

# Very Low Temperature Growth of ZnO Thin Films on Si Substrates Using the Metalorganic Chemical Vapor Deposition Technique

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We have deposited ZnO thin films on Si(100) substrates at low temperatures ranging from 25 to 300 °C by using the metalorganic chemical vapor deposition (MOCVD) technique. The x-ray diffraction (XRD) analysis revealed that the *c*-axis orientation of the ZnO thin films increased with increasing growth temperature. We demonstrated that ZnO thin films can be grown at a low temperature of 100 °C by using the MOCVD method. The room-temperature photoluminescence spectra of ZnO exhibited peaks in the violet region, as well as the ultraviolet region.

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## I. INTRODUCTION

In recent years, wide band-gap semiconductor materials have attracted a great deal of attention for use in blue-light-emitting and short-wavelength diodes [1–3]. Zinc oxide (ZnO) has rapidly emerged as a promising optoelectronic material due to its large band gap of 3.3 eV, low power threshold for optical pumping at room temperature (RT), and highly efficient UV emission resulting from a large exciton binding energy of 60 meV. Moreover, ZnO is thermally and chemically stable in ambient air. Additionally, due to its high conductance, chemical and thermal stability, and high piezoelectric coupling coefficient, ZnO is also used for piezoelectric devices, such as surface acoustic wave (SAW) devices [4] and bulk acoustic devices [5]. Various deposition techniques, including sputtering [6,7], pulsed laser deposition [8,9], ion beam deposition [10], chemical vapor deposition (CVD) [11,12], atomic layer deposition (ALD) [13], metal-organic CVD (MOCVD) [14–16], and molecular beam epitaxy [17] have been employed for the growth of ZnO films. However, MOCVD has an advantage in achieving commercial-level devices since a high deposition rate and high-quality films are attainable, especially at low pressure.

High-quality ZnO films grown on Si substrates pave the way from the integration of devices with Si IC technology. Also, amorphous substrates, such as SiO<sub>2</sub> and glass substrate, have obvious technological advantages and potential applications [18]. Because most researchers grow ZnO films on sapphire substrates, there are not many reports on growing ZnO thin films on Si or Si-based materials by using the MOCVD technique. Furthermore, there are rare reports on the MOCVD growth of ZnO at low temperatures below 300 °C.

In this research, we employed the MOCVD technique to grow high-quality ZnO films on Si(100) substrates. Since the material properties strongly affect the performance of a device, the influence of substrate temperature on the structural properties of the samples is presented. The crystallinity and the surface morphology of ZnO films were investigated using X-ray diffraction (XRD), atomic force microscopy (AFM), and scanning electron microscope (SEM). The optical properties of the films were studied via photoluminescence (PL).

## II. EXPERIMENT

ZnO films were grown on Si(100) substrates by using a MOCVD system with Zn(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> (99.9999 % purity DEZn (Diethylzinc)) and O<sub>2</sub> (99.999 % purity). The

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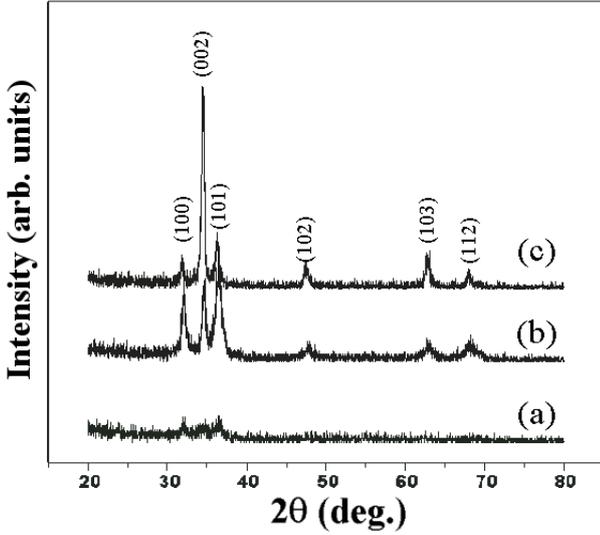


Fig. 1. XRD patterns of ZnO thin films on Si substrates at growth temperatures of (a) 100 °C, (b) 150 °C, and (c) 200 °C.

