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Structural Characterization of ZnO Thin Film Grown on Si-Based Substrates by Metal Organic Chemical Vapor Deposition

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ZnO thin films have been grown using the metal organic chemical vapor deposition (MOCVD) technique on Si(100), Si(111) and SiO_2 substrates. We investigated the structural properties of ZnO thin film depending on growth temperature and substrate material in the range of 200∼300 °C. The XRD analysis revealed that the c-axis orientation of ZnO thin films increases up to 250 °C with increasing growth temperature, regardless of substrate material and orientation. The film grown at 250 °C showed a strong ZnO (002) diffraction peak, indicating that the ZnO film was highly c-axis oriented.

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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]. 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 (PLD) [8,9], ion beam deposition [10], chemical vapor deposition (CVD) [11,12], atomic layer deposition (ALD) [13], metal-organic chemical vapor deposition (MOCVD) [14, 15], and molecular beam epitaxy (MBE) [16] have been employed for the growth of ZnO films. However, MOCVD has an advantage in achieving devices at commercial level since high deposition rate and high-quality film is attainable, especially at low pressure. 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 [17]. Although 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 the MOCVD technique. In this paper, we employ the MOCVD technique to grow high-quality ZnO films on various substrates such as Si(100), Si(111), and SiO_2. Since the material properties strongly affect the performance of a device, the influence of growth condition including substrate temperature of 200∼300 °C and substrate material on the structural properties of the samples is presented. The crystallinity and surface morphology of ZnO films are investigated by X-ray diffraction (XRD), atomic force microscopy (AFM), and scanning electron microscopy (SEM).

II. EXPERIMENTAL

ZnO films grown in a vertical cool wall reactor by an MOCVD system were deposited on p-type Si(100), Si(111) and SiO_2 substrates by the MOCVD system using $Zn(C_2H_5)_2$ (99.9999 % purity DEZn (Diethylzinc)) and O_2 (99.999 % purity). The SiO_2 substrates were made by thermally depositing a 60 nm-thick SiO_2 layer on Si(100) substrate. Fig. 1 shows a schematic diagram of the MOCVD reactor used in our experiments. Before loading into the reactor, the substrate was cleaned in acetone for 10 min, HF (20:1) for 1 min and then rinsed by deionized water for 1 min. High-purity Ar was passed through the DEZn bubbler and saturated with DEZn vapor to the reactor. For MOCVD growth of ZnO films, the gas phase reaction will result in particle formation, which will degrade the ZnO film quality. In order to minimize the gas phase reaction, $Zn(C_2H_5)_2$ 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 a temperature of −2 °C.

In preliminary experiments, we could not find any evidence that the ratio of Ar and O_2 gas flow rate affected

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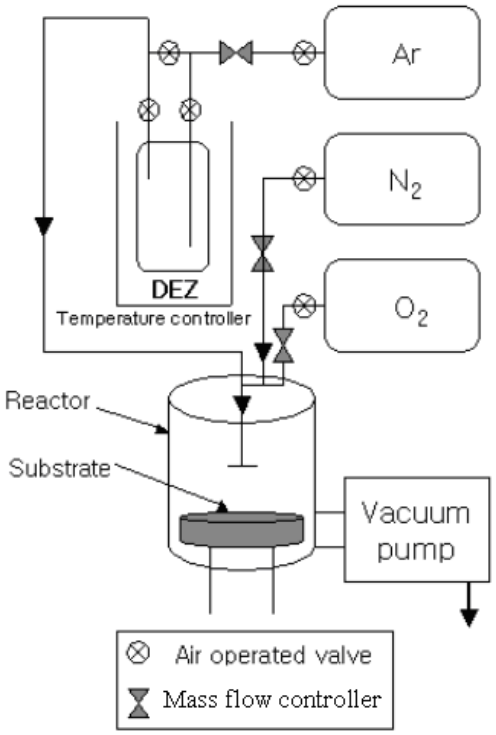

Fig. 1. Schematic diagram of MOCVD reactor.

