Ceramics International 30 (2004) 1669–1674

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

ZnO thin films produced by filtered cathodic vacuum arc technique

K.Y. Tse [a], H.H. Hng [a,*], S.P. Lau [b], Y.G. Wang [b], S.F. Yu [b]

[a] *School of Materials Engineering, Nanyang Technological University, Nanyang Avenue, Singapore 639798, Singapore*
[b] *School of Electrical and Electronic Engineering, Nanyang Technological University, Nanyang Avenue, Singapore 639798, Singapore*

Received 19 November 2003; received in revised form 11 December 2003; accepted 22 December 2003

Available online 7 May 2004

Abstract

High quality *c*-axis oriented ZnO thin films have been successfully deposited on silicon substrates using filtered cathodic vacuum arc (FCVA) technique. Two deposition temperatures, namely room temperature and 420 °C, were studied. The films were characterised by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). XRD revealed that the ZnO films exhibited (0 0 2) orientation. An amorphous layer between the substrate and the ZnO film was observed in both samples using TEM. Both samples showed *c*-axis oriented ZnO columns. However, for the ZnO thin film deposited at room temperature, the *c*-axis oriented ZnO columns were observed to grow on a layer of randomly oriented nanocrystals.

Keywords: A. Films; B. Electron microscopy; D. ZnO

1. Introduction

ZnO is a II–VI compound semiconductor with wide band gap, high exciton binding energy and optical transparency [1]. These properties make ZnO a promising material for short wavelength light emitting diode and lasers. With appropriate doping, ZnO thin films can be used as transparent electrodes in liquid crystal displays [2]. However, in order to realise these applications, high quality *c*-axis ZnO thin films are necessary. Current techniques used for the deposition of ZnO thin films include molecular beam epitaxy (MBE) [3], pulsed laser deposition [4], metal organic chemical vapour deposition (MOCVD) [5] and spray pyrolysis [6]. High quality ZnO films were usually grown at relatively high temperatures above 450 °C using MOCVD and MBE techniques [7]. In order to prevent interdiffusion between different layers, to protect substrates of low melting point and to reduce the strain effect caused by the difference in thermal expansion of the deposited film and the substrate [8], it is advantageous to deposit ZnO thin films at lower temperature. Recently, *c*-axis oriented ZnO thin films have been successfully deposited by filtered cathodic vacuum arc (FCVA) technique at approximately 200 °C [7,9]. Electrical and optical properties of the films were reported in these studies, however, a detailed study of the microstructures of these films were not undertaken. In this work, the effects of deposition temperatures on the microstructures of ZnO thin films prepared by FCVA technique were investigated. Two deposition temperatures, namely, room temperature and 420 °C were studied. The texture and surface morphology of the films were characterised by X-ray diffraction (XRD) and scanning electron microscopy (SEM) respectively, while the interface microstructure was analysed using transmission electron microscopy (TEM).

2. Experimental procedure

2.1. Film deposition

ZnO thin films were deposited on (1 0 0) silicon substrates using FCVA technique. The details on the apparatus is described elsewhere [7,9]. High purity zinc (99.9% purity) was used as the cathode material and oxygen gas was used as the reactant gas. Typically, the base pressure was kept at approximately 2.7×10^{-4} Pa, and the pressure during deposition is about 1.3×10^{-2} Pa. An arc current of 60 mA was used to generate the plasma and the axial and curvilinear fields were produced by a torodial magnetic field of strength about 40 mT to steer the plasma.

* Corresponding author. Tel.: +65-67904140; fax: +65-67909081.
E-mail address: ashhhng@ntu.edu.sg (H.H. Hng).

0272-8842/$30.00 © 2004 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2003.12.156

2.2. Characterisation methods

Crystal structures of the films were analysed using Cu Kα radiation on X-ray diffractometer (Rigaku Ultima) while surface morphologies of the samples were studied using field emission SEM (JEOL JSM-6340F) operated at 5 kV. The average grain sizes of the samples were estimated directly from the micrographs using the linear intercept method described by Mendelson [10]:

$$\text{Average grain size,}\ \bar{G} = 1.56\bar{L}$$

where $\bar{L}$ is the average grain boundary intercept length of a series of random lines on the micrographs.