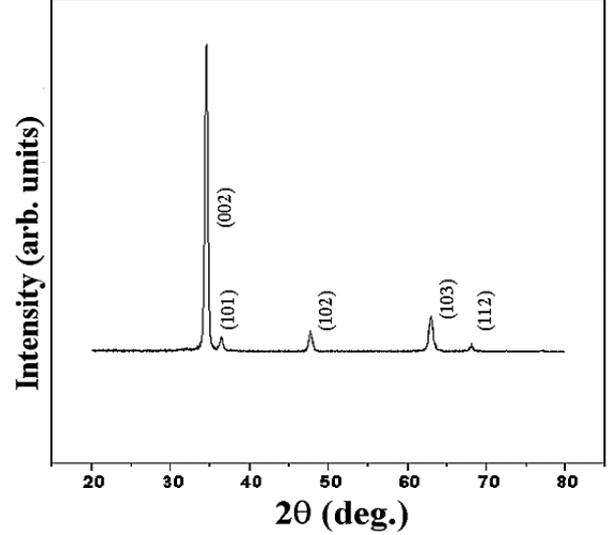


Fig. 2. XRD pattern of ZnO thin films on Si substrates at a growth temperature of 250 °C.

MOCVD reactor used in our experiments has been described elsewhere [16, 19]. Before loading the substrate into the reactor, it was cleaned in acetone for 10 min and in HF (20:1) for 1 min, and then rinsed with deionized water for 1 min. High-purity Ar was passed through the DEZn bubbler, was saturated with DEZn vapor, and was passed into the reactor. In the MOCVD growth of the ZnO films, the gas phase reaction will result in particle formation, which will degrade the ZnO film's quality. In order to minimize the gas phase reaction, we introduced  $\text{Zn}(\text{C}_2\text{H}_5)_2$  and  $\text{O}_2$  into the reactor separately and mixed them just before the inside of chamber. The  $\text{Zn}(\text{C}_2\text{H}_5)_2$  bubbler was maintained at a temperature of  $-2$  °C, and the ratio of the Ar to the  $\text{O}_2$  gas flow rates was set to 2.

The growth temperature ranged from 25 to 300 °C at a pressure of  $5.0 \times 10^{-1}$  Torr. The structural characteristics of the films were analyzed using XRD with  $\text{CuK}\alpha 1$  radiation ( $\lambda = 0.15405$  nm) and by scanning electron microscopy (SEM: Hitachi S-4200). The surface roughness was measured using a Digital Instruments Nanoscope III atomic force microscope (AFM). PL measurements were carried out at room temperature with a Shimadzu fluorescence spectrophotometer (RF-5301PC). The excitation light was the monochromatic light from a xenon short arc lamp with a wavelength of  $\lambda = 325$  nm.

### III. RESULTS AND DISCUSSION

Figure 1 shows XRD patterns of ZnO thin films on Si substrates in the temperature range of 100-250 °C. Figure 1(c) shows that the  $\theta$ - $2\theta$  scan data of ZnO films exhibit a strong  $2\theta$  peak, corresponding to the (002) peak of ZnO, at  $34.53^\circ$  in the sample grown at 200 °C. The ob-

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

Figure 2 shows XRD patterns of ZnO thin films on Si substrates at a temperature of 250 °C, revealing that a highly c-axis-oriented film was grown. By comparing Fig. 2 to Fig. 1, we reveal that the relative intensity 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 with increasing growth temperature, the c-axis orientation of the ZnO films grown on Si substrates increases with increasing growth temperature in the range of 100-250 °C.

