-7]. These applications entail ZnO films with higher optical transmittance and lower resistivity over the visible wavelength region. It is well known that the quality and properties of thin films depend on various process parameters, such as the deposition rate, thickness of the film, the molar concentration of the starting solution and post-heat treatment, etc. Therefore, to enhance the functionality of ZnO thin films, the effect of preparation conditions and parameters on the properties has to be studied for its economic and effective technological applications.

A variety of techniques have been used to fabricate ZnO thin films such as pulsed laser deposition (PLD), RF/DC magnetron sputtering, chemical vapor deposition, sol–gel and spray pyrolysis, etc. [8–12]. Among these methods, the sol-gel spin coating technique has several benefits of controllability of compositions, simplicity in processing, safety, homogeneity and low cost of the equipment and raw materials. In the present study, we show that the post-heating treatment is an important parameter which enhances the optoelectronic properties of sol-gel derived spin coated ZnO thin films making it suitable for transparent electronics.

2   Experimental

ZnO thin films were deposited by the sol-gel spin coating method on a glass substrate (Corning 1737). Zinc acetate dehydrate $(Zn(COOCH_3)_2\text{-}2H_2O)$ was used as the starting salt material. 2-methoxyethanol and Monoethanolamine (MEA) were used as solvent and stabilizing agent, respectively. The molar ratio of MEA to zinc acetate was maintained at 1.0 and the total concentration of the sol was maintained at 0.5 mol L^{-1}. The solution was stirred at 50°C for 1 hour using a magnetic stirrer to form a clear and homogeneous solution. The glass substrate was cleaned using standard cleaning procedure and then ZnO films were spin-coated on the glass substrate at room temperature with a spinning rate of 3000 rpm for 30 seconds. The deposited thin films were preheated at 150°C for 10 min to evaporate the solvent and to remove organic residuals. The films with desired thickness were achieved by multiple spin-bake processes and then the films were post-heated at 250°C, 350°C, 450°C and 550°C in the air for an hour.

The crystalline structures and orientations of ZnO thin films were investigated by RigakuMiniflex 600 Table Top Powder X-ray diffractometer using Cu Kα radiation having a wavelength of 0.154059 nm. The surface topography of the films was studied using the atomic force microscope (AFM-Nanosurf Easy Scan 2). An Ellipsometer is used to measure the film thickness. Optical transmittance of the films was measured by a UV−visible spectrophotometer (SHIMADZU 1800) in the wavelength range 300-800 nm. The photoluminescence (PL) of the film was measured using a PL spectrometer. A He-Cd laser with a wavelength of 325 nm was used for the excitation of the samples. Electrical properties of the films were studied using the van der Pauw method and the Hall measurement system. The measurements were carried out in air and at room temperature.

3 Results and Discussion

3.1 Structural Properties

The X-ray diffractograms of ZnO thin films, post-heated at different temperatures are exhibited in Figure 1. XRD pattern shows that all the films have polycrystalline and hexagonal wurtzite structure with a (0 0 2) preferred orientation [13]. It is known that the preferred orientation is due to the internal stress and minimization of surface energy [14]. The c-axis orientation might have resulted from the lowest surface energy found along the (0 0 2) plane and the higher atomic packing density along the same plane[15]. The intensity of (0 0 2) peak gradually increased with the increasing post-heating temperature up to 450°C. This indicates that the crystallinity of ZnO films enhanced by increasing the post-heating temperature up to 450°C. A further increase in the temperature deteriorates the crystallinity of the film. The grain size of the film is calculated from the full width at half maxima (FWHM) of the (002) peak using the XRD patterns and Debye–Scherrer's formula [16]

$$D = \frac{0.9\lambda}{\beta cos\theta} \qquad (1)$$

where D is the grain size, λ is the X-ray wavelength (0.154059 nm), β is the full width at half maximum of the peak in radians and θ is the angle of diffraction. The larger D values indicate the improved crystallization of the thin film. The lattice constant 'c' can be calculated by the following formula:

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

The values of FWHM, grain size and the lattice constants are shown in Table 1. It can be seen that, when the post-heating temperature is increased from 250°C to 450°C, the FWHM decreases. The trend of FWHM values indicate the improved crystallinity and crystal size of the ZnO thin films. The reason for the increase in the grain size may be because; the thermal treatment leads to coalescence of small grains by grain boundary diffusion, which results in major grain growth [17]. The observed deviation of the lattice constants from the standard values

