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Temperature Effect on ZnO/Si Thin Film Grown Using Metal Organic Chemical Vapor Deposition

Kwang-Sik Kim, Jung-Ho Lee, and Hyoun Woo Kim

School of Materials Science and Engineering, Inha University
253 Yonghyeon 3-dong, Nam-gu, Incheon 402-751, Korea

We investigated the effect of deposition temperature on the growth and structural quality of ZnO films on Si(100) substrate 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 400 °C. The film crystallinity improved and the surface smoothness decreased with increasing growth temperature.

Keywords : MOCVD, ZnO, surface smoothness, 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 resulting from a large exciton binding energy of 60 meV, it has received 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 the advantage in achieving devices of a commercial level since a high deposition rate and high crystallinity is attainable.

High quality ZnO films grown on a Si substrate pave the way for integration of devices with Si IC technology. Although most researchers grow ZnO films on sapphire substrates, there are not many reports on growing ZnO thin films on Si substrates by the MOCVD technique. In this paper, we demonstrate the depositing of ZnO films with a c-axis (002) orientation on the Si substrate by MOCVD. We investigate the effect of deposition temperature on the structural quality of thin films. We also investigate the relationship between the crystallinity and surface smoothness of ZnO thin films.

2. EXPERIMENTAL PROCEDURE

ZnO films were deposited on p-type silicon with (100) orientation by MOCVD using $Zn(C_2H_5)_2$ (99.9999 % purity diethylzinc ($Zn(C_2H_5)_2$) and O_2 (99.999 % purity) gas as source gases. Ar (99.999 % purity) was used as a carrier gas of the $Zn(C_2H_5)_2$ source. Before being loaded 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 in 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 the chamber. The $Zn(C_2H_5)_2$ bubbler was maintained at the temperature of 10 °C. The Ar/O_2 gas flow rate ratio of 1 and 2 were used. The substrate temperature during deposition was varied in the range of 250-500 °C. The deposition time was set to 10 min. The crystal structures were characterized by x-ray diffraction (XRD: CuKa1 λ=1.5405). The surface morphology of these films were evaluated by atomic force microscopy (AFM: Topomatrix corporation, Accurex II). Scanning electron microscopy (SEM: Hitachi S4200) was used to characterize the surface morphology and structural quality of the films.

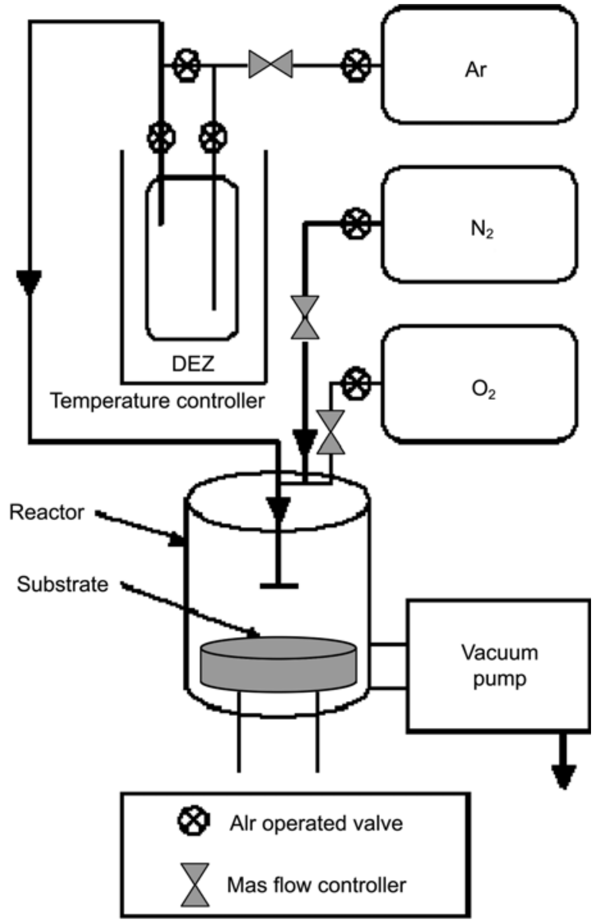

Fig. 1. Schematic diagram of MOCVD system.

