Sains Malaysiana 40(3)(2011): 209–213

Effects of Annealing Conditions on the Surface Morphology and Crystallinity of Sputtered ZnO Nano Films

(Kesan Keadaan Penyepuhlindupan Terhadap Morfologi Permukaan dan Kehabluran Filem Nano ZnO yang Dipercik)

J. KARAMDEL, C.F. DEE* & B. YEOP MAJLIS

ABSTRACT

The effects of annealing parameters on crystallinity and surface morphology of RF sputtered zinc oxide nano films were investigated. The structure and morphology of the nano films were dependent on temperature, gas flow rate and time of annealing. The results from atomic force microscopy (AFM), field emission scanning electron microscopy (FESEM) and X-ray diffraction (XRD) showed smooth and uniform growth of c-axis orientation films with an average grain sizes from 10 to 30 nm. Increments of the annealing temperature from 400 to 800°C led to bigger grain size, better crystallinity and also increase of the surface roughness. Moreover, the results showed that the crystallinity was independent of the annealing time up to 40 min after starting the annealing process. Increase in the percentage of oxygen in the O/Ar (mixture of annealing gases) from 50% to 100% results in no changes in AFM results, but XRD revealed that the (100) peak intensity was decreased, the position of (002) peak was slightly shifted towards higher angle and FWHM of (002) peak was improved.

Keywords: Annealing; sputtering; ZnO nano film

ABSTRAK

Kesan pelbagai parameter penyepuhlindapan terhadap morfologi permukaan dan kehabluran bagi filem nano ZnO yang dipercik secara RF telah dikaji. Struktur dan morfologi nanofilem ini bergantung pada suhu, kadar aliran gas dan masa bagi proses sepuhlindapan. Keputusan daripada mikroskop daya atom (AFM), mikroskop elektron imbasan jenis pancaran medan (FESEM) dan pembelauan sinaran-X (XRD) menunjukkan filem-filem berorientasi pada paksi-c adalah licin dan seragam dengan butiran bersaiz purata daripada 10 ke 30 nm. Peningkatan suhu sepuh lindapan daripada 400 ke 800°C memberi saiz butiran yang lebih besar, kehabluran yang lebih baik namun menambahkan kekasaran permukaan. Hasil kajian juga menunjukkan kehabluran tidak bergantung kepada masa sepuh lindapan sehingga 40 min selepas permulaan proses penyepuhlindapan. Apabila ditambahkan peratusan oksigen dalam O/Ar (campuran gas penyepuhlindupan) daripada 50% menjadi 100%, didapati tiada perubahan pada keputusan AFM tetapi keputusan XRD menunjukkan bahawa keamatan puncak (100) telah berkurangan, kedudukan puncak (002) sedikit menganjak ke arah sudut lebih besar dan FWHM bagi puncak (002) bertambah baik.

Kata kunci: Nanofilem ZnO; percikan; sepuh lindap

INTRODUCTION

Thin films of transparent conductive oxides play essential roles in a wide range of nanoelectronic and optoelectronic applications such as sensors, solar cells, flat panel displays and piezoelectric (Kang et al. 2005; Lee et al. 2004; Poortmans & Arkhipov 2006). Particularly, zinc oxide with a wide direct band gap around 3.37 eV and other physical properties is a promising material for light emitting diodes (LEDs), transistors and microelectronic devices (Dang et al. 2007; Dee et al. 2008). Also due to its large exciton binding energy (60 meV), ZnO structures are suitable candidates for producing UV light emitting devices with better efficiency compared to other competitive materials (Jeong et al. 2003; Kang et al. 2003; Kim et al. 2008; Lee et al. 2005; Lin et al. 2006). Moreover, crystalline ZnO films with hexagonal wurtzite structure can be used as buffer layer for epitaxial growth of subsequent layers or nanorods (Bang et al. 2003; Eom et al. 2008; Lin et al. 2008; Wang et al. 2005). It is reported that ZnO buffer layers offer advantages such as lattice-match, no metal catalysts and cost-effective (Bang et al. 2003; Wang et al. 2005; Wellings et al. 2008). For realizing and developing these applications based on ZnO thin films, we need highly preferred *c*-axis orientation and highly stable crystal of ZnO.