The full-width at half-maximum (FWHM) of the (002) diffraction peak of the ZnO thin films deposited on Si(100) substrates at 150, 200, 250, and 300 °C are 0.4907, 0.4431, 0.4177, and 0.3856, respectively. Thus, the FWHM of the (002) diffraction peak decreases with increasing growth temperature for ZnO films deposited on Si substrates. Since the FWHM of the (002) diffraction peak is inversely proportional to the grain size of the film, the grain size of the ZnO thin film increases with increasing growth temperature in the range of 150-250 °C.

Figure 3 shows the cross-sectional SEM images of ZnO thin films deposited on Si substrates at a growth temperatures in the range of 100-250 °C. According to SEM images, most of the film structure is composed of columnar-type c-axis-oriented grains. However, at the low temperature of 100 °C, we are not able to clearly observe the

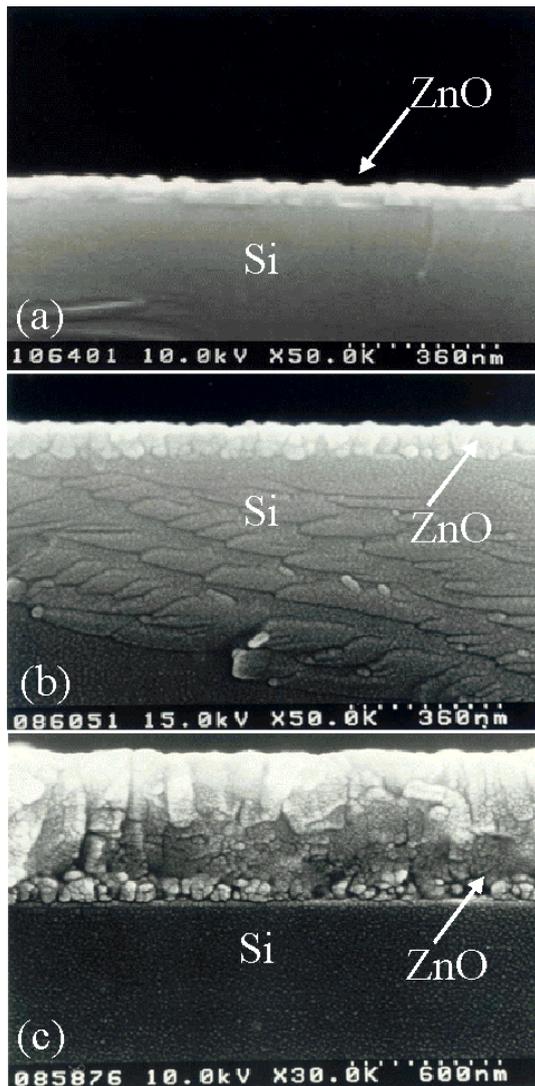


Fig. 3. Cross-sectional SEM images of ZnO films grown on Si substrates at growth temperatures of (a) 100 °C, (b) 200 °C, and (c) 250 °C.

c-axis-oriented grains. We surmise that at high temperatures, the atoms have enough diffusion activation energy to occupy the correct site in the crystal lattice so that grains with lower surface energy will become larger at high temperature. Then, the growth orientation develops in the one crystallographic direction of the low surface energy.

In order to investigate the surface roughness of the ZnO films grown on Si(100) substrate, we present AFM data. Figure 4 shows the AFM root-mean-square (RMS) surface-roughness data measured. It is noteworthy that the RMS surface roughness measured by using an AFM increases slightly with increasing growth temperature from 100 °C to 250 °C. This agrees with previous reports [20,21]. This observation on the surface smoothness may be related to the SEM observation, indicating that the c-axis orientation of ZnO films improves with increasing

