Materials Science and Engineering B98 (2003) 135–139

MATERIALS SCIENCE & ENGINEERING B

www.elsevier.com/locate/mseb

Effect of growth temperature on ZnO thin film deposited on SiO_2 substrate

Kwang-Sik Kim, Hyoun Woo Kim *, Chong Mu Lee

School of Materials Science and Engineering, Inha University, Incheon 402-751, South Korea

Received 21 November 2002; accepted 16 December 2002

Abstract

We investigated the effect of deposition temperature on the growth and structural quality of ZnO films on SiO_2 substrate in the range of 100–250 °C using the metal organic chemical vapor deposition (MOCVD) technique. We revealed that highly *c*-axis oriented ZnO thin films were obtained at the temperature of 200–250 °C and the ZnO thin film was successfully deposited at the lower temperature of 100–150 °C. The c-axis orientation of the film improved and the grain size increased by increasing growth temperature.

Keywords: MOCVD; ZnO; Low temperature; Thin film

1. Introduction

Thin ZnO films are of importance due to their unique optical and physical properties. They have a wide variety of applications, such as surface acoustic wave (SAW) band pass filters, optical wave guides, and laser deflectors using piezoelectric or piezo optic properties [1,2]. Also, they are used as transparent conducting oxide coatings, gas sensors, and varistors. Since the ZnO has a large band gap of 3.37 eV, low power threshold for optical pumping at room temperature, and highly efficient UV emission resulted from a large exciton binding energy of 60 meV, it has received a great attention as a luminescence material for display panels [3].

The main property of ZnO for these applications results from the polar nature of the crystalline structure of ZnO thin films. Many efforts have been made to grow high-quality c-axis-oriented ZnO films, using various deposition techniques such as sputtering [4], pulsed laser deposition (PLD) [5,6], chemical vapor deposition (CVD) [7,8], atomic layer deposition (ALD) [9], spray pyrolysis [10], and also molecular beam epitaxy (MBE) [11]. However, MOCVD has an advantage in achieving devices in commercial level since high deposition rate and high crystallinity is attainable.

High quality ZnO films grown on Si substrate pave the way for integration of devices with Si IC technology. Also, amorphous substrates such as SiO_2 and glass substrate have obvious technological advantages and potential applications [12]. Although most researchers have grown ZnO films on sapphire substrates, there are not many reports on growing ZnO thin films on Si or Si-based materials by MOCVD technique. Furthermore, there are rare reports on the MOCVD growth of ZnO at low temperatures below 300 °C.

In this paper, we demonstrate to deposit ZnO films with a c-axis (002) orientation on the SiO_2 substrate at the low temperature of 100–250 °C by MOCVD. We investigate the effect of deposition temperature on the structural quality of thin films.

2. Experimental

The SiO_2 substrates were prepared by depositing a 60-nm thick SiO_2 layer on Si(100) substrate thermally. The ZnO films were deposited on the SiO_2 substrate by MOCVD using $Zn(C_2H_5)_2$ (99.9999% purity diethylzinc

* Corresponding author. Tel.: +82-32-860-7544; fax: +82-32-862-5546.

E-mail address: hwkim@inha.ac.kr (H.W. Kim).

0921-5107/03/$ - see front matter
doi:10.1016/S0921-5107(02)00754-7

($Zn(C_2H_5)_2$) and O_2 (99.999% purity) gas as source gases. Ar (99.999% purity) was used as a carrier gas of $Zn(C_2H_5)_2$ source. Before loading into the reactor, the substrate was cleaned in acetone for 10 min, in HF (20:1) for 1 min and then rinsed in deionized water for 1 min. Fig. 1 shows a schematic diagram of the MOCVD reactor used in our experiments.