In order to satisfy these conditions, different methods have been employed to deposit ZnO films including sol-gel (Ghamsari & Vafaee 2008), molecular beam epitaxy (MBE) (Tang et al. 1998), metal organic chemical vapor deposition (MOCVD) (Gorla et al. 1999), pulsed laser deposition (Jin et al. 2000) and RF magnetron sputtering (Dang et al. 2007; Hamzah et al. 2008). Among these methods, RF magnetron sputtering has the advantages of simplicity and working in desired temperature. However, it is reported that the quality of as-sputtered ZnO films is low and a post annealing process can improve the crystallinity of ZnO thin films (Alivov et al. 2006; Özgur et al. 2005; Shan et al. 2005). Therefore, besides the sputtering conditions, the annealing factors such as temperature, gas types, gas flow rate and time are indeed important parameters for ZnO thin films deposition.

In this article, we deposited ZnO thin films on Si substrates by using RF magnetron sputtering method and subsequently annealed in different conditions. The effects of annealing conditions on the properties of the film have been investigated.

Experimental Details

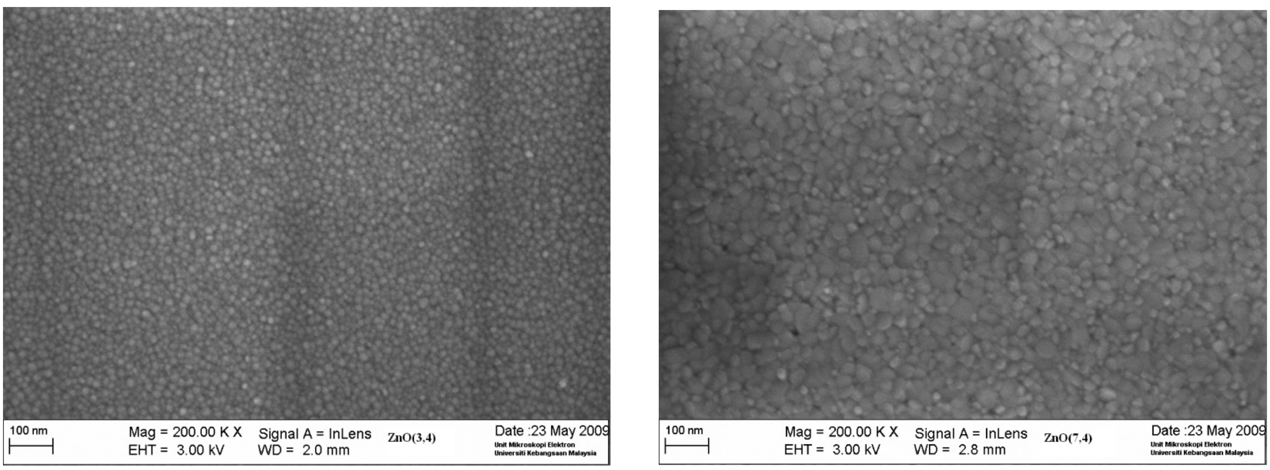
RF magnetron sputtering was employed to deposit a thin layer of ZnO on Si substrates. The substrates were cleaned in an ultrasonic bath with methanol, acetone and isopropyl alcohol for 20 min. To remove any native oxide from the surface they were cleaned with HF acid and rinsed with DI water, respectively. The cleaned Si substrates were loaded into the chamber and thin film of ZnO with approximately 60 nm thickness was deposited. The target was a 15.36 cm diameter ZnO with purity of 99.99% reacted with the pure 99.99% argon gas. The flow rate of argon gas was 25 sccm and the target to substrate distance was 12 cm. The RF power was 150 watts and sputtering pressure was fixed on 12 mtorr. The chamber was evacuated down to base pressure around 10^{-6} torr using a turbo pump. The target was pre-sputtered for 15 min with the shutter closed to clean the surface of target. Then the shutter was opened and ZnO was deposited on the Si substrate in which the temperature of substrate holder was 100°C. The as deposited substrates having uniform thickness of ZnO over whole the surface were divided into equal pieces. Subsequently the films were annealed in horizontal furnace with different conditions.

