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Influence of the substrate on the structural properties of sputter-deposited ZnO films

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We have deposited ZnO films on various substrates using the r.f. magnetron sputtering method. X-ray diffraction and scanning electron microscopy coincidentally revealed that the larger grain size and the higher crystallinity were attained when the ZnO films were deposited on sapphire substrates, compared to the films on Si substrates. The XRD analysis revealed that the *c*-axis lattice constant decreased and increased, respectively, by thermal annealing for the ZnO films deposited on Si and sapphire substrates. Atomic force microscopy indicated that the surface roughness was higher for the films deposited on the sapphire substrates.

1 Introduction Zinc oxide (ZnO) thin films received much attention due to its unique piezoelectric and piezooptic properties made suitable for surface acoustic devices [1], low loss optical waveguides [2], optoelectronic devices [3, 4], and gas sensors [5]. Additionally, ZnO has been developed as a promising alternative to transparent conducting indium tin oxide and tin oxide coating due to its low cost and non-toxicity [6]. ZnO have been prepared by various physical vapor deposition techniques such as evaporation, r.f./d.c. sputtering, ion beam sputtering, atomic layer epitaxy etc., as well as a plethora of chemical methods. Among these methods, r.f. magnetron sputtering has gained importance due to its potential for low-cost and low temperature process. Although many researchers have grown ZnO films by various techniques, the effects of substrate material on the structural characteristics of ZnO thin films have not been sufficiently investigated [7, 8].

In this paper, we have deposited the *c*-axis oriented ZnO films by the r.f. magnetron sputtering method. We have studied the dependence of the structural properties on the substrate material, i.e. silicon (Si) and sapphire.

2 Experimental A schematic description of the r.f. sputtering system is provided elsewhere [9]. ZnO films were deposited by an r.f. magnetron sputtering system using a ZnO (99.99% purity) target with a diameter and a thickness of 75 mm and 6 mm, respectively. The sputtering was carried out in a 30 sccm Ar (99.99% purity) gas atmosphere by supplying 80–250 W r.f. power. The magnetron is capacitively powered with 13.56 MHz radio-frequency. In ordet to exclude the thickness effect, we have fixed the ZnO film thickness to about 500–600 nm.

The ZnO thin films were sputtered on Si and sapphire substrates. The Si substrate was p-type silicon with (001) orientation and the resistivity was 1–30 ohm–cm. The Si substrate was rinsed in acetone for 10 min, HF (20:1) for 10 seconds and then rinsed by deionized water for 1 minute before loading into the sputtering system. The sapphire substrate was of (001) orientation and were cleaned in acetone for 10 min.

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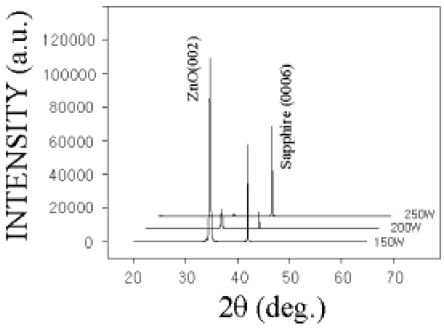

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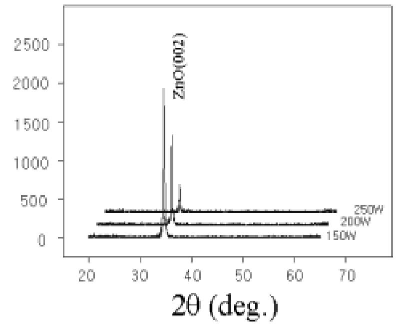

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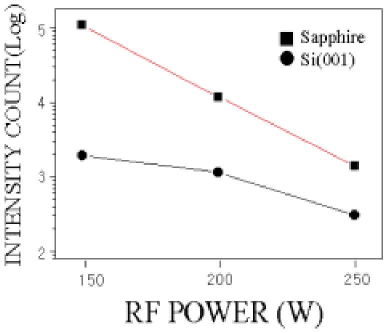
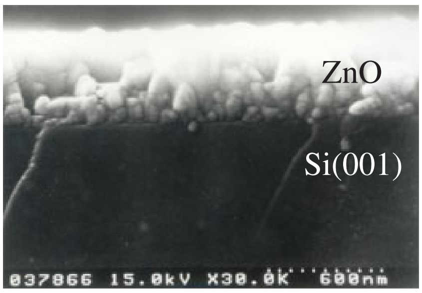


c)

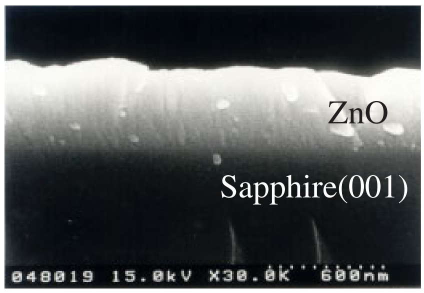
Fig. 1 (online colour at: www.interscience.wiley.com) Relative intensity of (002) diffraction peak of ZnO films deposited on a) Si and b) sapphire substrates with varying the r.f. power. c) Comparison between Si and sapphire substrates in terms of the relative intensity (log scale).