High-purity Ar was passed through the $Zn(C_2H_5)_2$ bubbler and saturated with $Zn(C_2H_5)_2$ vapor to the reactor. In order to minimize the gas phase reaction causing the generation of particles and thus degrading the ZnO film quality, $Zn(C_2H_5)_2$ and O_2 are introduced into the reactor separately and mixed just before the inside of chamber. The $Zn(C_2H_5)_2$ bubbler was maintained at a temperature of −2 °C. The Ar/O_2 gas flow rate ratio of 2 was used. The substrate temperature during deposition was varied in the range of 100–250 °C. The deposition time was set to 30 min. The crystal structures were characterized by X-ray diffraction (XRD: CuK_{a1} ? = 1.5405 Å). Scanning electron microscopy (SEM: Hitachi S4200) was used to characterize the surface morphology and structural quality of the films. The surface roughness was measured using a Digital Instruments Nanoscope III AFM.

3. Results and discussion

Fig. 2 shows XRD patterns of ZnO thin films on SiO_2 substrates in the temperature range of 100–200 °C, with an Ar/O_2 ratio of 2. The θ–2θ scan data of ZnO films exhibit a strong 2θ peak at 34.53° in the sample grown at 200 °C, corresponding to the (002) peaks of ZnO.

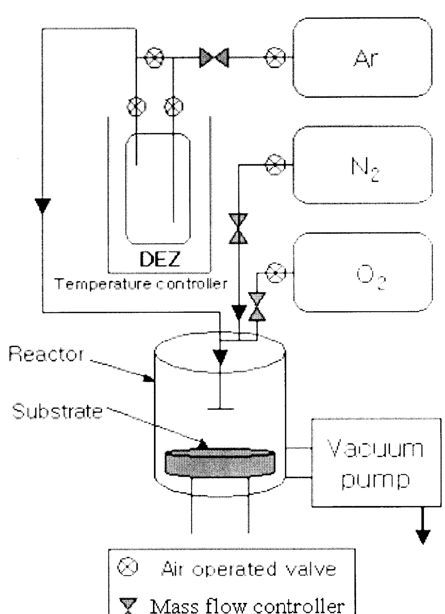

Fig. 1. Schematic diagram of MOCVD reactor.

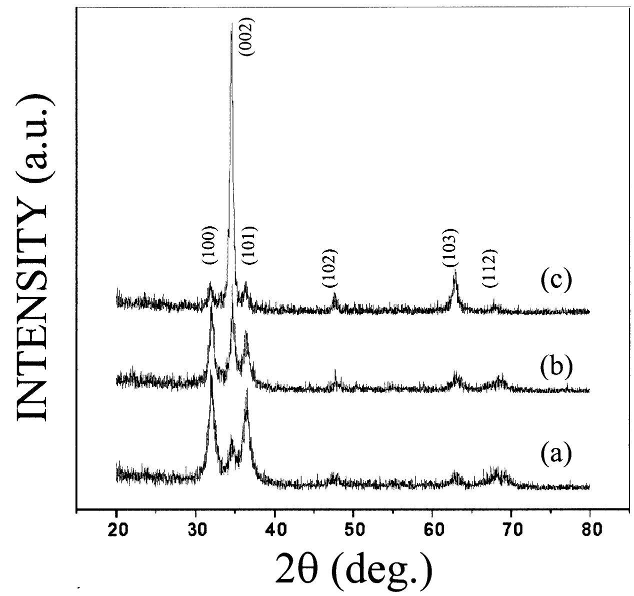

Fig. 2. XRD patterns of ZnO thin films on SiO_2 substrate at a growth temperature of (a) 100 °C, (b) 150 °C, and (c) 200 °C.

The observation of the strong (002) peak indicates that the highly c-axis oriented film is grown. The films have other peaks, which may correspond to granular structure of the film. The relative intensity of the (002) diffraction peak compared to the neighboring (100) and (101) peaks increases by increasing the growth temperature in the range of 100–200 °C.