The effects of temperature, oxygen/argon gas flow rate and duration of annealing were studied. Field emission scanning electron microscopy (FESEM) measurements were performed in order to study the surface structure and morphology of samples. X-ray diffraction (XRD) measurements were carried out to investigate the crystallization of the ZnO thin films and the surface morphology of samples was characterized by using atomic force microscopy (AFM).

Results and Discussion

Surface morphology of samples were studied by FESEM (Zeiss model SUPRA 55VP). The typical FESEM results of samples annealed at 400°C and 800°C are shown in Figure 1(a) and 1(b), respectively. It can be seen that by increasing the annealing temperature from 400°C to 800°C, the average grain size of ZnO films increased from 10 to 30 nm.

X-ray diffraction patterns of the samples were investigated by Panalytical Diffractometer system (XPERT-PRO). Shown in Figure 2 are the XRD patterns of ZnO thin films which were annealed at different temperatures. The diffraction peak around 30.87° corresponding with the index of (100), together with the diffraction peak around 34.4° corresponding with the indexes of (002) (ICCD-PDF NO. 01-075-1533) are clearly observed. The predomination of (002) peak in the pattern proved that the ZnO nano films have wurtzite crystalline structures with a preferential orientation along the c-axis and without formation of any secondary phases. The XRD patterns indicated that the grown nano films had a weak c-axis orientation, but increment of annealing temperature led to superior and narrower diffraction peaks with smaller full width at half maximum (FWHM), which correspond with increase in crystallite sizes and qualities. The increase of annealing temperature from 400 to 800°C increased the (002) peak intensity, while decreased slightly those of the (100) orientation. Furthermore, the peak (002)



(a) (b)

FIGURE 1. Top-view FESEM images of the ZnO thin film on Si substrates with different annealing temperatures of (a) 400°C and (b) 800°C

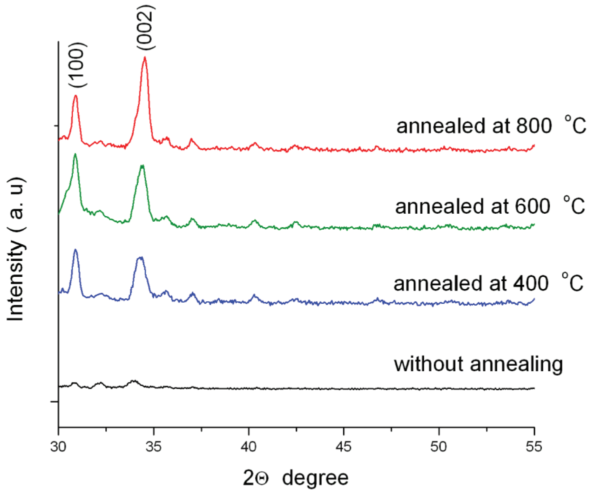


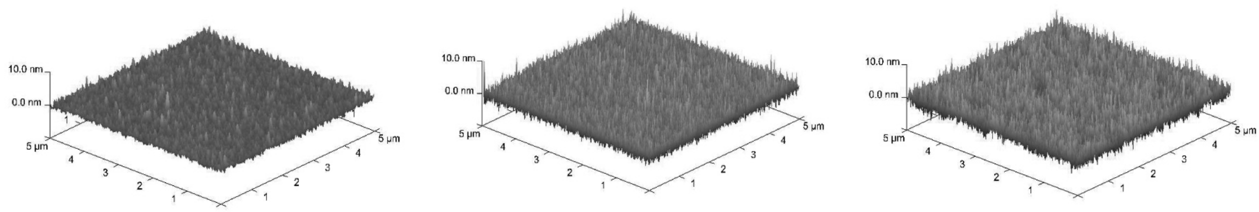
FIGURE 2. XRD patterns of the as deposited and annealed ZnO thin films at different temperatures.

was slightly shifted towards higher angle by increasing the annealing temperature. The rise of (002) peak intensity and shift in position of (002) peak can be attributed to better crystallinity with more relaxation caused by annealing.

