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Influence of post-annealing condition on the properties of ZnO films

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Abstract

The study of the properties of zinc oxide (ZnO) films has gained popularity recently due to its potential in a wide range of applications, such as thin-film solar cells, transistors, sensors and other optoelectronic devices. In this work, low cost sol–gel spin coating technique was employed to fabricate the ZnO films. The influences of post-annealing condition on the properties of the ZnO films were investigated. The ZnO films were annealed under ambient, nitrogen and vacuum environments at 450 °C and the environment effects on the ZnO films were compared. Furthermore, the effect of cooling period allowed for the ZnO films after the post-annealing process was examined. The ZnO films were characterized using surface profilometer, atomic force microscopy, X-ray diffractometer, and ultraviolet–visible transmission spectroscopy in order to study the thickness, surface morphology, crystallinity, and optical properties of the ZnO films. The optical band gap of the ZnO films was estimated based on the thickness and the optical transmittance data. These investigations serve to clarify the effects of different post-annealing conditions in order to optimize the properties of the ZnO films.

Keywords: A. Sol–gel process; B. X-ray methods; C. Optical properties; D. ZnO

1. Introduction

Zinc oxide (ZnO) film features a wide band gap of 3.37 eV and high excitonic binding energy of 60 meV at room temperature, which has received an increasing demand for various applications including opto–electronic devices, sensors, and thin film solar cells [1]. Various growth techniques can be used to fabricate the ZnO films. The common methods are pulsed laser deposition [2], molecular beam epitaxy [3], metal-organic chemical vapor deposition [4], and sputtering deposition [5]. These fabrication techniques require sophisticated equipment and often result in higher manufacturing cost. The sol–gel spin coating method offers a simple, easy to control, and cost efficient way to fabricate ZnO films [6]. This method consists of a few stages which are: preparation of solution, spin coating, pre-heating and post-annealing process. Processing parameters can be altered to produce films with different properties. Precursor concentration [7], substrate types and annealing temperature [8] are among the popular parameters that have been studied intensively in the last few years. Nunes et al. [9] had conducted a research on the effect of annealing treatment under forming gas (95% N_2+5% H_2), vacuum and air on ZnO films based on spray pyrolysis method. Their findings showed that annealing treatment under forming gas yields better quality ZnO films. In the present investigation, the objective was to elucidate the influences of post-annealing environment and the cooling period after the annealing treatment on the crystallinity, structural and optical properties of the ZnO films deposited by sol–gel spin coating method.

2. Experimental

The ZnO solution was prepared with a mixture of zinc acetate dihydrate [$Zn(CH_3COO)2.2H_2O$], isopropanol (IPA) [C_3H_3OH], and monoethanolamine (MEA) as precursor, solvent, and stabilizer, respectively. The ZnO concentration was maintained at 0.5 Mol (M) while the molar ratio of precursor and MEA was kept at 1:1. The solution was then stirred on a hot-plate for 2 h, and was left for ageing process for 22 h. Next, the solution was spin-coated on glass substrates. Finally, the film was

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post-annealed at 450 °C in furnace under ambient, nitrogen, and vacuum environments for 1 h. Different cooling periods were tested in order to identify the best cooling duration. The ZnO films were characterized using surface profilometer, atomic force microscopy (AFM), X-ray diffractometer (XRD), and ultraviolet–visible (UV–vis) transmission spectroscopy to examine the thickness, surface morphology, crystallinity, and optical properties of the ZnO films, respectively. The optical band gap of the ZnO films was estimated based on the thickness and optical transmittance data.