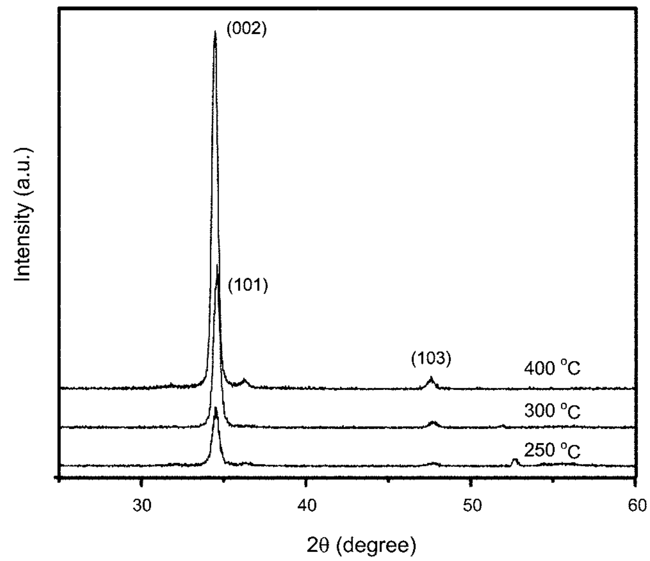

Fig. 2. XRD patterns of ZnO thin films with varying growth temperatures.

3. RESULTS AND DISCUSSION

Fig. 2 shows XRD patterns of ZnO thin films on Si(100) substrates in the temperature range of 250–400 °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 400 °C, corresponding to the (002) peaks of ZnO. The observation of the strong (002) peak indicates that the highly c-axis oriented film is grown. The films have other peaks such as (101), (103), etc., which may correspond to the granular structure of the film. Furthermore, an investigation of the XRD patterns of the ZnO film grown on the Si(100) substrate indicates that full-width at half-maximum (FWHM) of the (002) diffraction peak is about 0.4° at a growth temperature of 400 °C.

Since the intensity of the (002) diffraction peak increases gradually with increasing growth temperature, we assume that the c-axis orientation of ZnO films increases with increasing growth temperature in the range of 250–400 °C. The right-hand side of Fig. 3 shows the cross-sectional SEM images at growth temperatures of 250, 300, and 400 °C at an Ar/O_2 ratio of 2. According to SEM images, we reveal that most film structure is composed of columnar-structured grains, representing c-axis oriented grains. However, there are some granular structures especially on the bottom part of the film, corresponding to the initial growth which agree with XRD data. We surmise that the ZnO films have a granular structure in the beginning and as the growth proceeds, the granular growth changed into columnar growth.

At a 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 a high temperature. Then the growth orientation develops into one crystallographic direction of the low surface energy, leading to the improvement of ZnO crystallinity. The left-hand side of Fig. 3 shows the plan-view SEM image of ZnO thin films, revealing that the grain size becomes larger with increasing growth temperature.

Fig. 4 shows the cross-sectional SEM images at growth temperatures of 250, 300, and 400 °C at an Ar/O_2 ratio of 2, indicating that most of the film structure consists of columnar-structured grains, representing c-axis oriented grains, with some granular structure on the bottom part of the film.

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 250–400 °C. Fig. 5 shows the root mean square (RMS) data measured by AFM, revealing that surface smoothness decreases with increasing growth temperature and they agree with the previous reports [12,13]. This observation on the surface smoothness can be related to the observation of SEM, indicating that the crystallinity of ZnO films improves with increasing substrate tem-