The surface of as deposited and annealed samples was imaged by AFM. The results illustrated in Figures 3(a) to 3(c) show smooth and uniform surfaces for all samples, which are consistent with the FESEM results. The roughness measurements of samples revealed that the average roughness of ZnO thin films increased with temperature, in which, the average roughness of 0.5, 0.9 and 1.1 nm have been measured for as sputtered, annealed at 400°C and at 800°C, respectively. As a result, higher annealing temperature resulted in a uniform surface with more roughness, which is suitable for using thin film as a buffer layer for growth of nano wires (Wang et al. 2005).

To study the effect of annealing time on morphology and crystallinity of ZnO thin films, sputtered samples were annealed for various periods. XRD patterns showed that after 40 min, no changes were observed in crystallinity of annealed samples. However, the AFM results revealed that the surface of samples became smoother when annealing time was increased up to 2 h. Smoother surface is preferred in solar cell applications and device fabrications (Bang et al. 2003).

In order to investigate the influence of annealing atmosphere on the properties of ZnO thin films, the percentage of O_2 in O_2/Ar inlet gases was varied from 50% to 100%, with each annealing process lasted for 1 h. Figure



(a) (b) (c)

FIGURE 3. Typical AFM images of (a) as sputtered, (b) annealed at 400°C and (c) annealed at 800°C ZnO thin films exhibited average roughness of 0.5 nm, 0.9 nm and 1.1 nm, respectively

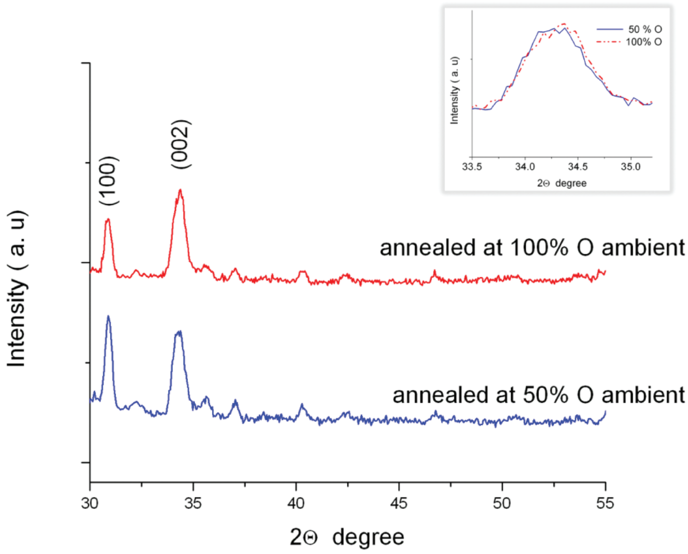


FIGURE 4. The XRD patterns of ZnO thin films which were annealed at different gas flow rates. The inset demonstrates a small shift of (002) peak

4 shows the XRD patterns of specimens which have been annealed at different gas flow rates. Figure 4 reveals that by increasing the O_2 percentage, the (100) peak intensity is decreased, the position of (002) peak is slightly shifted towards higher angels (the inset of Figure 4 exhibits the amount of this shift around 0.1° and the FWHM of (002) orientation was improved, but no affect was observed on AFM results. It is suggested that rich O_2 causes lower oxygen vacancy (V_O), which results in better crystallinity with lower defects.