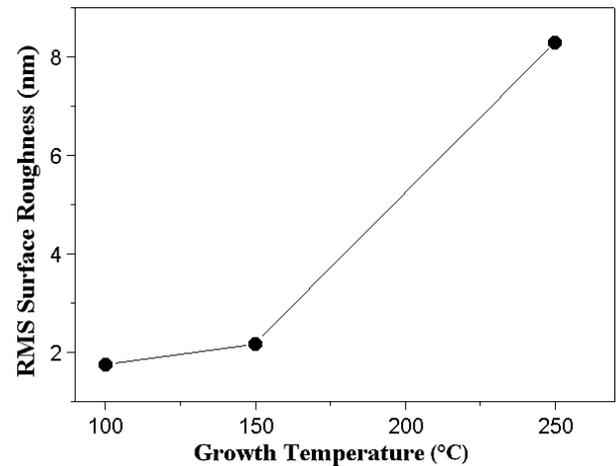


Fig. 4. The AFM root-mean-square (RMS) surface roughness for various temperatures in the range of 100-250 °C for ZnO thin films deposited on Si substrates.

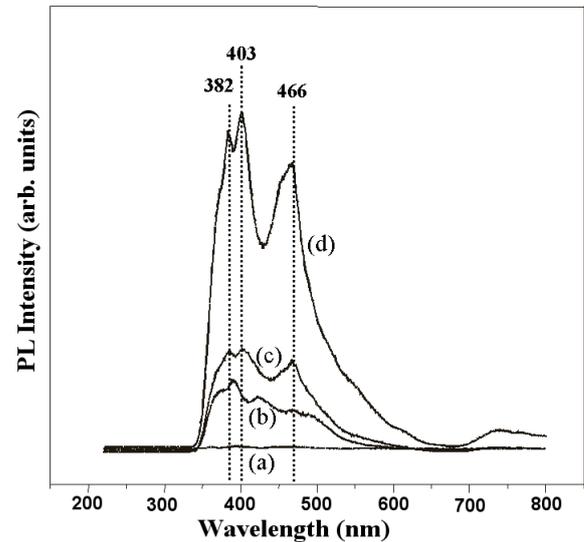


Fig. 5. Photoluminescence (PL) spectra of ZnO films deposited at (a) 25, (b) 150, (c) 200, (d) 250 °C and recorded at room temperature (300 K).

substrate temperature. A high substrate temperature may cause the grains to overgrow and induce a rough surface [22]. Further studies are necessary to reveal the detailed mechanism of ZnO thin-film formation at low temperatures.

Figure 5 shows the PL spectra of ZnO films deposited at 25, 150, 200, and 250 °C and recorded at room temperature (300 K). The band in the UV region corresponds to near band-edge emission, and the other one in the visible region ( $\lambda = 466$  nm) is possibly due to structural defects and impurities in ZnO film [23]. The position of the peak or band in the UV region is close to the reported energy of 3.26 eV ( $\lambda = 380$  nm) for the free exciton in high-quality ZnO thin films [24-27]. It is noteworthy

that a violet PL located at 403 nm is clearly observed. Although there are reports on violet light emission for sapphire [28] and Si substrates [29], reports on the violet light emission for films deposited on Si substrates by using MOCVD are rare. Further systematic study is underway in order to explain the observed emissions. The films grown at 25 °C exhibited very weak emission, indicating poor optical properties. However, as the growth temperature was increased, the emission intensity became stronger. The emission was strongest for the film grown at 250 °C, revealing that the optical properties of the films are improved with increasing growth temperature.

#### IV. CONCLUSIONS

We deposited the ZnO thin films on Si(100) substrates at temperatures in the range of 25-300 °C by using the MOCVD technique. The c-axis orientation, based on XRD analysis, improved with increasing substrate temperature up to 250 °C, regardless of the substrate material. XRD revealed that the linewidth of the ZnO (002) peak is very small and that a FWHM of less than 0.5° was achieved by using Si(100) substrates in the temperature range 200-300 °C. PL measurements on the ZnO films showed a band-edge emission in the UV region and a violet emission, indicating that the optical properties of the films were improved with increasing growth temperature. The growth temperature of high-quality ZnO films could be lowered significantly by using MOCVD, and this shed light on the potential applications of ZnO films in electronic and optoelectronic devices.

