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Formation mechanism of preferential *c*-axis oriented ZnO thin films grown on p-Si substrates

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Recently, ZnO thin films grown on various substrates have proved particularly attractive for their promising applications in optoelectronic devices, such as solar cells [1], photodetectors [2], ultra-violet laser diodes [3], and light emitting diodes [4], because of their strong exiton binding energies and thermal stabilities [5, 6]. In particular, ZnO/Si heterostructures are of current interest since Si substrates with large areas and high quality are relatively cheap and extensively available in comparison with sapphires [7]. Even though some studies concerning the formation and physical properties of the preferential *c*-axis oriented ZnO thin films on Si substrates have been reported [8–10], the formation mechanisms of preferential *c*-axis oriented ZnO thin films have not yet been established.

This letter reports the formation mechanism of preferential *c*-axis oriented ZnO thin films grown on Si substrates by using the radio-frequency magnetron sputtering method. Auger electron spectroscopy (AES) measurements were carried out to characterize the composition of the ZnO/Si heterostructures, and X-ray diffraction (XRD) measurements were performed to investigate the crystallization of the ZnO thin film. Transmission electron microscopy (TEM) measurements were carried out in order to investigate the microstructural properties of the ZnO/p-Si (100) heterostructures. Furthermore, a possible formation mechanism is described on the basis of the experimental results.

Polycrystalline stoichiometric ZnO with a purity of 99.999% was used as a target material and was precleaned by repeated sublimation. The carrier concentration of the B-doped p-Si substrates with the (100) orientation used in this experiment was 1×10^{15} cm^{-3}. The substrates were degreased in trichloroethylene (TCE), rinsed in de-ionized water, etched in a mixture of HF and H_2O (1:1) at room temperature for 5 min, and rinsed in TCE again. After the Si wafers were cleaned chemically, they were mounted onto a susceptor in a growth chamber. After the chamber was evacuated to 8×10^{-7} Torr, the deposition was carried out at substrate temperatures between 300 and 600 °C. Ar gas with a purity of 99.999% was used as the sputtering gas. Prior to ZnO growth, the surface of the ZnO was polished by Ar^+ sputtering. The ZnO deposition was performed at a system pressure of 0.021 Torr and a radio-frequency power (radio frequency = 13.26 MHz) of 100 W. The flow-rate ratio of the Ar/O_2 was 2, and the growth rate was approximately 1.17 nm/min.

The AES measurements were performed using a Perkin-Elmer Phi 400 scanning Auger microprobe. The XRD measurements were performed using a Rigaku D/Max-B diffractometer with Cu K_α radiation. The TEM measurements were performed using a Jeol JEM 3010 transmission electron microscope operating at 300 keV. The samples for cross-sectional TEM measurements were prepared by cutting and polishing with diamond paper to a thickness of approximately 30 μm and then argon-ion milling at liquid-nitrogen temperature to electron transparency.

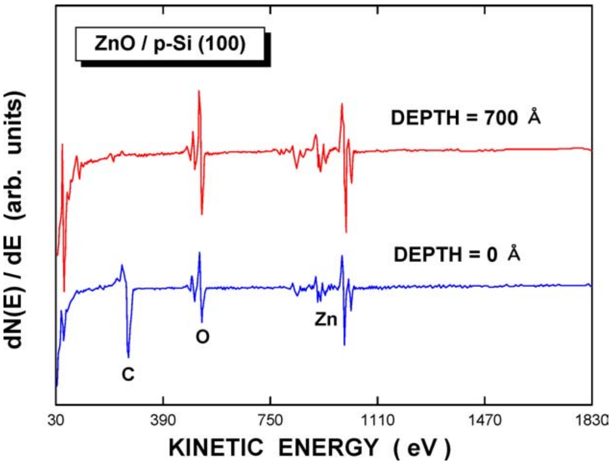

Figure 1 Auger electron spectroscopy spactra obtained from the ZnO/p-Si (100) heterostructure. The lower curve was obtained at the surface of the grown ZnO/p-Si (100) heterostructure, and the upper one was obtained at a 700 Å depth.