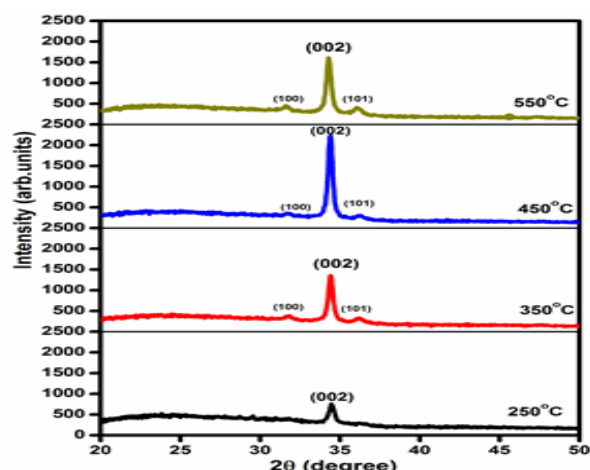of ZnO can be attributed to the presence of the lattice strain in the thin films.

Figure 1: XRD patterns of ZnO thin films post-heated at different temperature.

Table 1: Structural properties of ZnO thin films at different post-heating temperature.

Post-heating Temp.	FWHM (o)	D (nm)	d (Å)	C (Å)	S_a (nm)
250°C	0.332	25.074	2.599	5.199	22.346
350°C	0.304	27.360	2.603	5.206	12.834
450°C	0.294	28.223	2.605	5.210	6.293
550°C	0.302	27.513	2.615	5.230	11.982

Three-dimensional AFM images of ZnO films post-heated at different temperatures are depicted in Figure 2. It can be seen that the ZnO grains get more and more uniform when the post-heating temperature is increased from 250°C to 450°C and the surface roughness decreases steadily (Table 1). However, on further increase in the temperature, the grains become smaller and surface roughness increases. A rougher surface certainly leads to a more severe surface scattering, which in turn leads to a further decrease in the carrier mobility.
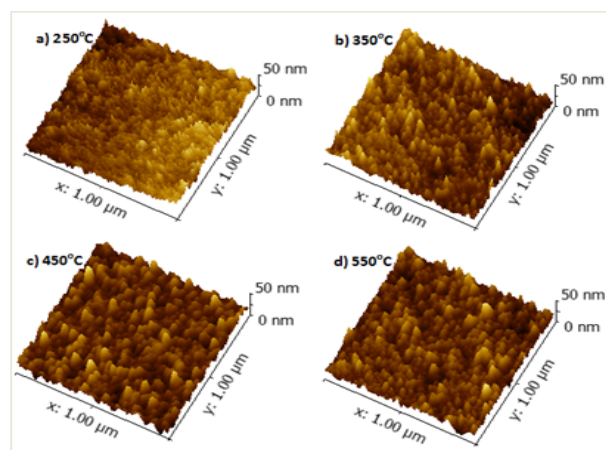

Figure 2: Three-dimensional AFM images of ZnO thin films deposited at different post-heating temperature.

3.2 Optical Properties

The optical transmittance spectra of the ZnO films deposited at various post-heating temperatures are compared in Figure 3(a). All the films exhibited transparency, higher than 67% in the visible region. The average transmittance was calculated from transmittance spectra between 350-800 nm wavelengths. It was found that the average transmittance of the films increases with post-heating temperature and can be attributed to an improvement in the crystallinity and the structural homogeneity of the films [18]. A blue shift of the absorption edge of the film was observed. This shift of the absorption edge may be ascribed to the difference in grain size.
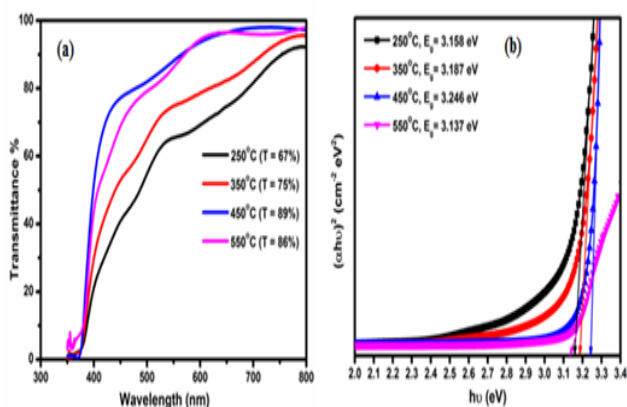

Figure 3: (a) Transmittance spectra (b) Plots $(\alpha h\upsilon)^2$ versus hυ of ZnO thin films with different post-heating temperatures.