the surface morphology and film crystallinity in our system. Fig. 2 shows the change of root mean square (RMS) data measured according to the ratio of Ar and O_2 flow rate in the temperature range of 250∼300 °C. It is noteworthy that the RMS value measured by atomic force microscopy (AFM), representing surface roughness, increases slightly with increasing growth temperature from 250 °C to 300 °C. Here, the ratio of Ar to O_2 gas flow rates was set to 2. The growth temperature ranged from 200 to 300 °C at a pressure of 5.0×10^{-1} Torr. The structural characteristics of the films were analyzed by x-ray diffraction (XRD) using CuKa1 radiation (λ=0.15405 nm) and by scanning electron microscopy (SEM: Hitachi S-4200). The surface roughness was measured using a Digital Instruments Nanoscope III AFM.

III. RESULTS AND DISCUSSION

Fig. 3(a) shows XRD patterns of ZnO thin films on Si(100) substrates in the temperature range of 200∼300 °C. The $\theta-2\theta$ scan data of ZnO films exhibits a strong 2θ peak at 34.53° in the sample grown at 250 °C, corresponding to the (002) peaks of ZnO. The observation of the strong (002) peak indicates that the film is grown with a c-axis orientation. Since the peak intensity of the neighboring peak ((101) peak) is not so dependent on the growth temperature, we regard the strength of

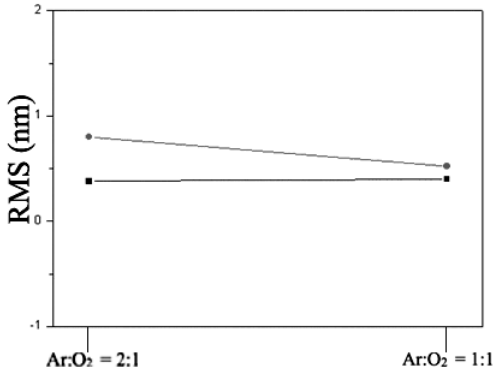

Fig. 2. Root mean square (RMS) data by AFM with varying the ratio of Ar and O_2 flow rate in the temperature range of 250-300 °C.

the (002) peak intensity as the relative intensity of the (002) peak compared to the neighboring peak. The film has other peaks such as (101), (102), *etc.*, which may correspond to a granular structure of the film. Furthermore, investigation of the XRD patterns of the ZnO film grown on Si(100) substrate indicates that full-width at half-maximum (FWHM) of the (002) diffraction peak is 0.41° at a growth temperature of 250 °C.

Fig. 3(b) and (c) show XRD patterns of ZnO thin films on SiO_2 substrates and Si(111) substrate in the temperature range of 200∼300 °C. The $\theta-2\theta$ scan data of ZnO films grown on SiO_2 substrates at 250 °C exhibits a strong 2θ peak at 34.55°, corresponding to the (002) peaks of ZnO. Also the FWHM of the (002) diffraction peak is 0.42°, on SiO_2 substrate at a growth temperature of 250 °C. However, it is notable that the ZnO films grown on Si(111) substrate at 250 °C show the strong 2θ peak at 34.55° with a FWHM of 0.39°, but the relative intensity is comparable to samples grown at 300 °C.

In order to investigate the temperature effect on c-axis orientation, we plotted XRD data of ZnO film grown on each substrate. Fig. 4 shows the dependence of intensity and FWHM of the (002) diffraction peak of samples on substrate temperature on Si(100), SiO_2 and Si(111) substrate. The FWHM of the (002) diffraction peak decreases with increasing growth temperature in the range of 200∼300 °C, regardless of substrate material and orientation. The intensity of the (002) diffraction peak shows a maximum value at about 250 °C, regardless of substrate material and orientation. Since the intensity of the (002) diffraction peak increases and the FWHM of the (002) diffraction peak decreases with increasing growth temperature from 200 to 250 °C, we assume that the c-axis orientation of ZnO film increases with increasing temperature in the range of 200∼250 °C. We have shown that the c-axis-oriented ZnO films are grown even at a low temperature (250 °C), regardless of substrate, including Si(100), SiO_2 and Si(111).