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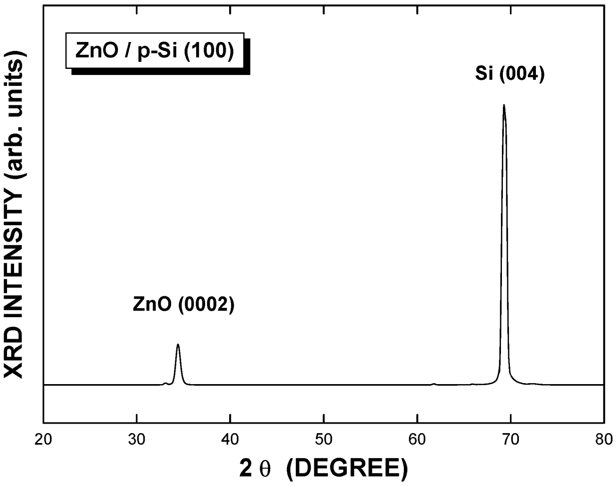

Figure 2 X-ray diffraction pattern of the ZnO thin films grown on Si (10) substrates.

The as-grown ZnO films had mirror-like surfaces without any indication of pinholes, which was confirmed by using Normarski optical microscopy and scanning electron microscopy measurements. The compositions and the interfacial qualities of the grown samples on Si substrates were investigated by AES measurements, and AES results are presented in Fig. 1, which shows that the as-grown films consisted of zinc, oxygen, and carbon at the surface and of zinc and oxygen at a 700 Å depth. The carbon impurities at the ZnO surface might originate from contamination due to the target material during growth or to air pollution after growth. Auger depth profiles of the ZnO/p-Si (100) heterostructure show that the stoichiometry of the ZnO film was uniform regardless of the depth and that the interfaces between the ZnO thin film and the Si substrate were not abrupt. The thickness of the ZnO, determined from the AES depth profile, was approximately 140 nm, and this value was in reasonable agreement with that obtained from the ellipsometer measurements.

Fig. 2 shows the XRD pattern for the as-grown ZnO thin films grown on p-Si (100) substrates. The (0002) K_α diffraction peak corresponding to the ZnO (0001) film, together with the (004) diffraction peak related to the Si (100) substrate, is clearly observed. The result of the XRD pattern for the ZnO film grown on the Si (100) substrate indicates that the grown ZnO films have a strong *c*-axis orientation. The epitaxial relationship between the ZnO thin film and the Si substrate was investigated by using the pole figure method. The pole figure, obtained by using the ZnO $(10\bar{1}1)$ planes, for the as-grown ZnO/p-Si heterostructure is shown in Fig. 3. The pole figure indicates that as-grown ZnO thin films have columnar grains, the grains having their [0002] crystallographic axis perpendicular to the Si (100) substrate, indicative of the random rotational orientations along the *c*-axis.