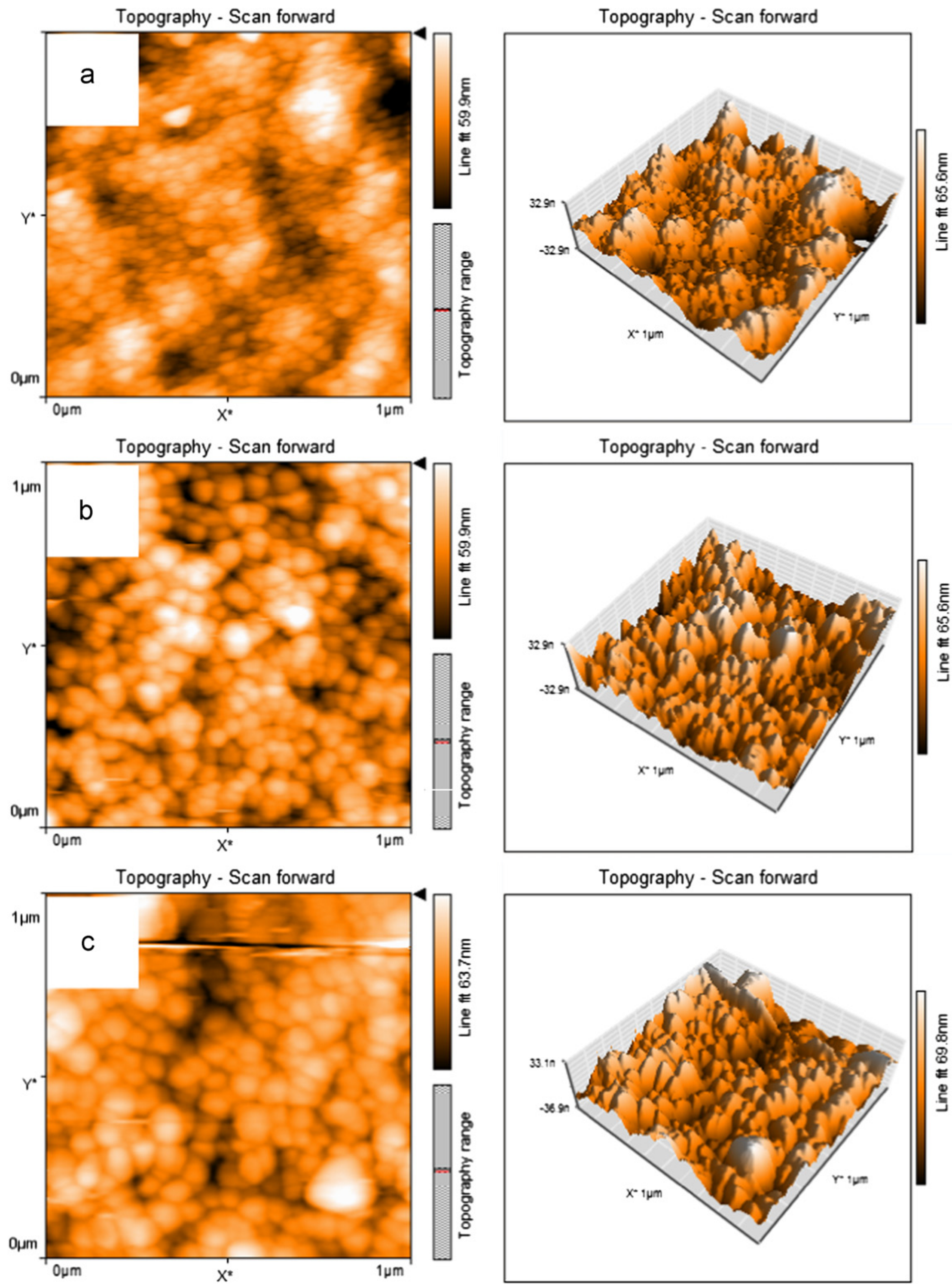

Fig. 1. AFM images of ZnO films annealed in (a) vacuum, (b) nitrogen, and (c) ambient environments.

3. Results and discussions

3.1. Post-annealing environment

The surface morphology of the ZnO films captured by AFM is shown in Fig. 1. It is found that the surface consists of randomly distributed granular structure. All films have thickness of around 500 nm.

It was observed that the films annealed in ambient and nitrogen environments have developed slightly larger grains as compared to the film annealed in vacuum environment. The lack of oxygen atoms in vacuum environment may be the cause of smaller grain size as the adsorption of oxygen atoms on the film's surface contributes to the development of ZnO granular structure [10].

Fig. 2 shows the XRD patterns on ZnO films post-annealed in different environments. All films are polycrystalline in nature with hexagonal wurtzite ZnO structure. The XRD patterns reveal high intensity peaks representing the (100), (002), and (101) on the diffraction planes, which corresponds to the peaks of standard ZnO (JCPDS no. 751526). Higher peaks can be seen on the films annealed in nitrogen and ambient environments, which implies higher crystallinity. However, the ZnO film annealed in vacuum environment exhibited weaker peaks. This may be due to the absence of the oxygen gas. Oxidation is defined as the interaction between oxygen molecules and the substances they may contact. It is an important factor in forming metal oxide layer including ZnO films and the ozone atmosphere acts as an effective oxidizing agent [11].

The optical transmittance spectra of the ZnO films are shown in Fig. 3. The average optical transmittance of the ZnO films is approximately 80% of the visible light. It is observed that the annealing environment neither affects the transmittance nor the absorption edge. The optical band gap of the ZnO films estimated using Tauc method is 3.25 eV, which is close to the band gap of intrinsic ZnO of 3.37 eV [12].