When we raise the substrate temperature to about 300 °C, the peak intensity is reduced significantly. Although

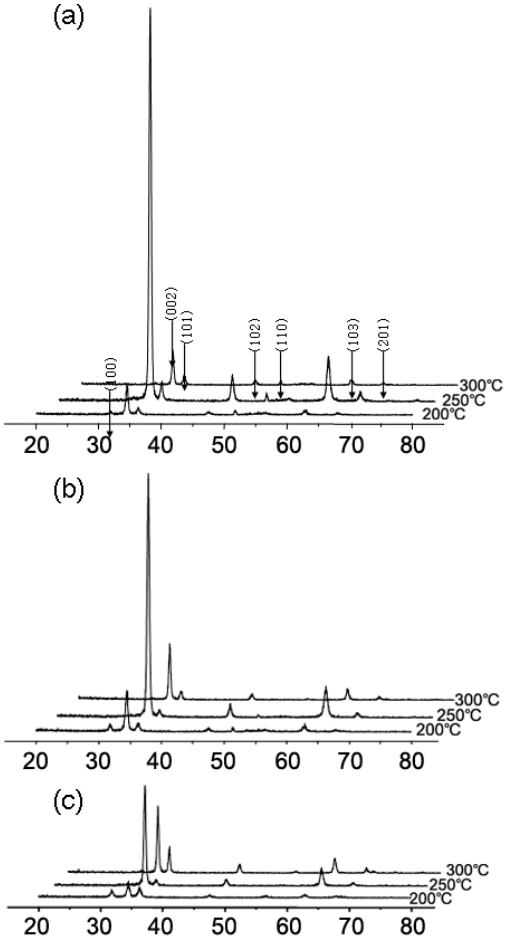

Fig. 3. XRD patterns of ZnO thin films with varying temperature at 200-300 °C grown (a) on Si(100) substrate, (b) on SiO_2 substrate, and (c) on Si(111) substrate.

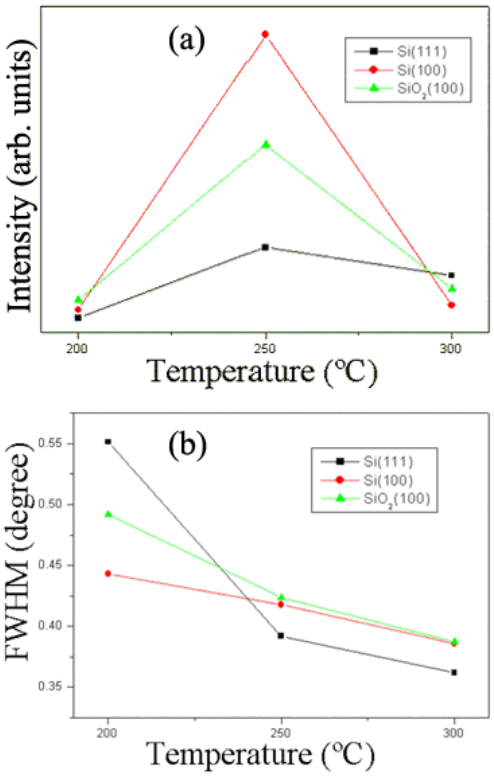

Fig. 4. Dependence of (a) intensity and (b) FWHM of (002) diffraction peak of ZnO films on substrate temperature on Si(100), SiO_2, and Si(111) substrate.

the FWHM decreases slightly from 0.41° to 0.38°, 0.42° to 0.38°, and 0.39° to 0.36°, respectively, using the substrates of Si(100), SiO_2 and Si(111), when the temperature increases from 250 °C to 300 °C, we are not sure about the degree of c-axis orientation, due to the low peak intensities.

Fig. 5(a), (c) and (e) are cross-sectional SEM images, revealing that c-axis oriented ZnO thin films are grown on Si(100), SiO_2 and Si(111) substrate at 250 °C. They show that most film structure consists 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. They agree with XRD data. We surmise that the ZnO films have granular structure at the beginning and as the growth proceeds, the granular growth changes into columnar growth. It is noteworthy that this phenomenon is observed regardless of substrate material and orientation. Although we cannot explain the growth mechanism at this moment, further study is underway to understand this observation.