The preparation of TEM specimens for cross-section observation were prepared first by ultrasonically cutting two pieces of sample and four pieces of silicon wafers of the size of 4 mm × 5 mm. The samples were then glued face to face with two pieces of silicon wafer on each side with epoxy. A 2.3 mm diameter cylinder was then cut ultrasonically from the rectangle block. It was introduced into a copper tube and secured with epoxy. The composite was sliced into 600 μm thick disks with the low speed diamond saw. The disks were then mechanically ground with a disk grinder to a thickness of about 100 μm. The centre portions of these disks were further ground by the dimple grinder to approximately 20 μm. The samples were then thinned in the precision ion polishing system with argon ions at an accelerating voltage of 5 kV which incident at both surfaces at an angle of 4°. A hole is finally created at the centre of the specimen to provide larger transparent areas for observation. The detailed study of the interface microstructure was then carried out through cross-section observation using TEM (JEOL JEM-2010) operating at 200 kV.

3. Results

3.1. XRD results

Fig. 1 shows the XRD patterns of the ZnO thin films. ZnO thin film deposited at room temperature has very weak (0 0 2) preferred orientation as indicated by the broad diffraction peak. As the deposition temperature was increased to 420 °C, a sharp (0 0 2) diffraction peak was observed, showing that the ZnO films are strongly c–axis oriented. It was found that the FWHM of the (0 0 2) peak decreased from 0.5 to 0.24° when the deposition temperature was increased from room temperature to 420 °C, indicating that crystal quality improves with deposition temperature. Similar results are reported for ZnO thin films produced by radio frequency reactive sputtering [11] and plasma enhanced chemical vapour deposition [12].

3.2. SEM observation

SEM micrographs of the surface morphologies of the samples are shown in Fig. 2. The film deposited at room temperature consisted of small and hexagonally shaped grains. The average grain size is approximately 27 nm. When the deposition temperature was increased to 420 °C, the grain size increased significantly to about 126 nm. Such variation of grain size with deposition temperature was also observed

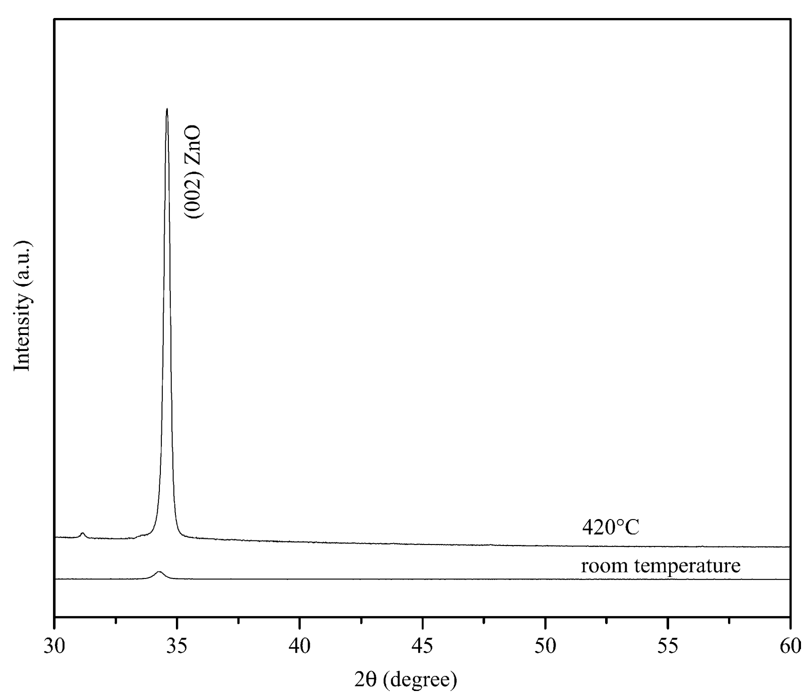

Fig. 1. X-ray diffraction patterns of ZnO thin films deposited at room temperature and 420 °C.