The chamber was down to 6×10^{-6} torr using a turbo-molecular pump before introducing the Ar sputtering gas into the chamber. The ZnO film was grown at room temperature at a pressure of 5.0×10^{-2} torr. The thermal annealing was performed in a furnace using quartz tube reactor in the temperature of 500−900 °C in oxygen gas flow of 3 standard liter per minute for 10 minutes. The structural properties of the films (crystalline structure or microstructure) were analyzed by X-ray diffraction (XRD) using CuKa1 radiation ($\lambda = 0.154056$ nm), by scanning electron microscopy (SEM) (Hitachi S−4200), and by atomic force microscopy (AFM) (Digital Instruments Nanoscope III) with a scan size of 10 µm × 10 µm.

3 Results and discussion In order to compare the structural properties of ZnO films on Si and sapphire substrates, we have deposited ZnO films with varying the r.f. power for each substrate. The dependence of growth rate on the r.f. power indicates that the film growth rate is almost linearly proportional to the r.f. power, regardless of the substrate material. In XRD analysis, the θ–2θ scan data of ZnO films exhibit a strong 2θ peaks at 34.53°, corresponding to the (002) peaks of ZnO. Since the *c*-axis (002) diffraction



a)



b)

Fig. 2 Cross-sectional SEM images of ZnO films grown on a) Si and b) sapphire substrates.

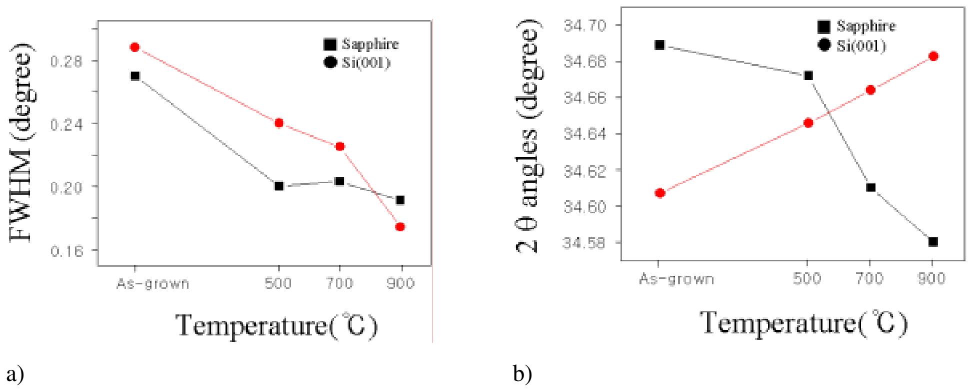


Fig. 3 (online colour at: www.interscience.wiley.com) a) FWHM and b) peak angle (2θ) of (002) diffraction peak from ZnO films deposited with an r.f. power of 150 W.

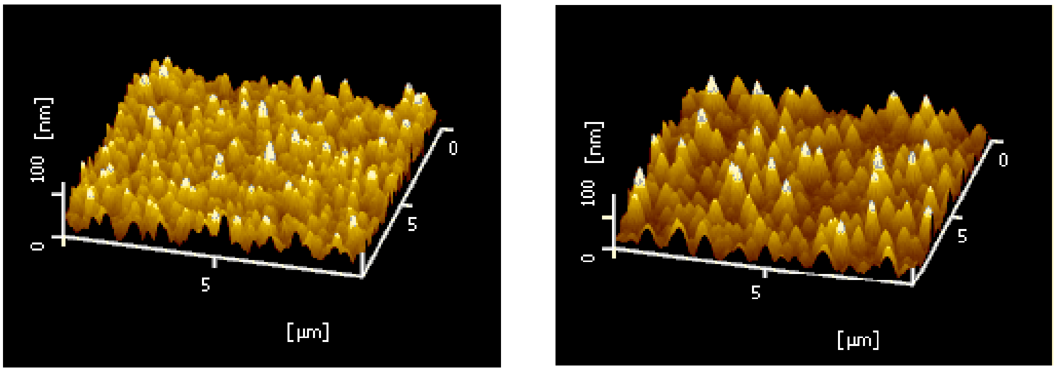
peaks were distinguishably observed in the grown ZnO films, we suppose that the *c*-axis oriented ZnO film is obtained, regardless of the substrate material. Figure 1 shows the relative intensity of ZnO film-with the (002) orientation, deposited on Si and sapphire substrates, as a function of r.f. power ranging from 150 to 250 W, indicating that the relative intensity is significantly higher when ZnO films are deposited on sapphire substrates.