Conclusion

The ZnO nano films were prepared on Si substrates by RF magnetron sputtering and then were annealed at different conditions. FESEM, XRD and AFM have been used for characterization of the films morphologies and crystal structures. Increment of the annealing temperature from 400 to 800°C leads to larger grain size, better crystallinity and also increment of the surface roughness, which is suitable for using thin film as a buffer layer for growth of nano wires. After 40 min of annealing, the crystallinity was independent of annealing time, but the AFM results revealed that the roughness of samples become better when annealing time was increased up to 2 h which is preferred in solar cell applications and thin film device fabrications. The percentage of oxygen in the O/Ar, was varied from 50%t to 100%. No changes were observed in AFM results but the peak intensities decreased by increasing the percentage of oxygen. It can be concluded that the ZnO thin films with desired properties can be achieved with certain annealing conditions.

Acknowledgements

The authors thank the Higher Education Ministry of Malaysia and Islamic Azad University-South Tehran Branch of Iran for their financial supports of this work.

References

Alivov, Y.I., Bo, X., Akarca-Biyikli, S., Fan, Q., Xie, J., Zhu, N. Biyikli, K., Johnstone, D. & Morkoc, H. 2006. Effect of annealing on electrical properties of radio-frequency-sputtered ZnO films. *Journal of Electronic Materials* 35(4): 520-524.

Bang, K.H., Hwang, D.K. & Myoung, J.M. 2003. Effects of ZnO buffer layer thickness on properties of ZnO thin films deposited by radio-frequency magnetron sputtering. *Applied Surface Science* 207(1-4): 359-364.

Dang, W.L., Fu, Y.Q., Luo, J.K., Flewitt, A.J. & Milne, W.I. 2007. Deposition and characterization of sputtered ZnO films. *Superlattices and Microstructures* 42(1-6): 89-93.

Dee, C.F., Majlis, B. Yeop & Salleh, M. Mat. 2008. Electrical characterization of cross-linked ZnO nanostructures grown on Si and Si/SiO_2 substrates. *Sains Malaysiana* 37(3): 281-283.

Eom, S.H., Senthilarasu, S., Uthirakumar, P., Hong, C.H., Lee, Y. S., Lim, J., Yoon, S.C., Lee, C. & Lee, S. H. 2008. Preparation and characterization of nano-scale ZnO as a buffer layer for inkjet printing of silver cathode in polymer solar cells. *Solar Energy Materials and Solar Cells* 92(5): 564-570.

Ghamsari, M. & Vafaee, M. 2008. Sol-gel derived zinc oxide buffer layer for use in random laser media. *Materials Letters* 62: 1754-1756.

Gorla, C.R., Emanetoglu, N.M., Liang, S., Mayo, W.E., Lu, Y., Wraback, M. & Shen, H. 1999. Structural, optical, and surface acoustic wave properties of epitaxial ZnO films grown on (012) sapphire by metalorganic chemical vapour deposition. *Journal of Applied Physics* 85(5): 2595.

Hamzah, A.A., Yunas, J., Majlis, B.Y. & Ahmad, I. 2008. Sputtered encapsulation as wafer level packaging for isolatable MEMS devices: A technique demonstrated on a capacitive accelerometer. *Sensors* 8(11): 7438-7452.

Jeong, M.C., Hwang, D.K., Myoung, J.M., Ko, Y.D., Kim, M.S. & Yun, I. 2003. The formation of p-type ZnO films by using a diffusion process. *Defect and Diffusion Forum* 218-220: 17-22.

Jin, B.J., Im, S. & Lee, S.Y. 2000. Violet and UV luminescence emitted from ZnO thin films grown on sapphire by pulsed laser deposition. *Thin Solid Films* 366(1-2): 107-110.

Kang, D.J., Kim, J.S., Jeong, S.W., Roh, Y., Jeong, S.H. & Boo, J.H. 2005. Structural and electrical characteristics of R.F. magnetron sputtered ZnO films. *Thin Solid Films* 475:160-165.

