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Growth mechanisms of thin-film columnar structures in zinc oxide on *p*-type silicon substrates

J. W. Shin and J. Y. Lee
Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Daejeon 305-701, Korea

T. W. Kim[a] and Y. S. No
Research Institute of Information Display, Division of Electronics and Computer Engineering, Hanyang University, 17 Haengdang-dong, Seongdong-gu, Seoul 133-791, Korea

W. J. Cho
Nano Device Research Center, Korea Institute of Science and Technology, Hawolgok-dong, Seongbuk-gu, Seoul 136-791, Korea

W. K. Choi
Thin Film Material Research Center, Korea Institute of Science and Technology, Seoul 136-701, Korea

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X-ray diffraction analysis reveals that the crystallinity of (0001)-oriented columnar grains in ZnO thin films grown on *p*-Si (100) substrates is enhanced with increasing growth temperature, and transmission electron microscopy confirms that the columnar structures become more stable at higher growth temperature. The morphological evolution of the columnar structure in ZnO thin films is described on the basis of experimental measurements. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2174829]

Wide band-gap II–VI compound semiconductors structures have attracted much attention because of their many potential applications for optoelectronic devices.[1–3] Among these, ZnO thin films have been particularly interesting due to their potential applications in optoelectronic devices, such as light-emitting diodes,[4] laser diodes,[5] and solar cells,[6] because of their large band gaps, low dielectric constants, large exciton binding energies, and excellent chemical stabilities.[7–12] ZnO/Si heterostructures, which are fabricated by utilizing the combined advantages of the large excitonic binding energy of the ZnO thin film and the availability of low-cost, large-area Si substrates,[13] are particularly interesting due to their many possible applications in the blue region of the spectrum.[14] Since the optical properties of ZnO thin films are strongly affected by their microstructural properties, systematic studies of the stability of the columnar structures related to stress generation and relaxation in ZnO/Si heterostructures are necessary if high-quality optoelectronic devices utilizing ZnO/Si heterostructures are to be fabricated. Even though prior investigations of the surface and structural properties of columnar structures in ZnO thin films have been performed,[15–17] systematic studies of the morphological evolution of ZnO thin films grown on Si substrates have not been performed yet.

This letter reports data on the temperature-dependent growth of columnar structures in ZnO thin films on *p*-Si (100) substrates fabricated by radio-frequency magnetron sputtering. X-ray diffraction (XRD) measurements are used to investigate the crystallization of the ZnO thin film. Transmission electron microscopy (TEM) and selected-area electron diffraction pattern (SADP) are used to investigate the microstructural properties of the ZnO/*p*-Si (100) heterostructures. The evolution process and growth mechanism of the columnar structures in the ZnO thin films are described on the basis of these experimental results.

Polycrystalline stoichiometric ZnO with a purity of 99.999% was used as a source target material and was precleaned by repeated sublimation. The carrier concentration of the B-doped *p*-Si substrates with (100) orientation used in this experiment was 1×10^{15} cm^{-3}. The substrates were degreased in trichloroethylene (TCE), rinsed in deionized 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 had been cleaned chemically, they were mounted onto a susceptor in a growth chamber. The depositions of the ZnO thin films were done at substrate temperatures of 27, 200, and 600 °C.

The XRD patterns of ZnO thin films grown on *p*-Si (100) substrates at (a) 27, (b) 200, and (c) 600 °C are shown in Fig. 1. 0002 $K\alpha_1$ diffraction peaks are clearly observed at 34.21°, 34.32°, and 34.45° for the ZnO (0001) films grown at 27, 200, and 600 °C, respectively, indicating that the films have strong *c*-axis orientations, which give the lowest surface energy.[18,19] The full width at half maximum for the 0002 ZnO diffraction peak for the ZnO/Si heterostructure decreases with increasing growth temperature, indicative of an enhancement in the crystallinity of the ZnO film. The peak position of the 0002 ZnO diffraction peak shifts toward the higher angle side with increasing growth temperature and approaches the peak position of the ZnO bulk (34.47°). The crystal lattice constants of the *c* axis of the ZnO thin films grown on Si substrates at 27, 200, and 600 °C, determined from the Bragg equation, are 0.5242, 0.5226, and 0.5206 nm, respectively. The peak position corresponding to the 0002 diffraction peak for the ZnO thin film grown on Si substrates at 600 °C is almost the same as that of the ZnO bulk, indicative of a relaxation of the tensile stress existing along the *c* axis in the ZnO film grown at this high temperature.