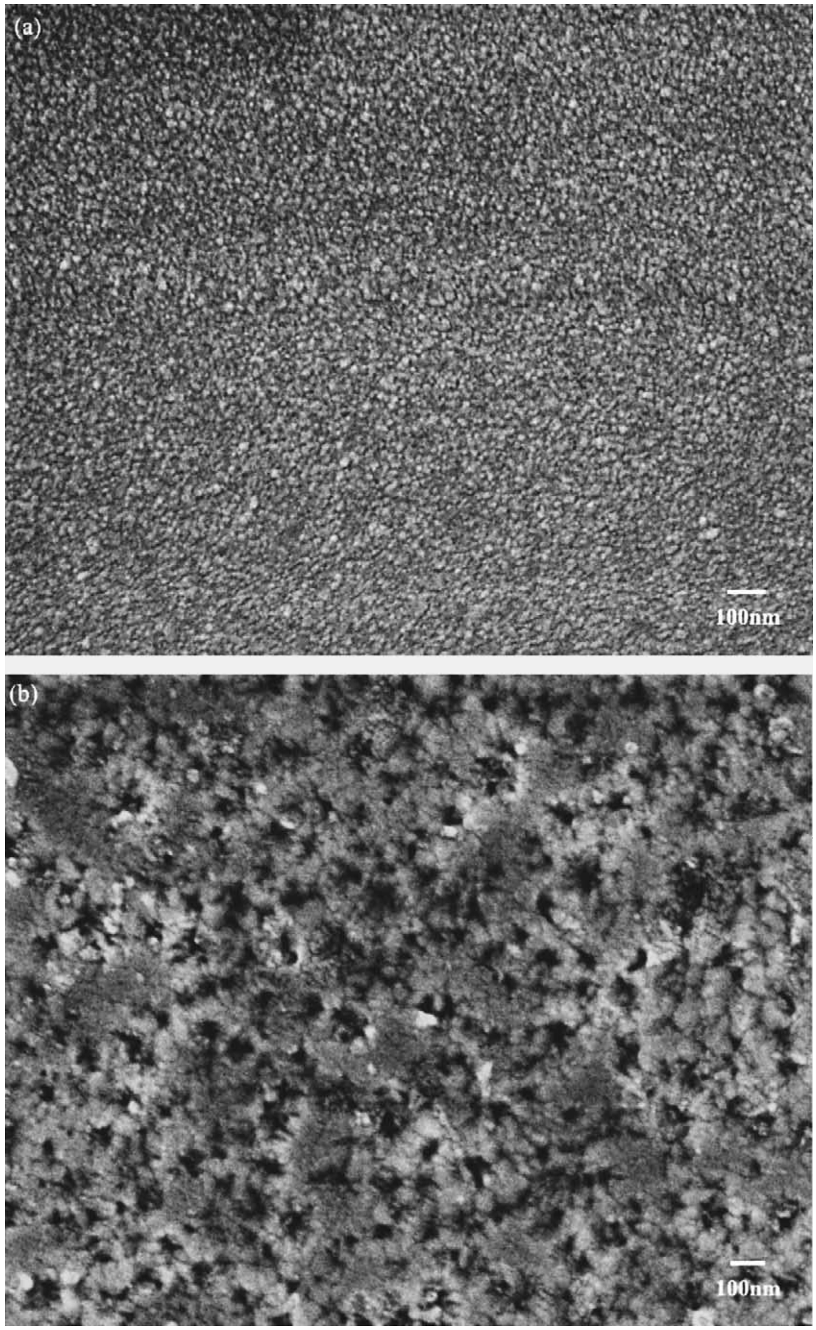

Fig. 2. SEM micrograph of ZnO thin films deposited at (a) room temperature and (b) 420 °C.

in other studies on ZnO thin films deposited by radio frequency reactive sputtering [11] and MOCVD [13]. It was reported that higher deposition temperature provides greater mass transfer and more energy for grain growth, leading to larger crystallites [14].