The optical band gap value (E_g) can be obtained by the absorption coefficient (α) and photon energies (hυ) using the equation [19]

$$(\alpha h\upsilon)^2 = A(h\upsilon - E_g) \qquad (3)$$

where hυ is the energy of the incident photon and A is the absorption edge width parameter. The absorption coefficient can be estimated using the relation [20]

$$\alpha = \frac{2.303A}{d} \qquad (4)$$

where 'A' is the absorbance and 'd' is the film thickness of the film. The values of the direct band gap were determined by plotting $(\alpha h\upsilon)^2$ against hυ and by linear extrapolation of $(\alpha h\upsilon)^2$ on hυ axis (Figure 3(b)). It can be seen that the band gap extends from 3.156 eV up to ~3.239 eV as the post-heating temperature increases from 250°C up to 450°C. In general, changes in the optical band gap energy of films have been related to the internal stress, variations in the mean crystallite size, and/or the free carrier concentration [21–22]. For the present samples, the observed widening of the band gap might have resulted due to the changes in the carrier density, well known as Burstein-Moss effect [23].

The room temperature Photoluminescence (PL) spectra (Figure 4) shows a dominant UV emission peak around 378 nm (3.29 eV) and a broad green emission peak in the visible range 522-535 nm (2.38-2.32 eV). The band emission in the UV range is due to excitonic recombination, while the band emission existing at the visible range is due to the recombination of deep-level holes and electrons [24]. All of the deep-level emissions correlate to the defects arising during the growth of crystallites in the film and are related to the change of crystallinity due to zinc interstitials, zinc vacancies, oxygen interstitials, oxygen vacancies, and dislocations [25-26].
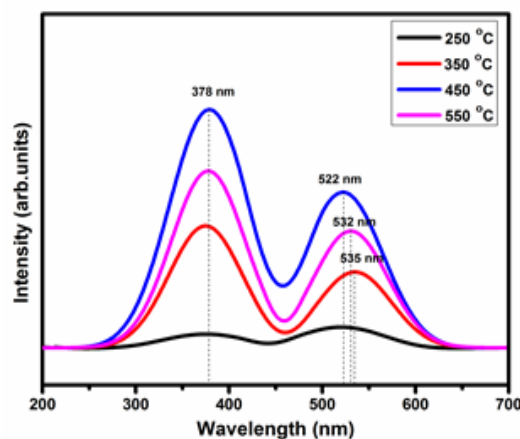

Figure 4: Room temperature PL spectra of ZnO thin films post-heated at different temperatures.

When the post-heating temperature increased to 450°C, the intensity of the UV emission peak is also increased. This indicates that the post-heating temperature improves the crystal quality by homogenizing the film. Post heating temperature also affects the broad green emission. The ZnO films post-heated at 450°C exhibits the strongest green emission compared to the other films. Generally, the green emission results from oxygen vacancy [27]. Therefore, the increase in the intensity of the green emission may be attributed to the increased concentration of oxygen vacancies in the zinc oxide films due to post-heating treatment. However, a further increase in the post-heating temperature decreases the oxygen vacancies and therefore the intensity of green emission decreases. The shift in the green emission band towards the blue region with an increase in post-heating temperature, confirms the widening of the energy band gap.

3.3 Electrical Properties

The variation of electrical resistivity, mobility and carrier concentration of ZnO films post-heated at different temperatures are shown in Figure 5.