Kang, H.S., Kang, J.S., Pang, S.S., Shim, E.S. & Lee, S.Y. 2003. Variation of light emitting properties of ZnO thin films depending on post-annealing temperature. *Materials Science and Engineering B* 102(1-3): 313-316.

Kim, Y.Y., Ahn, C.H., Kang, S.W., Kong, B.H., Mohanta, S.K., Cho, H.K., Lee, J.Y. & Kim, H.S. 2008. Temperature dependence of ZnO thin films grown on Si substrate. *Journal of Materials Science: Materials in Electronics* 19(8-9): 749-754.

Lee, H.S., Lee, J.Y., Kim, T.W., Kim, D.W. & Cho, W.J. 2004. Formation mechanism of preferential c-axis oriented ZnO thin films grown on p-Si substrates. *Journal of Materials Science* 39(10): 3525-3528.

Lee, S.Y., Shim, E.S., Kang, H.S., Pang, S.S. & Kang, J. 2005. Fabrication of ZnO thin film diode using laser annealing. *Thin Solid Films* 473(1): 31-34.

Lin, P.Y., Gong, J. R., Li, P. C., Lin, T.Y., Lyu, D.Y., Lin, D.Y., Lin, H.J., Li, T.C., Chang, K.J. & Lin, W.J. 2008. Optical and structural characteristics of Zno films grown on (0001) sapphire substrates by ALD using DEZn and N_2O. *Journal of Crystal Growth* 310(12): 3024-3028.

Lin, Y.S., Hsu, K.C. & Huang, Y.M. 2006. Surface roughness of sputtered ZnO films. *Physica Scripta* (T126): 68-71.

Liu, C.P., Wang, R.C., Kuo, C.L., Liang, Y.H. & Chen, W.Y. 2007. Recent patents on fabrication of nanowires. *Recent Patents on Nanotechnology* 1(1): 11-20.

Özgür, Ü., Alivov, Ya. I., Liu, C., Teke, A., Reshchikov, M.A., Doğan, S., Avrutin, V., Cho, S.-J. & Morkoç, H. 2005. A comprehensive review of ZnO materials and devices. *Journal of Applied Physics* 98: 041301.

Poortmans, J. & Arkhipov, V. 2006. *Thin Film Solar Cells Fabrication, Characterization and Applications*. New Jersey: John Wiley & Sons Inc.

Shan, F.K., Liu, G.X., Lee, W.J., Lee, G.H., Kim, I.S. & Shin, B.C. 2005. Aging effect and origin of deep-level emission in ZnO thin film deposited by pulsed laser deposition. *Applied Physics Letters* 86: 221910.

Tang, Z.K., Wong, G.K.L., Yu, P., Kawasaki, M., Ohtomo, A., Koinuma, H. & Segawa, Y. 1998. Room-temperature ultraviolet laser emission from self-assembled ZnO microcrystallite thin films. *Applied Physics Letters* 72: 3270.
Wang, L., Zhang, X., Zhao, S., Zhou, G., Zhou, Y. & Qi, J. 2005. Synthesis of well-aligned ZnO nanowires by simple physical vapor deposition on c-oriented ZnO thin films without catalysts or additives. *Applied Physics Letters* 86: 024108.
Wellings, J.S., Chaure, N.B., Heavens, S.N. & Dharmadasa, I.M. 2008. Growth and characterization of electrodeposited ZnO thin films. *Thin Solid Films* 516: 3893-3898.

J. Karamdel, C.F. Dee* & B. Yeop Majlis
Institute of Microengineering and Nanoelectronics (IMEN)
Universiti Kebangsaan Malaysia
43600 Bangi, Selangor D.E.
Malaysia

J. Karamdel
Electrical Department
Faculty of Engineering
Islamic Azad University – South Tehran Branch
No. 209, North Iranshahr Ave, Tehran
Iran

*Corresponding author; email: cfdee@vlsi.eng.ukm.my

Received: 23 August 2010
Accepted: 3 September 2010