3.3. TEM observations

A detailed study of the interface microstructures of the ZnO films was performed using TEM. Fig. 3 shows bright field (BF) images of the ZnO film deposited at room temperature. Small crystals of average size ∼8 nm were observed prior to the growth of ZnO columns as shown on Fig. 3(a). It is evident in Fig. 3(b) that these small crystallites were not *c*-axis oriented. Various orientations were observed. This is because at low deposition temperature, the ions have low thermal energy which is less than the crystallisation energy of energetically stable crystals [15]. The ions locate randomly on the substrate and the initial crystal nuclei grow in the direction of available reactant flux, leading to the formation of small crystals with random orientations [12]. After crystallisation, the crystals will grow in the preferred *c*-axis

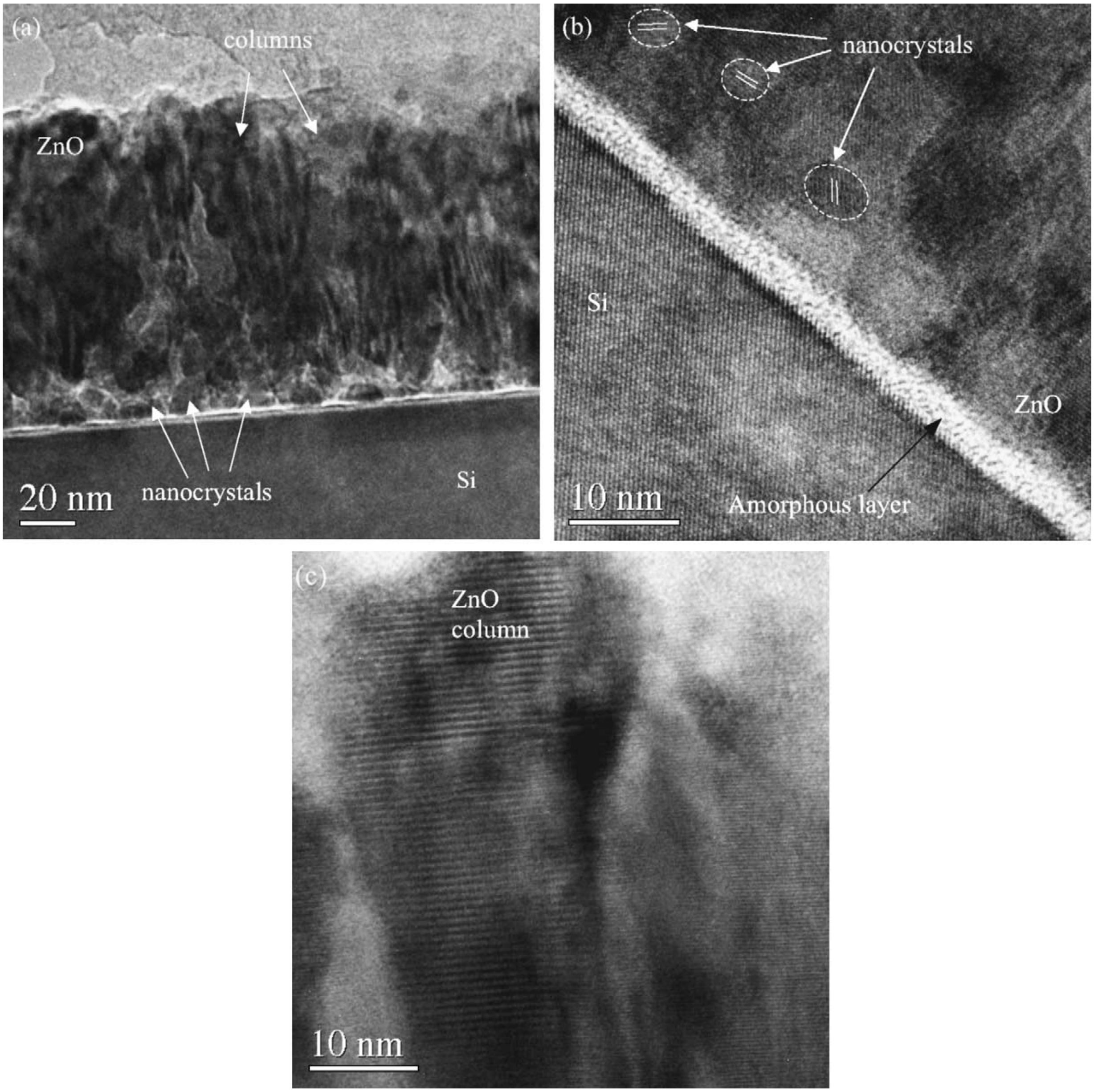

Fig. 3. TEM micrograph of ZnO thin films deposited at room temperature (a) BF image, (b) lattice image at the interface and (c) lattice image of a ZnO column.

direction, which is the most stable direction [16]. Fig. 3(c) shows the lattice image of these ZnO columns which was taken away from the interface. The interplanar spacing of the columns is approximately 0.26 nm, which corresponds to the (0 0 2) plane of ZnO. This indicates that these columns are *c*-axis oriented which is consistent with the XRD results. In addition, an interfacial layer with a thickness of approximately 3 nm existed between the substrate and the nanocrystals. This layer has the typical random structure characteristic of an amorphous layer.

BF TEM micrograph of the ZnO film deposited at 420 °C is shown in Fig. 4(a). No small crystals were observed below the ZnO columns and the columns are more uniform. From Fig. 4(b), it can be seen that growth of ZnO does not start immediately from the substrate, an amorphous layer of approximately 3.4 nm in thickness was observed. Similarly, the interplanar spacing between the ZnO planes is approximately 0.26 nm, which is equivalent to the (0 0 2) planes. This shows that *c*-axis oriented columns are also obtained under this condition.

4. Discussion

The preferred *c*-axis orientation of ZnO grains are generally observed in both of the samples studied. However, the *c*-axis orientation of the film deposited at room temperature is weaker. This suggests that a deposition temperature of