[a]Author to whom correspondence should be addressed; electronic mail: twk@hanyang.ac.kr

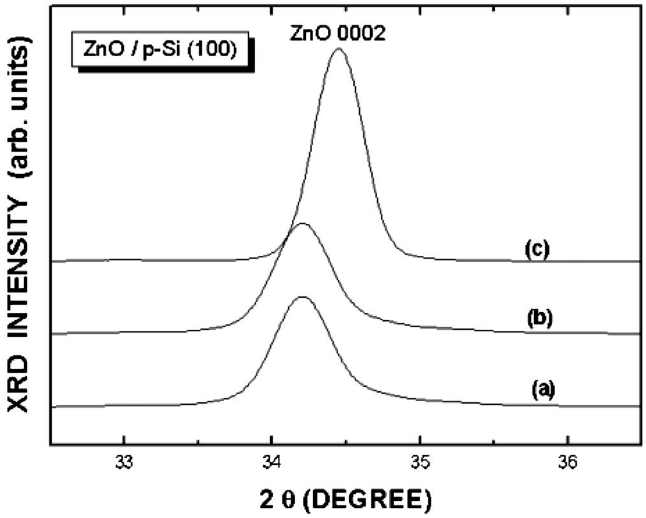

FIG. 1. XRD patterns of ZnO thin films grown on *p*-Si (100) substrates at (a) 27, (b) 200, and (c) 600 °C.

Figure 2 shows cross-sectional bright-field TEM images of the ZnO thin films grown on *p*-Si substrates at (a) 27, (b) 200, and (c) 600 °C. The thickness of the ZnO thin film, determined from the TEM image, is approximately 670 nm. The grain size of the ZnO thin film increases with increasing growth temperature because of enhanced kinetics and coalescence in the ZnO thin film. Since the atomic diffusivity contributing to the coalescence increases with increasing growth temperature, the grain size of the ZnO thin film during coalescence increases with increasing growth temperature.[20]

The columnar structures in the ZnO thin film become more stable with increasing growth temperature, resulting in

(a)

(b)

(c)

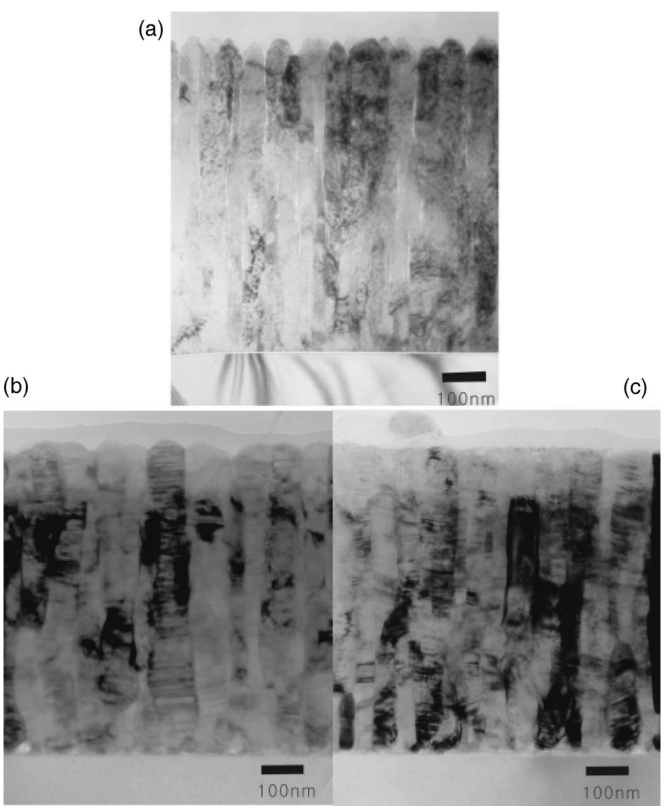

FIG. 2. Cross-sectional bright-field TEM images of ZnO thin films grown on *p*-Si (100) substrates at (a) 27, (b) 200, and (c) 600 °C.