Fig. 3 shows XRD patterns of ZnO thin films on SiO_2 substrates at the temperature of 250 °C, revealing that the highly c-axis oriented film is grown. By comparing Fig. 3 with Fig. 2(c), we reveal that the relative intensity

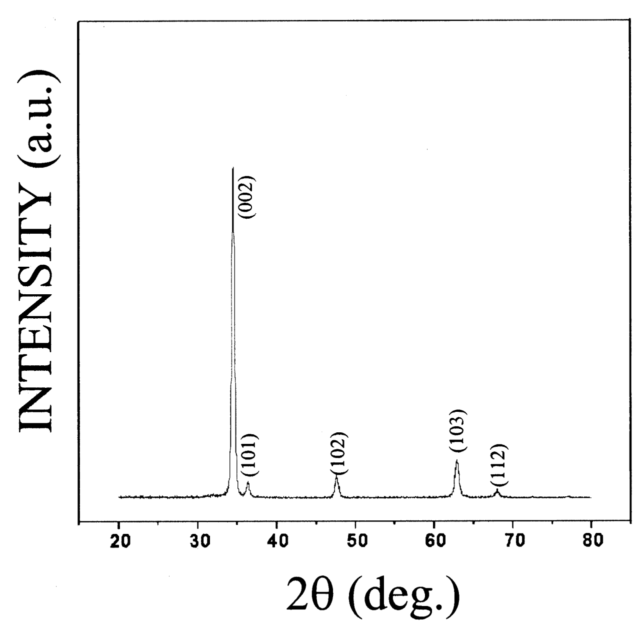

Fig. 3. XRD patterns of ZnO thin films on SiO_2 substrate at a growth temperature of 250 °C.

of the (002) diffraction peak compared to the neighboring (100) and (101) peaks at 250 °C is even higher than the relative intensity at 200 °C. Since the relative intensity of the (002) diffraction peak increases gradually by increasing growth temperature, we assume that the c-axis orientation of ZnO films increases by increasing growth temperature in the range of 100–250 °C.

Fig. 4 indicates that the half-maximum (FWHM) of the (002) diffraction peak at a growth temperature of 150, 200, and 250 °C, respectively, are 0.6384, 0.4918, and 0.4234. Since the FWHM of the (002) diffraction peak inversely proportional to the grain size of the film, we reveal that the grain size of the ZnO thin film increases by increasing the growth temperature in the range of 150–250 °C. Investigation of the XRD patterns of the ZnO film indicates that FWHM of the (002) diffraction peak is less than 0.5° at a growth temperature of 200–250 °C.

The left-hand side of Fig. 5 shows the cross-sectional SEM images at a growth temperature of 100, 150, 200 and 250 °C. According to SEM images, we reveal that most film structure is composed of columnar-structured grains in the temperature range of 150–250 °C, representing c-axis oriented grains. However, at the low temperature of 100 °C, we are not able to clarify the c-axis oriented grains. We surmise that at high temperature, the atoms have enough diffusion activation energy to occupy the correct site in the crystal lattice and grains with the lower surface energy will become larger at high temperature. Then the growth orientation develops into one crystallographic direction of the low surface energy.

The right-hand side of Fig. 5 shows the plan-view SEM image of ZnO thin films, revealing that the grain size becomes larger by increasing growth temperature and this result agrees with the XRD analysis. The role of temperature on the grain growth and c-axis orientation in the ZnO thin film needs to be fully understood and more systematic study is necessary. In order to investigate the effect of substrate temperature on the surface smoothness of ZnO films, we have performed an AFM measurement on the ZnO film deposited in the temperature range of 100–250 °C, revealing that surface smoothness decreases with increasing growth temperature (not shown here) and they agree with the previous reports [13,14]. This observation on the surface smoothness may be related to the observation of SEM, indicating that the c-axis orientation of ZnO films improves with increasing substrate temperature. The high substrate temperature may cause the grain to overgrow and induce the rough surface [15]. Further studies are necessary to reveal the detailed mechanism of formation of ZnO thin films at low temperature.