It can be seen that the resistivity (ρ) decreases and the carrier concentration and mobility increase with increasing the post-heating temperature up to 450°C. It is well known that in nonstoichiometric ZnO the n-type conductivity is due to the presence of oxygen vacancies

and zinc interstitials. The reason may be because the electrical conductivity of ZnO directly depends on the electron density. Moreover, the electrons formed by the ionization of the interstitial zinc and the oxygen vacancies will affect the electrical conductivity of ZnO. Therefore, the decrease in electrical resistivity in the present study might have resulted from the increase in electron concentration in the film. A minimum resistivity of 4.92×10^{-2} Ω cm was obtained after the film was heated at a temperature of $450°C$ and the corresponding carrier concentration was 1.075×10^{-19} cm^{-3}. It can be observed that the mobility and the grain size are linearly dependent, resulting in high mobility for the larger grain size of the films.
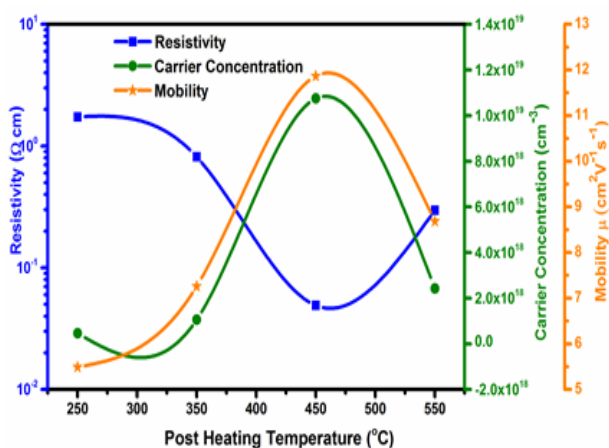

Figure 5: Variation of electrical properties of ZnO films post-heated at different temperatures.

4 Conclusions

Transparent and conducting ZnO thin films were deposited onto a glass substrate using sol-gel spin coating method. The effects of post-heating temperatures on the optoelectronic properties of the ZnO films were investigated. Experimental results showed that the post-heating temperature affected the morphological, electrical and optical properties of the films. Highly c-axis oriented ZnO thin films were obtained at $450°C$. The ZnO film post-heated at $450°C$ showed the maximum transmittance about 89% and minimum resistivity of 4.92×10^{-2} Ω cm. The results indicate that the post-heating treatment is an important parameter which influences the properties of sol-gel derived ZnO thin films for transparent electronics.

References

[1] B. Z. Dong, G. J. Fang, J. F. Wang, W. J. Guan and X. Z. Zhao, "Effect of thickness on structural, electrical, and optical properties of ZnO: Al films deposited by pulsed laser Deposition", J. Appl.Phys., vol. 101, pp.033713, 2007.

[2] B. Lin, Z. Fu and Y. Jia, "Green luminescent center in undoped zinc oxide films deposited on silicon substrates", Appl. Phys. Lett., vol. 79, pp. 943, 2001.

[3] T. V. Vimalkumar, N. Poornima, C. Sudha and K. P. Vijayakumar, "Effect of precursor medium on structural, electrical and optical properties of sprayed polycrystalline ZnO thin films", Mater.Sci. Eng., B, vol. 175, pp. 29-35, 2010.

[4]]C.Y. Tsay, K.S. Fan and C.M. Lei, "Synthesis and characterization of sol-gel derived gallium-doped zinc oxide thin films", J. Alloys Compd., vol. 512, pp.216–222, 2012.

[5] S. Benramache, F. Chabane and B. Benhaoua, "Influence of growth time on crystalline structure, conductivity and optical properties of ZnO thin films", J. Semicond., vol. 34, pp. 023001–023004, 2013.

[6] D.P. Norton, Y.W. Heo, M.P. Ivill, S.J. Pearton, M.F. Chisholm and T. Steiner, "ZnO: growth, doping processing", Mater. Today, vol. 7, pp. 34-40, 2004.

[7] F. Chowdhury, S.M. F-Hasan and M.S. Alam, "Morphological and optical properties of vacuum evaporated ZnO thin films", Turk. J. Phys., vol. 36, pp. 1-7, 2012.

[8] J. Mass, P. Bhattacharya and R.S. Katiyar, "Effect of high substrate temperature on Al-doped ZnO thin films grown by pulsed laser deposition", Mater. Sci. Eng. B, vol. 103, pp. 9, 2003.

[9] R.O. Ndong, H.Z. Moussambi and H. Gnanga, "Optical properties of ZnO thin films deposed by rf magnetron", Phys. Sci., vol. 10, pp. 173–181, 2015.

[10]]N. Nithya and S.R. Radhakrishnan, "Effect of thickness on the properties ZnO thin films", Appl. Sci. Res.,vol. 3, pp. 4041−4047, 2012.