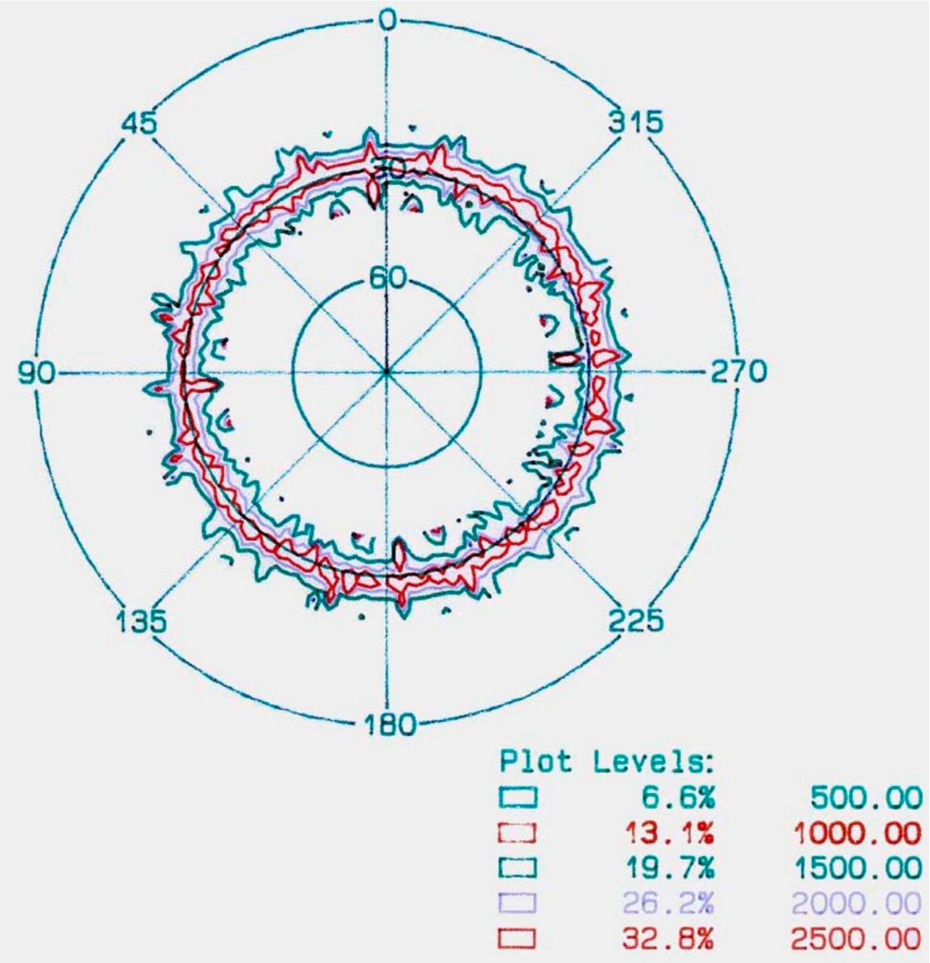

Figure 3 Pole figure of the ZnO/Si (100) heterostructures.

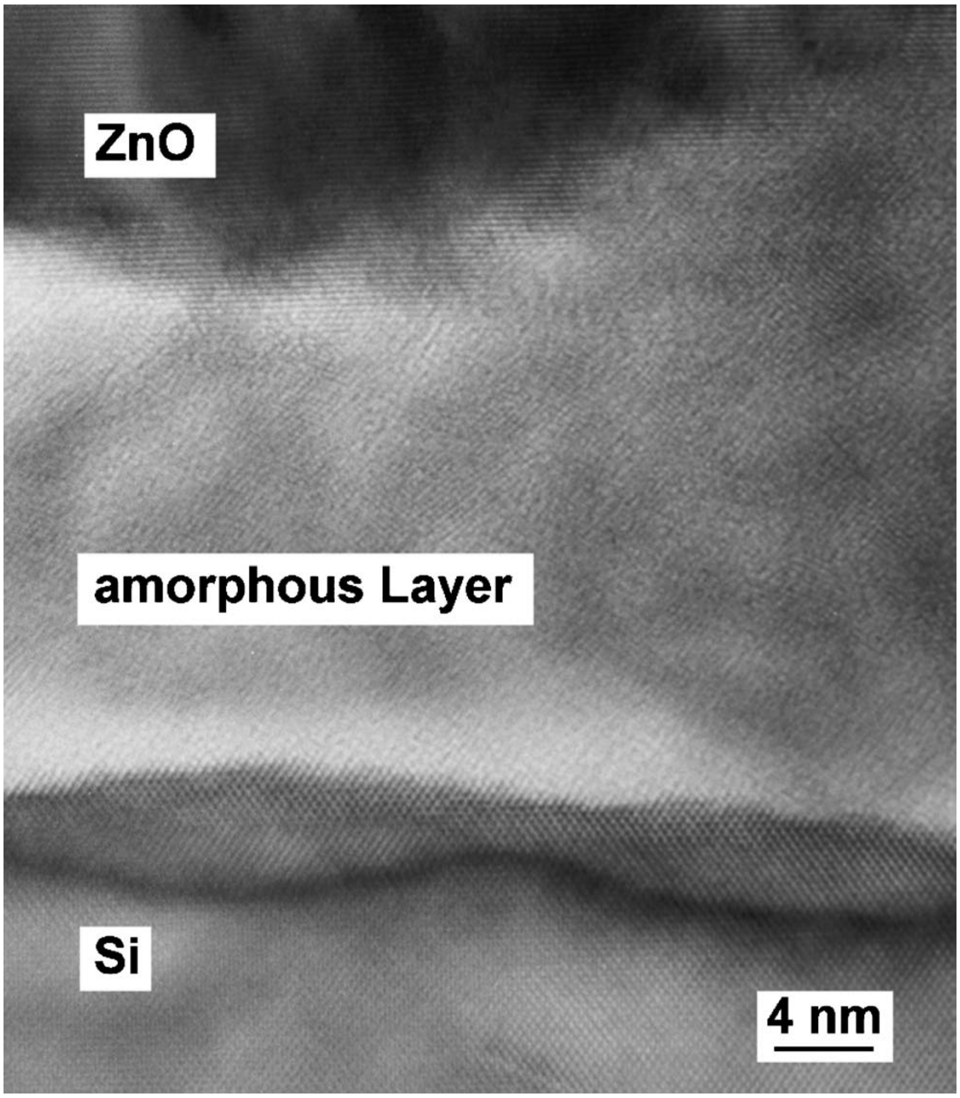

Figure 4 High resolution transmission electron microscopy image of the ZnO/Si (100) heterostructures.