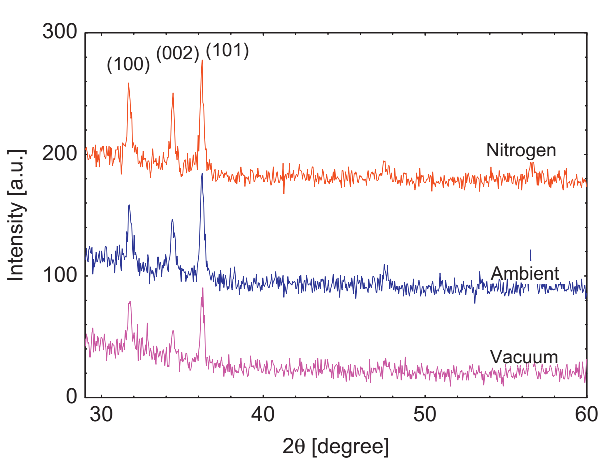

Fig. 2. XRD patterns of ZnO films annealed in different environments.

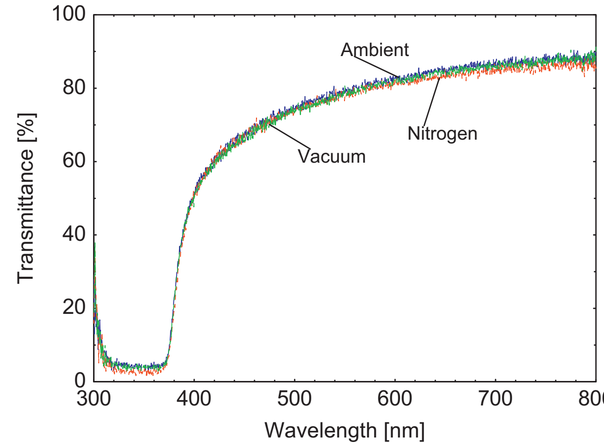

Fig. 3. Transmittance spectra of ZnO films annealed in different environments.

3.2. Cooling period

The AFM images of the films with cooling period 0, 6, and 12 h after annealing process are shown in Fig. 4. All films were annealed under ambient environment and were cooled at the average rate of 1 °C/min. A significant change on the surface morphology with longer cooling period of 12 h can be observed. The prolonged cooling period may have contributed to the excessive agglomeration of the structure from fine grains to bigger grains. Such effect could be critical in the sensor applications, where the sensitivity of the sensor is mostly affected by the topology of the film's surface.

The XRD patterns in Fig. 5 shows slight decrease on the peaks with extended cooling period. The preferential crystal growth may have halted due to the decreasing temperature during cooling period and therefore it does not further improve the crystallinity of the films. Instead of this, the longer cooling period may have degraded the crystallinity of ZnO films due to the formation of random structures [13]. Furthermore, the extended cooling period may lead to the association of contaminants into the ZnO structure under elevated temperature environment [14].

In Fig. 6, the increasing cooling period has decreased the slope of the absorption edge and lowers down the overall optical transmittance. This may be due to the formation of random structures and the incorporation of the contaminants with extended cooling period, as suggested above [13,14].

4. Conclusion

In this work, ZnO films were fabricated with low cost sol–gel spin coating technique. The influence of post-annealing condition was elucidated. The ZnO films post-annealed in ambient and nitrogen environments have developed more promising characteristics, such as larger grain size and stronger peaks on *c*-axis orientation, as