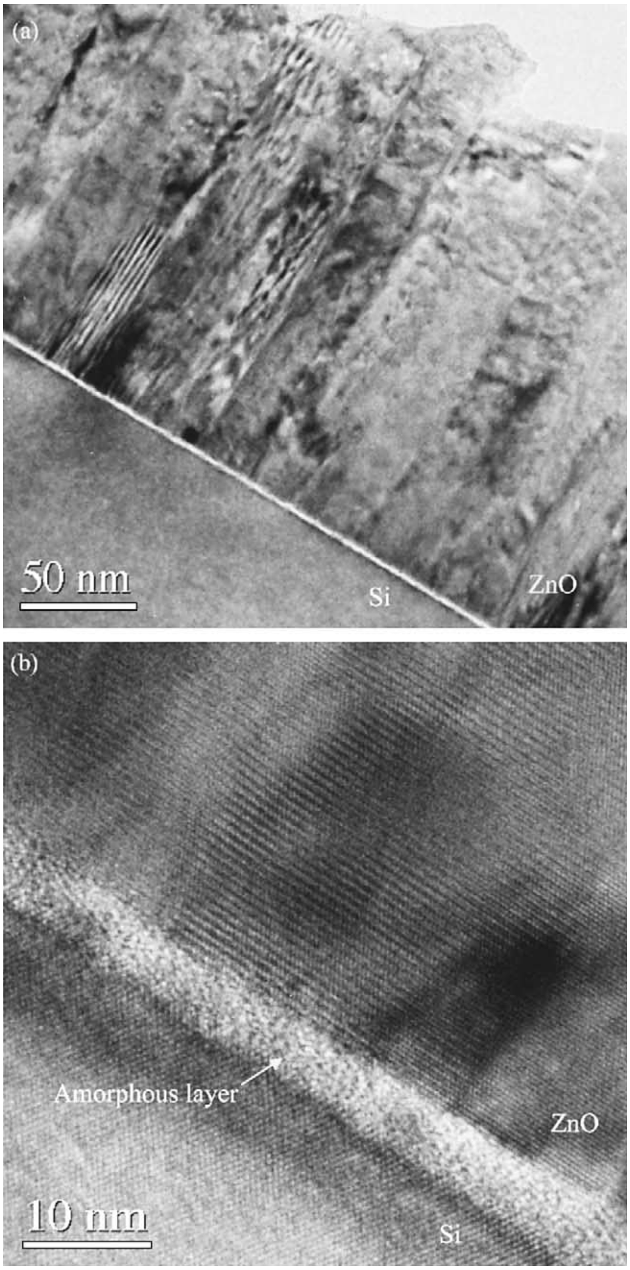

Fig. 4. TEM micrograph of ZnO thin films deposited at 420 °C (a) BF image and (b) lattice image at the interface.

420 °C is more favourable in producing *c*-axis oriented ZnO grains. The preferred orientation can be analysed from the energy minimisation consideration. The total energy in any film deposited on a substrate consists of three components, namely, surface energy of the film, film–substrate interface energy and the strain energy in the film [17]. Films tend to grow in such a way that the total energy is minimised. Jiang et al. [18] predicted that *c*-axis oriented ZnO thin films deposited by magnetron sputtering grown in the direction with the lowest surface energy. It was reported that among the various low index ZnO planes, the (0 0 1) plane has the lowest surface energy. Thus, (0 0 1) textured ZnO thin films can be formed through the minimisation of surface energy. However, the calculations are based on the fact that ZnO has tetragonal co-ordination. When the films are not grown under the optimum range of deposition conditions, tetragonal co-ordination is deteriorated and other textures are feasible [19]. Aita et al. [20] studied the evolution of texture in ZnO thin films produced by sputtering with various O_2/Ar gas compositions. It was found that the ratio of the number of Zn^+ to ZnO^+ in the plasma varied with different O_2/Ar gas compositions. It was reported that the ZnO films were most (0 0 2) textured films when the ratio of Zn^+ to ZnO^+ was a minimum with a 25% O_2 to 75% Ar gas mixture. It was explained that the films were more crystallographically ordered when the arriving species were already in an oxide form, hence satisfying the tetragonal co-ordination. This suggests that an optimum deposition conditions for (0 0 2) textured