4. Conclusions

We demonstrated to grow the ZnO thin films on the SiO_2 substrate at the temperature of 100–250 °C using the MOCVD technique. We reveal that the growth temperature plays a key role in determining the ZnO film properties. The c-axis orientation of thin films improved and the grain size increased by increasing

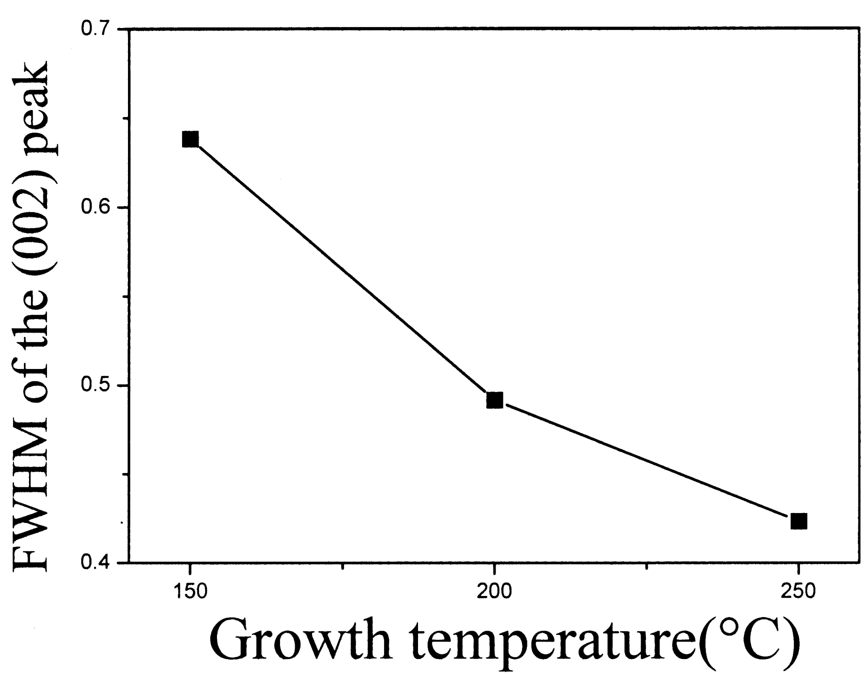

Fig. 4. The half-maximum (FWHM) of the (002) diffraction peak at a growth temperature of 150, 200, and 250 °C.