Fig. 5(b), (d) and (f) indicate that the grown ZnO thin films have some columnar grains almost regularly, representing c-axis orientation on Si(100), SiO_2 and Si(111) substrate at 300 °C. Further study is necessary to reveal the dependence of ZnO film quality on growth temperature above 250 °C.

As ZnO films are to be used for SAW device application, the rough surface will impede wave transmittance and increase propagation loss. In order to investigate the surface roughness of the ZnO films grown on Si(100) and SiO_2 substrate, we have presented the AFM data. Fig. 6b and d show that the mean surface roughness measured by AFM is about 11.1 nm and 4.4 nm, respectively, when deposited on Si(100) and SiO_2 substrate. Fig. 6a and c show that the SEM images agree with AFM measurement, because larger grain size may induce the rougher surface. The surface morphology depending on substrate material needs to be studied further, related to the growth mechanism of ZnO films.

IV. CONCLUSION

Good structural-quality ZnO thin films are achieved on Si(100), Si(111) and SiO_2 substrates at a low substrate temperature of 250 °C by using MOCVD. The

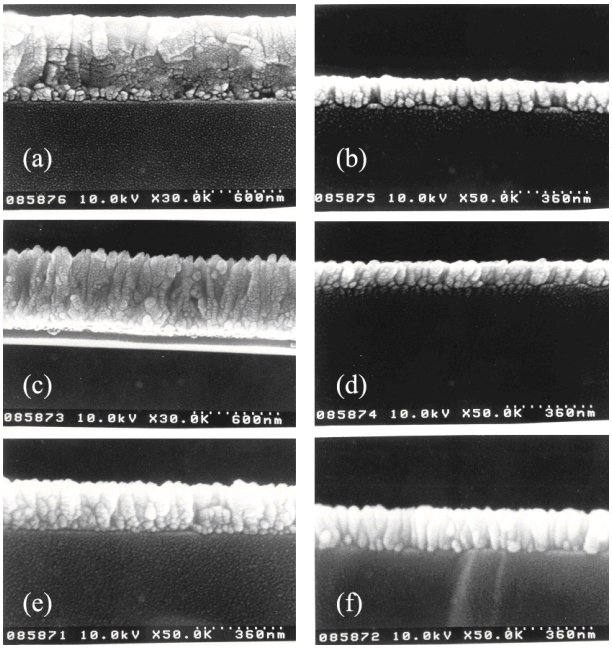

Fig. 5. Cross-sectional view of ZnO film grown (a, b) on Si(100) substrate, (c, d) on SiO_2 substrate, and (e, f) on Si(111) substrate. (a, c, e): grown at 250 °C. (b,d,f): grown at 300 °C.

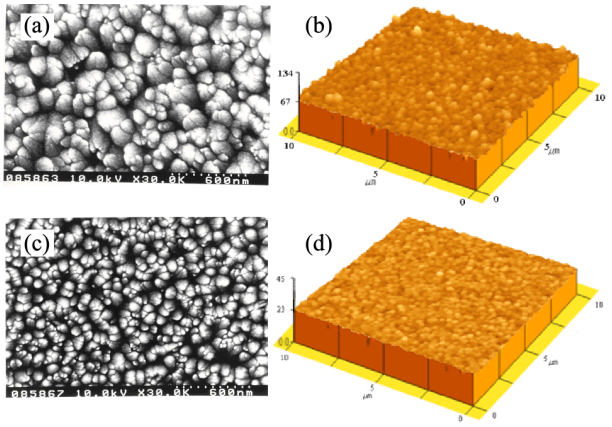

Fig. 6. Plan view of ZnO film grown (a,b) on Si(100) substrate, (c,d) on SiO_2 substrate at 250 °C. (a,c) SEM images. (b,d) AFM images.

structural quality based on XRD analysis improves with increasing substrate temperature up to 250 °C, regardless of substrate material and orientation. X-ray diffraction reveals that the ZnO films are highly c-axis-oriented and the line width of the ZnO(002) peak is significantly small, and the full width at half maximum (FWHM) of 0.4 ° was achieved using both Si(100) and SiO_2 substrates at 250 °C. Growth temperatures of high-quality ZnO films are significantly lowered using MOCVD, shedding light on the potential application of ZnO film in electronic and optoelectronic devices.

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