ZnO existed. Hence, in the present work, a higher deposition temperature of 420 °C is more favourable for the formation of (0 0 2) textured ZnO thin films, while at room temperature, it may not be within the optimum range of deposition conditions, which explained the formation of the ZnO nanocrystals at the interface.

5. Conclusion

The texture and microstructures of ZnO thin films deposited by FCVA technique at room temperature and 420 °C have been studied using XRD, SEM and TEM. XRD revealed that the ZnO grains are *c*-axis oriented, which became stronger as the deposition temperature increased. In addition, the average grain size increased significantly with increasing deposition temperature. The interface microstructures were studied using cross section TEM. An amorphous layer between the substrate and the ZnO film was observed in both samples. Both samples showed *c*-axis oriented ZnO columns. However, for the sample deposited at room temperature, the *c*-axis oriented ZnO column grew on a layer of randomly oriented nanocrystals. It is believed that the low thermal energy of the ions at low deposition temperature caused the formation of such randomly oriented layer.

References

[1] D.M. Bagnall, Y.F. Chen, Z.Q. Zhu, T. Yao, Optically pumped lasing of ZnO at room temperature, Appl. Phys. Lett. 70 (17) (1997) 2230–2232.

[2] A. Martin, J.P. Espinos, A. Justo, J.P. Hologado, F. Yubero, A.R. Gouzalez-Elipe, Preparation of transparent and conductive Al-doped ZnO thin films by ECR plasma enhanced CVD, Surf. Coat. Technol. 151152 (2002) 289–293.

[3] Y.F. Chen, D.M. Bagnall, Z.Q. Zhu, T. Sekiuchi, K.T. Park, K. Hiraga, T. Yao, S. Koyama, T. Goto T, Growth of ZnO single crystal thin films on *c*-plane (0 0 0 1) sapphire by plasma enhanced molecular beam epitaxy, J. Cryst. Growth 181 (1997) 165–169.