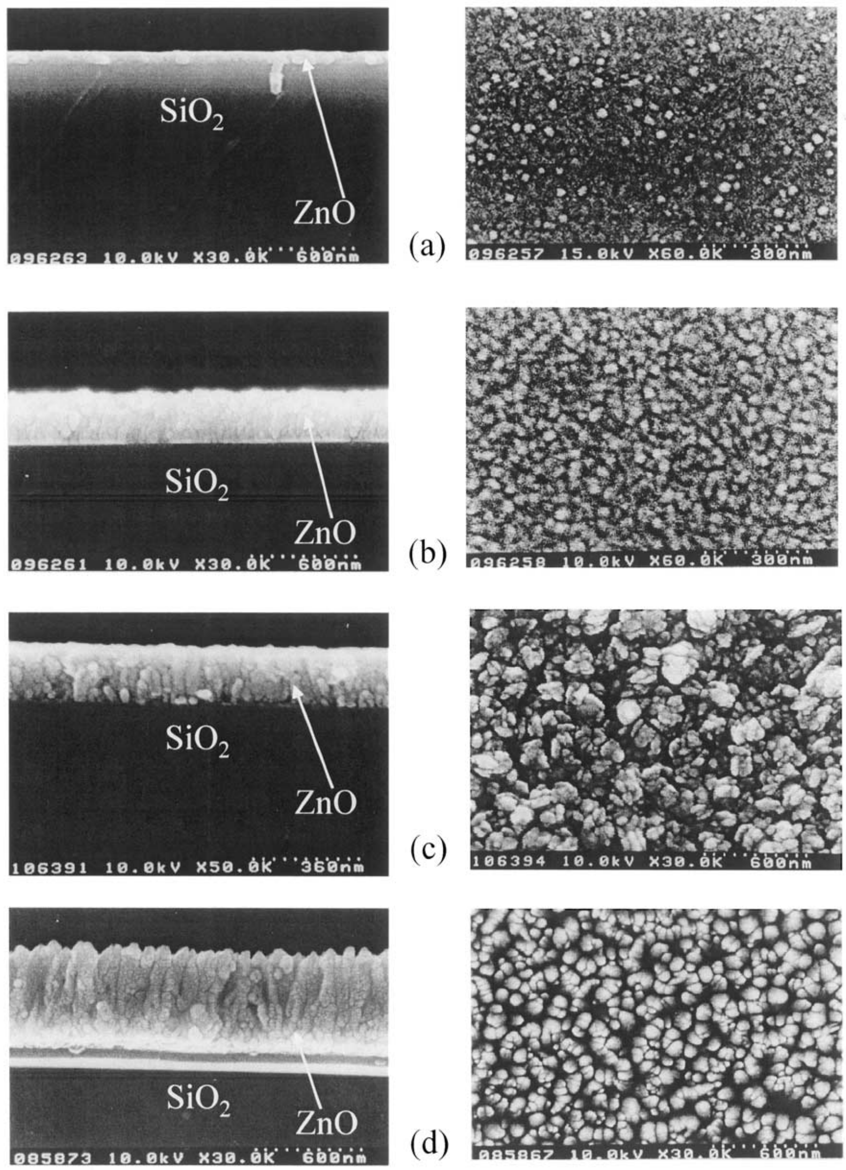

Fig. 5. Cross-sectional view (left-hand side) and plan-view SEM images (right-hand side) of ZnO film grown on SiO_2 substrate at a growth temperature of (a) 100 °C, (b) 150 °C, (c) 200 °C, and (d) 250 °C.

growth temperature. In x-ray diffraction analysis with respect to ZnO (002) peak, the full width at half maximum (FWHM) of less than 0.5° is achieved at 200–250 °C.

Acknowledgements

This work was supported by grant No.R05-2001-000-00843-0 from the Basic Research Program of the Korea Science & Engineering Foundation.

References

[1] F.S. Hickernell, IEEE Trans. Sonics Ultrason. SU-32 (1985) 621.
[2] M. Kadota, Jpn. J. Appl. Phys. 36 (1997) 3076.
[3] D.C. Reynolds, D.C. Look, B. Jogai, H. Morkoc, Solid State Commun. 101 (1997) 643.
[4] Y.M. Lu, W.S. Hwang, W.Y. Liu, J.S. Yang, Mater. Chem. Phys. 72 (2001) 269.
[5] X.W. Sun, H.S. Kwok, J. Appl. Phys. 86 (1999) 408.
[6] M. Joseph, H. Tabata, T. Kawai, J. Appl. Phys. 74 (1999) 2534.
[7] N.W. Emanetoglu, C. Gorla, Y. Liu, S. Liang, Y. Lu, Mater. Sci. Semicond. Process. 2 (1999) 247.
[8] B.P. Zhang, Y. Segawa, Appl. Phys. Lett. 79 (2001) 3953.

[9] A. Yamada, B. Sang, M. Konagai, Appl. Surf. Sci. 112 (1997) 216.
[10] F. Paraguay D., W. Estrada L., D.R. Acosta N., E. Andrade, M. Miki-Yoshida, Thin Solid Films 350 (1999) 192.
[11] K. Iwata, P. Fons, S. Niki, A. Yamada, K. Matusubara, K. Nakahara, T. Tanabe, H. Takasu, J. Cryst. Growth 214/215 (2000) 50.
[12] S. Guha, N.A. Bojarczuk, Appl. Phys. Lett. 73 (1998) 1487.
[13] S. Muthukumar, C.R. Gorla, N.W. Emanetoglu, S. Liang, Y. Lu, J. Cryst. Growth 225 (2001) 197.
[14] R. Groenen, J. Loffler, P.M. Sommeling, J.L. Linden, E.A.G. Harners, R.E.I. Schropp, M.C.M. van de Sanden, Thin Solid Films 392 (2001) 226.
[15] K.B. Sundaram, A. Khan, Thin Solid Films 295 (1997) 87.