We have compared the cross-sectional SEM images of ZnO films grown on Si and sapphire substrates in Fig. 2, in which the RF power was set to 150 W for the same growth time. The images indicate that the crystallinity of the film on sapphire substrate is higher than that on Si substrate, agreeng with the XRD intensity data. We suppose that relatively little lattice mismatch between ZnO and sapphire substrates helps to grow the higher crystalline films.

In order to analyze the effect of substrate on the structural properties of ZnO films, we have annealed the samples at the temperature of 500–900 °C. Figure 3a and 3b, respectively, show the full width at half maximum (FWHM) and the peak angle (2θ) of (002) diffraction peak measured in ZnO thin films when deposited with the r.f. power of 150 W. Figure 3a indicates that the FWHM decreases with increasing the annealing temperature, regardless of substrate material. This observation also indicates that the grain size becomes larger and thus the crystallinity may be improved with increasing the annealing temperature.

Figure 3b indicates that the 2θ angle of the ZnO films with respect to the (002) diffraction peak grown on Si(001) and sapphire(001) substrates, respectively, are 34.61° and 34.69°. Since the XRD angle (2θ) of the bulk ZnO are 34.44° and by calculating with the Bragg law [10], we reveal that *c*-axis lattice constant becomes larger when deposited at room temperature, regardless of the substrate material. It is noteworthy that the 2(angle increases with increasing the annealing temperature for the ZnO films grown on Si substrates but decreases with increasing the annealing temperature for the films grown on sapphire substrates. The different substrates will lead to different crystal mismatch and thermal expansion between substrates and ZnO films, and the crystal lattice mismatch and difference of thermal expansion may cause different strains and stress in the films. In case of ZnO films on Si substrates, we suppose that increasing the annealing temperature increases the compressive stress along the c–axis direction and thus reduces lattice plane spacing and increases the 2(angle of XRD. On the other hand, in case of ZnO films on sapphire substrates, increasing the annealing temperature reduces the compressive stress along the c-axis direction and thus increases the lattice plane spacing and reduces the 2(angle of XRD. Further systematic study is necessary to reveal the detalied mechanism.

Figure 4 shows the AFM images of ZnO films deposited with the r.f. power of 150 W and subsequently annealed at 700 °C, indicating that the surface roughness (root-mean-square) of the films grown on sapphire substrates is higher than that on Si substrates. We have the similar results for the samples annealed at other temperatures and for the as-grown samples. Accordingly, the AFM data agree with the



a) b)

Fig. 4 (online colour at: www.interscience.wiley.com) AFM images of ZnO films deposited a) on Si(001) and b) on sapphire(001) substrates with the r.f. power of 150 W and subsequently annealed at 700 °C.

XRD data (Fig. 3a), implying that larger grain size corresponds to the higher surface roughness. The different substrates will lead to different crystal mismatch between substrates and ZnO films. We conclude that for the ZnO films grown on sapphire substrates, due to their relatively smaller lattice mismatch, the atoms have more chances to occupy the correct site in the crystal lattice and grains with the lower surface energy will become larger. Then the growth orientation develops into one crystallographic direction of the lower surface energy.

4 Conclusions ZnO thin films have been grown on Si and sapphire substrates at room temperature using the r.f. magnetron sputtering technique. The XRD of all ZnO films showed *c*-axis orientation, regardless of substrate material. The relative intensity of (002) diffraction peak is higher for ZnO films grown on sapphire substrates than for ZnO films on Si substrates. The FWHM of (002) diffraction peak decreases with increasing the annealing temperature, regardless of substrate material. The XRD (002) peak angle increases and decreases, respectively, with increasing the annealing temperature for ZnO films deposited on Si and sapphire substrates. The grain size is larger and the surface is more rough for ZnO films grown on sapphire substrate. We believe that the approach to investigate the very low temperature growth and annealing behavior of ZnO films depending on the substrate material are a step toward the efficient production of ZnO devices.

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