[4] J.H. Choi, H. Tabata, T. Kawai, Initial preferred growth in zinc oxide thin films on Si and amorphous substrates by pulsed laser deposition, J. Cryst. Growth 226 (2001) 493–500.
[5] A. Zeuner, H. Alves, M. Hofmann, B.K. Meyer, Structural and optical properties of epitaxial and bulk ZnO, Appl. Phys. Lett. 80 (12) (2002) 2078–2080.
[6] P. Nunes, B. Fernandes, E. Fortunato, P. Vilarinho, R. Martins, Performances presented by zinc oxide thin films deposited by spray pyrolysis, Thin Solid Films 337 (1999) 176–179.
[7] X.L. Xu, S.P. Lau, B.K. Tay, Structural and optical properties of ZnO thin films produced by filtered cathodic vacuum arc, Thin Solid Films 398/399 (2001) 244–249.
[8] B.S. Li, Y. C Liu, D.Z. Shen, Y.M. Lu, J.Y. Zhang, X.G. Kong, X.W. Fan, Z.Z. Zhi, Growth of high quality ZnO thin films at low temperature on Si(1 0 0) substrates by plasma enhanced chemical vapour deposition, J. Vac. Sci. Technol. A 20 (1) (2002) 265–269.
[9] X.L. Xu, S.P. Lau, J.S. Chen, G.Y. Chen, B.K. Tay, Polycrystalline ZnO thin films on Si(1 0 0) deposited by filtered cathodic vacuum arc, J. Cryst. Growth 223 (2001) 201–205.
[10] M.I. Mendelson, Average grain size in polycrystalline ceramics, J. Am. Ceram. Soc. 52 (8) (1969) 443–446.
[11] H.X. Gong, Y.Y. Wang, Z.J. Yan, Y.H. Yang, The effect of deposition condition on structure properties of radio frequency reactive sputtered polycrystalline ZnO films, Mater. Sci. Semicond. Process. 5 (2) (2002) 31–34.
[12] B.S. Li, Y. C Liu, D.Z. Shen, Y.M. Lu, J.Y. Zhang, X.G. Kong, X.W. Fan, Z.Z. Zhi, Growth of stoichiometric (0 0 2) ZnO thin films on Si (0 0 1) substrate by using plasma enhanced chemical vapour deposition, J. Vac. Sci. Technol. A 20 (5) (2002) 1779–1783.
[13] K.H. Guenther, Columnar and nodular growth of thin films, in: Proceedings of the International Society for Optical Engineering, vol. 346, 1982, pp. 9–18.
[14] K.S. Kim, H.W. Kim, C.M. Lee, Effects of growth temperature on ZnO thin film deposited on SiO_2 substrate, Mater. Sci. Eng. B 98 (2003) 135–139.
[15] E. Jacobsohn, D. Schechtman, Effects of reactive sputtering parameters on the growth and properties of acoustooptic ZnO films, in: Proceedings of the Materials Research Society Symposium, vol. 242, 1992, pp. 779–784.
[16] S. Hayamizu, H. Tabata, H. Tanaka, T. Kawai, Preparation of crystallised zinc oxide films on amorphous glass substrates by pulsed laser deposition, J. Appl. Phys. 80 (2) (1996) 787–791.
[17] C.V. Thompson, Grain growth in polycrystalline thin films in: Proceedings of the Materials Research Society Symposium, vol. 343, 1994, pp. 3–12.
[18] X. Jiang X, C.L. Jia, B. Szyszka, Manufacture of specific structure of aluminium-doped zinc oxide films by patterning the substrate surface, Appl. Phys. Lett. 80 (17) (2002) 3090–3092.
[19] S.V. Prasad, S.D. Walck, J.S. Zabinski, Microstructural evolution in lubricious ZnO films grown by pulsed laser deposition, Thin Solid Films 360 (2000) 107–117.
[20] C.R. Aita, A.J. Purdes, R.J. Lad, P.D. Funkenbuch, The effect of O_2 on reactively sputtered zinc oxide, J. Appl. Phys. 51 (1980) 5533–5536.