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#### REFERENCES

- [1] A. V. Nunmikko, Y.-K. Song, H. Zhou, M. Diagne, R. P. Schneider, T. Takeuchi and J. Han, *J. Korean Phys. Soc.* **39**, 558 (2001).
- [2] C. J. Youn, T. S. Jeong, M. S. Han, J. W. Yang, K. Y. Lim and H. W. Yu, *J. Korean Phys. Soc.* **41**, 778 (2002).
- [3] S.-R. Jeon and G. M. Yang, *J. Korean Phys. Soc.* **41**, 1021 (2002).
- [4] T. Yamamoto, T. Shiosaki and A. Kawabata, *J. Appl. Phys.* **51**, 3113 (1980).
- [5] H. Kim, *J. Korean Phys. Soc.* **32**, S1741 (1988).
- [6] Y. M. Lu, W. S. Hwang and W. Liu, *Mater. Chem. Phys.* **72**, 269 (2001).
- [7] M. Ginting, J. C. Lee and K. H. Kang, *J. Korean Phys. Soc.* **34**, S343 (1999).
- [8] X. W. Sun and H. S. Kwok, *J. Appl. Phys.* **86**, 408 (1999).
- [9] M. Joseph, H. Tabata and T. Kawai, *J. Appl. Phys.* **74**, 2534 (1999).
- [10] S. W. Whangbo, H. K. Jang and S. G. Kim, *J. Korean Phys. Soc.* **37**, 456 (2000).
- [11] N. W. Emanetoglu, C. Gorla and Y. Liu, *Mater. Sci. Semicon. Proc.* **2**, 247 (1999).
- [12] B. P. Zhang and Y. Segawa, *Appl. Phys. Lett.* **79**, 3953 (2001).
- [13] A. Yamada, B. Sang and M. Konagai, *Appl. Surf. Sci.* **112**, 216 (1997).
- [14] Z. Fu, B. Lin and J. Zu, *Thin Solid Films* **402**, 302 (2002).
- [15] W. I. Park and G. C. Yi, *J. Elec. Mater.* **30**, L32 (2001).
- [16] K.-S. Kim and H. W. Kim, *Physica B* **328**, 368 (2003).
- [17] K. Iwata, P. Fons and S. Niki, *J. Cryst. Growth* **214/215**, 50 (2000).
- [18] S. Guha S and A. Bojarczuk, *Appl. Phys. Lett.* **73**, 1487 (1998).
- [19] K.-S. Kim and H. W. Kim, *J. Korean Phys. Soc.* **42**, S316 (2003).
- [20] S. Muthukumar, C. R. Gorla and N. W. Emanetoglu, *J. Cryst. Growth* **225**, 197 (2001).
- [21] R. Groenen, J. Löffler and P. M. Sommeling, *Thin Solid Films* **392**, 226 (2001).
- [22] K. B. Sundaram and A. Khan, *Thin Solid Films* **295**, 87 (1997).
- [23] D. Basak, G. Amin, B. Mallik, G. K. Paul and S. K. Sen, *J. Cryst. Growth* **256**, 73 (2003).
- [24] D. M. Bagnall, Y. F. Chen, Z. Zhu, T. Yao, M. Y. Shen and T. Goto, *Appl. Phys. Lett.* **73**, 1038 (1998).
- [25] D. M. Bagnall, Y. Chen, M. Y. Shen, Z. Zhu, T. Goto and T. Yao, *J. Cryst. Growth* **184/185**, 605 (1998).
- [26] T. Minami, H. Nanto, S. Shooji and T. Tanaka, *Thin Solid Films* **111**, 167 (1984).
- [27] G. H. Lee, Y. Yamamoto, M. Kouroggi and M. Ohtsu, *Thin Solid Films* **386**, 117 (2001).
- [28] B. J. Jin, S. Im and S. Y. Lee, *Thin Solid Films* **366**, 107 (2000).
- [29] Q. P. Wang, D. H. Zhang, Z. Y. Xue and X. T. Hao, *Appl. Surf. Sci.* **201**, 123 (2002).