Fig. 4 shows a high resolution TEM (HRTEM) image of the ZnO/Si (100) heterostructures. The top ZnO preferential oriented film, the amorphous interfacial layer, and the Si substrate are observed. It is clearly observed that an amorphous interfacial layer between the top ZnO layer and the bottom Si substrate exists. The XRD pattern, the pole figure, and the HRTEM image indicate that the ZnO layers form a c-axis preferentially oriented film.

Even though Zn and O molecules contribute to probably quite a complicated growth process of the ZnO layer, a qualitative idea of the formation mechanism of the c-axis preferentially oriented ZnO thin film can be suggested on the basis of the experimental results and by considering the minimization of the surface free energy. Since the ZnO thin films are II–VI semiconductors with strong ionic bonds, when the deposition condition is controlled within the optimum range of the energetically stable state, the ZnO thin film should be grown with a c-axis orientation. According to the theoretical result of the surface free energy [11], the value of the surface free energy for the ZnO (0001) plane is minimum at the growth stage. Even though the formation of the ZnO textural thin film strongly depends on the growth condition, the growth conditions used in this study are suitable for the formation of the c-axis oriented ZnO thin film. Since the c-axis preferentially oriented ZnO thin film is grown on the amorphous interfacial layer, the effect of the surface energy of the thin film is more dominant than that of the strain energy in the thin film or the interface energy between the ZnO thin film and the Si substrate. Therefore, the minimization of the surface energy leads the ZnO thin film to form a (0001) textural structure regardless of the existence of the amorphous layer between the ZnO thin film and the Si (100) substrate.

In summary, the AES, XRD, and HRTEM results showed that the c-axis preferentially oriented ZnO thin films were grown on Si (100) substrates by using the radio-frequency magnetron sputtering technique. A possible formation of the c-axis oriented ZnO thin films was suggested on the basis of the experimental results. Even though our main purpose was the growth of ZnO epitaxial layer on the Si substrate, the amorphous layer might mask the growth of the ZnO epitaxial layer. These present observations can help improve understanding of the formation mechanism of the ZnO/Si heterostructures.

Acknowledgments

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References

1. U. RAU and M. SCHMIDT, *Thin Solid Film* **387** (2001) 141.
2. Y. LIU, C. R. GORLA, S. LIAN, N. EMANETOGLU, Y. LU, H. SHEN and M. WRABACK, *J. Electr. Mater.* **29** (2000) 60.
3. R. F. SERVICE, *Science* **276** (1997) 895.
4. T. SOKI, Y. HATANAKA and D. C. LOOK, **76** (2000) 3257.
5. D. M. BAGNALL, Y. F. CHEN, Z. ZHU, T. YAO, M. Y. SHEN and T. GOTO, *Appl. Phys. Lett.* **73** (1998) 1038.
6. C. G. GRANGVIST, *Thin Solid Films* **193/194** (1990) 730.
7. K. OGATA, T. KAWANISKI, K. MAEJIMA, K. SAKURAI, SZ. FUJITA and SG. FUJITA, *J. Crystal Growth* **237** (2002) 553.
8. J. H. CHOI, H. TABATA and T. KAWAI, *ibid.* **226** (2001) 493.
9. A. NAHHAS, H. K. KIM and J. BLACHERE, *Appl. Phys. Lett.* **78** (2001) 1511.
10. Y. ZHANG, G. DU, D. LIU, X. WANG, Y. MA, J. WANG, J. YIN, X. YANG, X. HOU and S. YANG, *J. Cryst. Growth* **243** (2002) 439.
11. N. FUJIMURA, T. NISHIHARA, S. GOTO, J. XU and T. ITO, *ibid.* **130** (1993) 269.

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