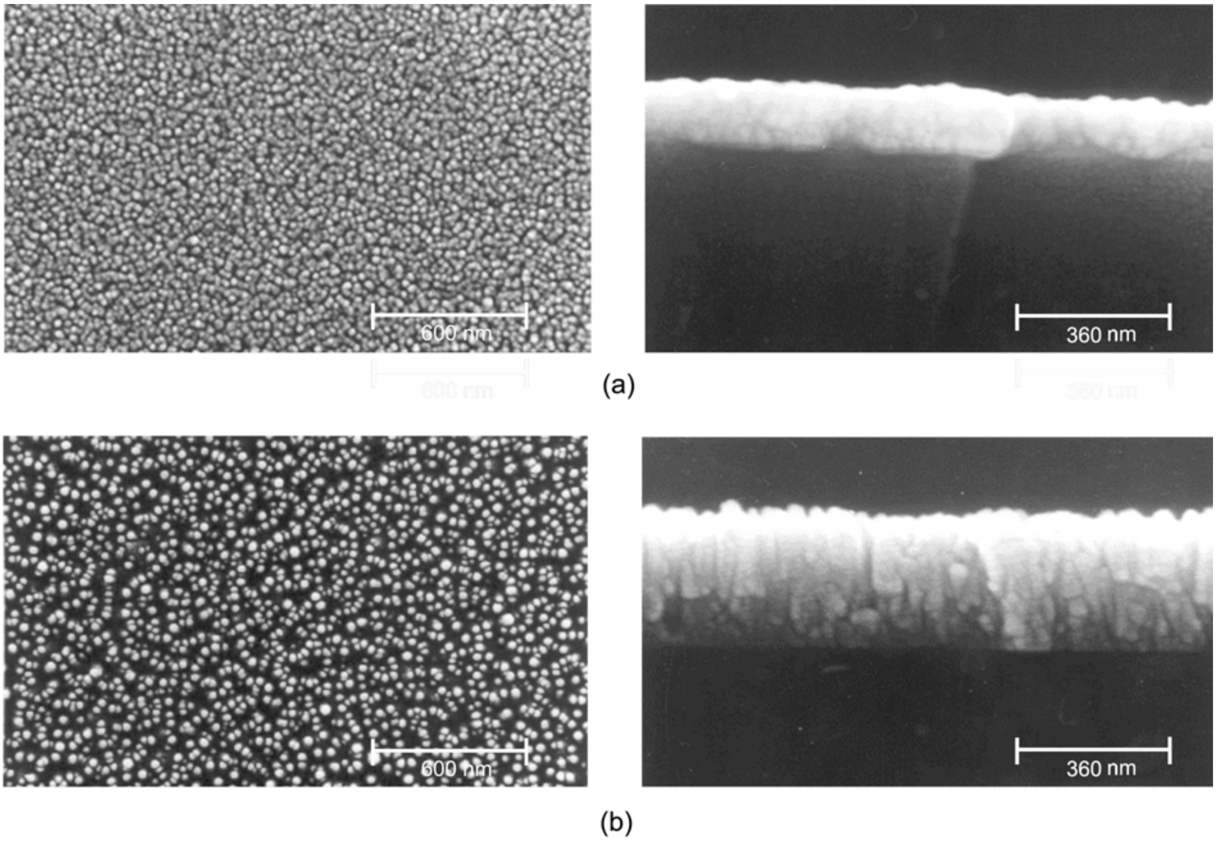

Fig. 3. SEM images of top view (left) and cross-sectional view (right) of ZnO films deposited at an Ar/O_2 ratio of 2: (a) 250 °C; (b) 300 °C; and (c) 400 °C.

perature. The high substrate temperature will cause the grain to overgrow and induce the rough surface [14]. It is noteworthy that the crystallinity of thin films improves and the surface smoothness decreases with increasing growth temperature.

As mentioned above, ZnO thin films were obtained in the temperature range of 250–400 °C. However, a large amount of ZnO rods were found to be deposited at 500 °C. Fig. 6 shows ZnO rods grown on the silicon substrate. The average diameter of the rods obtained was found to be 120 nm and the orientation of the rods appears to be randomized. Recently, the growth of highly oriented ZnO whiskers has also been reported [15]. The formation mechanism of ZnO thin films or ZnO rods is currently unknown. We surmise that the growth characteristics of ZnO thin films or ZnO rods are influenced by growth temperature. Further studies are necessary to reveal the detailed mechanism of formation of the ZnO thin films or rods.