[11] M. Wang, J. Wang, W. Chen, Y. Cui, L. Wang, "Effect of preheating and annealing temperatures on quality characteristics of ZnO thin film prepared by sol–gel method", Mater. Chem. Phys., vol. 97, pp. 219-225, 2006.

[12] P. Nunes, E. Fortunato and R. Martins, "Influence of the annealing conditions on the properties of ZnO thin films", Int. J. Inorg. Mater., vol. 3, pp. 1125-1128, 2001.

[13] B.Z. Dong, G.J. Fang, J.F. Wang, J.W. Guan and X.Z. Zhao, "Effect of thickness on structural, electrical, and optical properties of ZnO: Al films deposited by pulsed laser deposition", J. Appl. Phys., vol. 101, pp. 033713-2, 2007.

[14] D. Bao, H. Gu and A. Kuang, "Sol-gel-derived c-axis oriented ZnO thin films", Thin Solid Films, vol. 312, pp. 37-39, 1998.

[15] S. Amirhaghi, V. Craciun, D. Craciun, J. Elders and I.W. Boyd, "Low temperature growth of highly transparent c-axis oriented ZnO thin films by pulsed laser deposition", Microelectron. Eng., vol. 25, pp. 321-326, 1994.

[16] B. D. Cullity, "Elements of X-ray Diffraction", Addison-Wesley, pp. 102, 1978.

[17] V. Gupta and A. Mansingh, "Influence of postdeposition annealing on the structural and optical properties of sputtered zinc oxide film", J.Appl.phys., vol. 80, pp. 1063,1996.

[18] R. Al Asmar, D. Zaouk, Ph.Bahouth, J. Podleki and A. Foucaran, "Characterization of electron beam evaporated ZnO thin films and stacking ZnO fabricated by e-beam evaporation and rf magnetron sputtering for the realization of resonators", Microelectronic Engineering vol. 83, pp. 393-8, 2006.

[19] M. Girtan and G. Folcher, "Structural and optical properties of indium oxide thin films prepared by an ultrasonic spray CVD process", Surf. Coat. Technol., vol. 172, pp. 242-250, 2003.

[20] S.Suwanboon, P. Amornpitoksuk, A. Haidoux and J.C. Tedenac, "Structural and optical properties of undoped and aluminium doped zinc oxide nanoparticles via precipitation method at low temperature", J. Alloys Compd., vol. 462, pp. 335–339, 2008.

[21] M. Bouderbala, S. Hamzaoui, M. Adnane, T. Sahraoui and M. Zerdali, "Annealing effect on properties of transparent and conducting ZnO thin films", Thin Solid Films, vol. 517, pp. 572–576, 2009.

[22] S.S. Lin and J.L. Huang, "Effect of thickness on the structural and optical properties of ZnO films by rf magnetron sputtering", Surf. Coat. Technol., vol. 185, pp. 222–227, 2004.

[23] F. Paraguay, W. Estrada, D. R. Acosta, E. Andrade and M. Miki-Yoshida, "Growth, Structure and Optical Charac- terization of High Quality ZnO Thin Films Obtained by Spray Pyrolysis", Thin Solid Films, vol. 350, pp. 192-202, 1999.

[24] R.Hong, H. Qi, J. Huang, H. He, Z. Fan, and J. Shao, "Influence of oxygen partial ressure on the structure and photoluminescence of direct current reactive magnetron sputtering ZnO thin films", Thin Solid Films, vol. 473, pp. 58–62, 2005.

[25] A. B. Djurisic, W. C. H. Choy and V. A. L. Roy et al., "Photoluminescence and electron paramagnetic resonance of ZnO tetrapod structures", Advanced Functional Materials, vol. 14, pp. 856–864, 2004.

[26] Pramod Sagar, P.K. Shishodia, R.M. Mehra, H. Okada, Akihiro Wakahara, Akira Yoshida, "Photoluminescence and absorption in sol–gel-derived ZnO films", J. Lumin., vol. 126, pp. 800, 2007.

[27] K. Vanheusden, W.L. Warren and C.H. Seager et al. "Mechanisms behind green photoluminescence in ZnO phosphor powders", J. Appl. Phys., vol. 79, pp. 7983, 1996