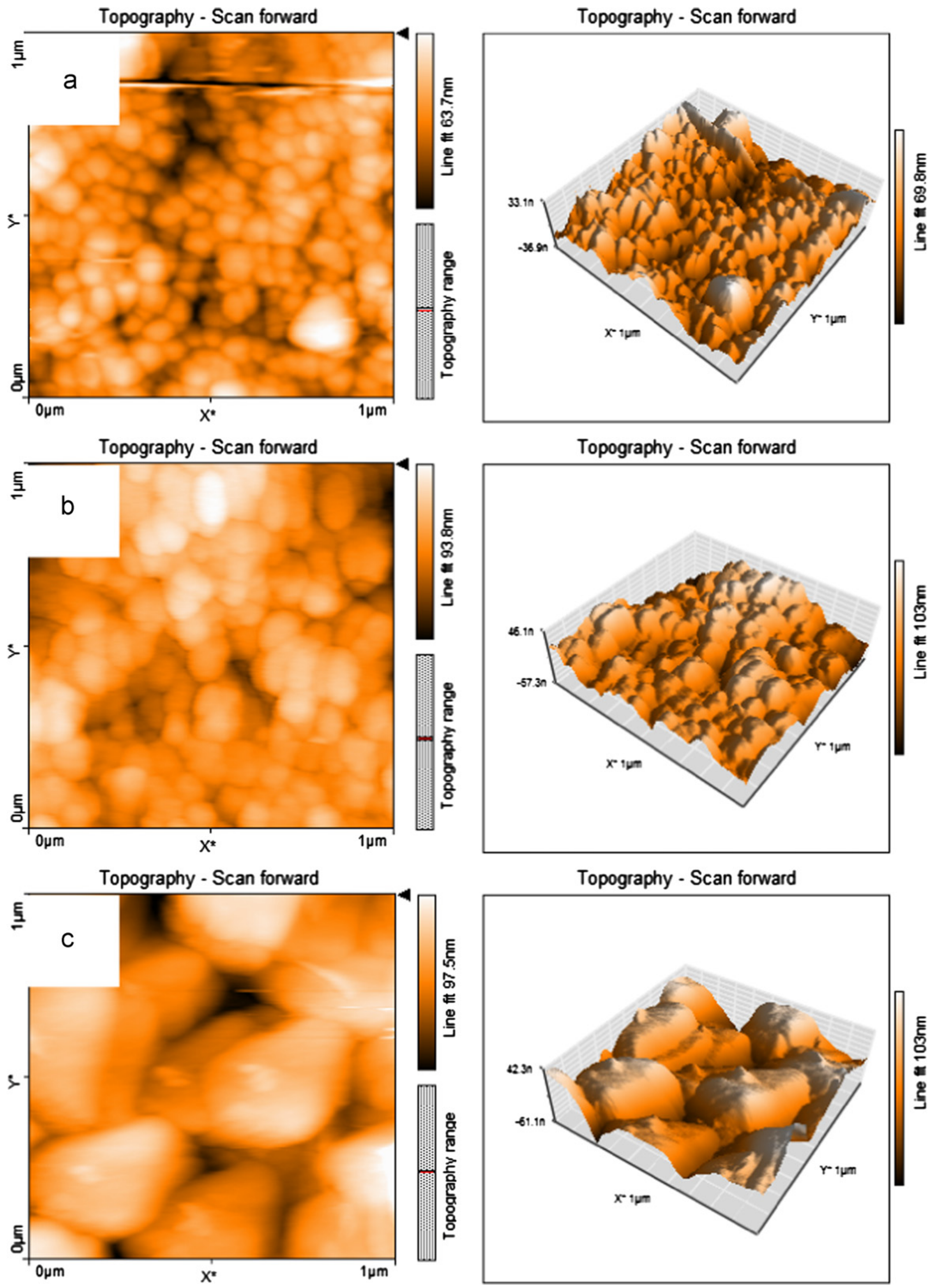

Fig. 4. AFM images of ZnO films cooled for (a) 0, (b) 6, and (c) 12 h.

shown in AFM and XRD results, respectively. However, the annealing environment has no significant effects on the optical properties. In the cooling period investigation, the grains grow as the cooling period is lengthened. This may due to the agglomeration of the structure from fine grains to bigger grains when the films undergo longer cooling period inside the furnace. However the XRD and the optical transmittance results show slight degradation over prolonged cooling period. Therefore it is recommended to shorten the cooling process. In conclusion, this paper has

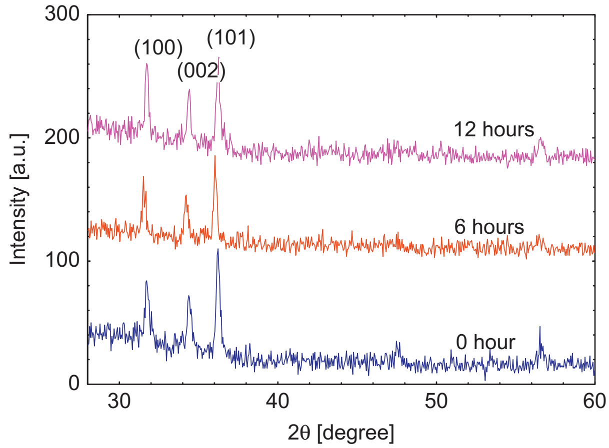

Fig. 5. XRD patterns of ZnO films with different cooling periods.

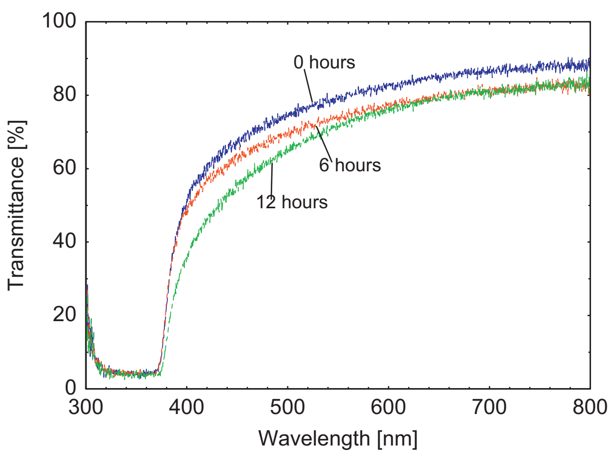

Fig. 6. Transmittance spectra of ZnO films with different cooling periods.

demonstrated significant role of annealing environment and cooling period in the sol–gel fabrication of ZnO films.

Acknowledgments

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