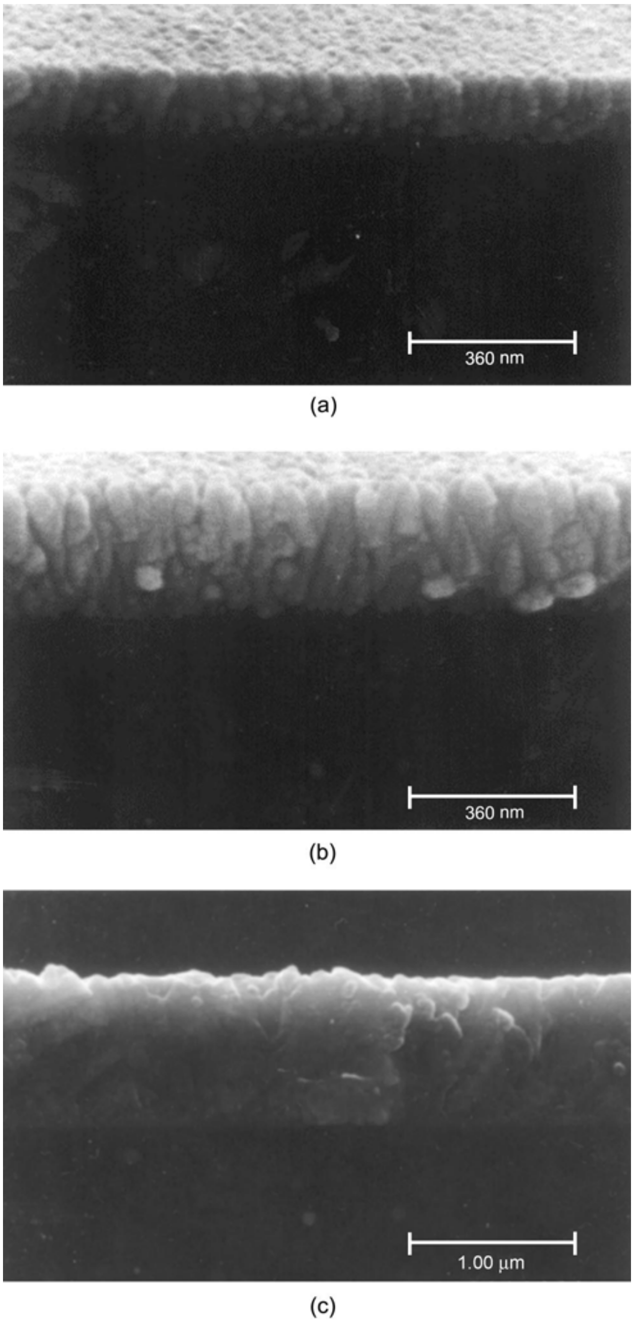

Fig. 4. SEM images of cross-section of ZnO films deposited at an Ar/O_2 ratio of 1: (a) 250 °C; (b) 300 °C; and (c) 400 °C.

4. CONCLUSIONS

The ZnO films are deposited on the Si substrate using the MOCVD technique. We reveal that the growth temperature plays a key role in determining the ZnO film properties. The crystallinity of thin films improved and the surface smoothness decreased with increasing growth temperature. In x-ray diffraction analysis with respect to the ZnO (002) peak, the full width at half maximum (FWHM) of 0.4° is achieved at 400 °C. ZnO rods are found to be grown on the silicon substrate at a temperature of 500 °C.

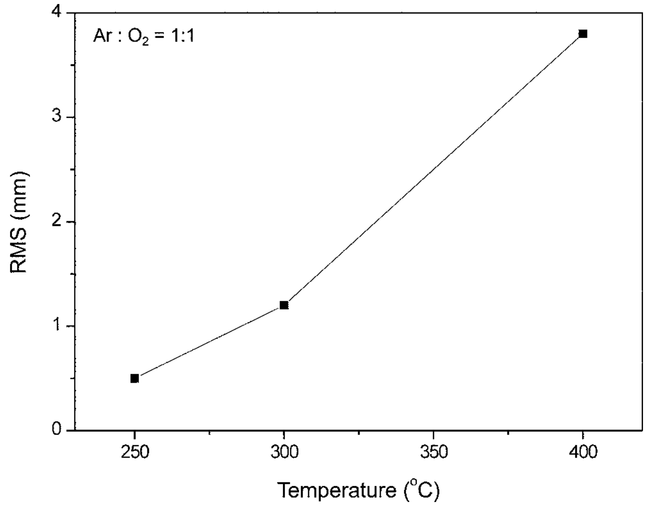

Fig. 5. Root mean square data measured by atomic force microscopy.

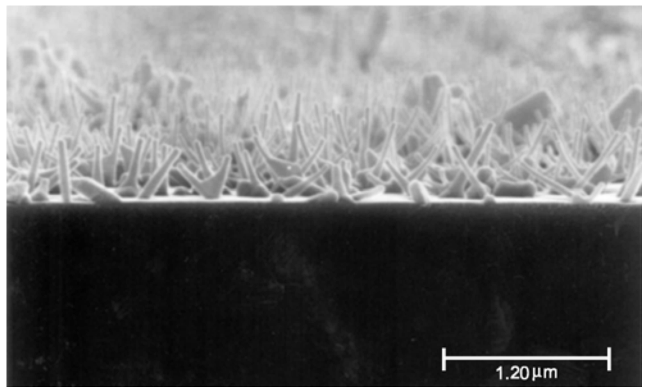

Fig. 6. SEM images of ZnO films deposited at 500 °C.

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