(a)

(b)

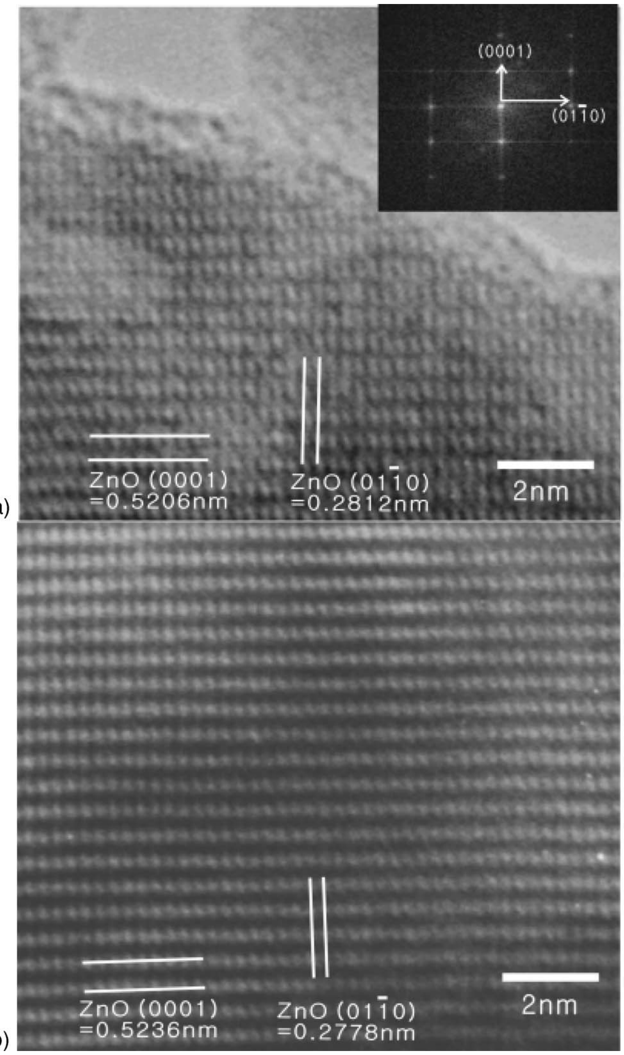

FIG. 3. HRTEM images of (a) the top region and (b) the middle region of the ZnO film grown on a *p*-Si substrate at 200 °C. The insert is the fast-Fourier transform result of the HRTEM image of the top region.

an enhanced crystallinity, which is in reasonable agreement with the XRD results. Although atoms have low mobility at low temperatures, thus preventing perfect crystallization in the ZnO films, they have high mobility at high temperatures, allowing them to occupy more suitable positions and enhancing the crystallinity. The upper region of the ZnO columnar structure is more stable than its lower region, as shown in Fig. 2. After coalescence, the ZnO columnar structure in the lower region consists of grains with a nonequilibrium state. Because the shape of the grain island is convex and because the upper region of the ZnO columnar structure is closer to equilibrium morphology due to atomic mobility, stress relaxation in the upper region is more fully achieved than in the lower region.

Figure 3 shows high-resolution TEM (HRTEM) images of (a) the upper region and (b) the middle region of a ZnO film grown on a *p*-Si substrate at 200 °C. The interplanar spacing distances of (0001_{ZnO}) and $(01\bar{1}0)_{\mathrm{ZnO}}$ of the upper region of the ZnO film are 0.5206 and 0.2812 nm, respectively. Therefore, the upper region of the ZnO film grown on the *p*-Si substrate at 200 °C does not receive any stress. However, since the interplanar spacing distance of the $(0001)_{\mathrm{ZnO}}$ of the middle region of the ZnO film is 0.5236 nm, the ZnO film grown on a *p*-Si substrate at

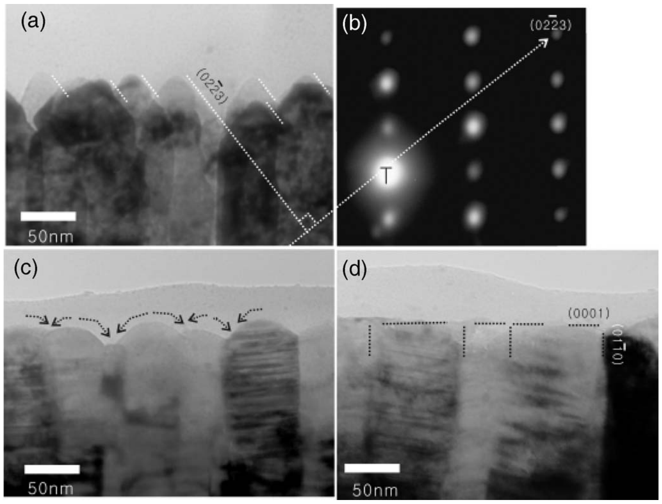

FIG. 4. Cross-sectional bright-field TEM images with high magnification of the top regions of the ZnO thin films grown on *p*-Si (100) substrates at (a) 27, (c) 200, and (d) 600 °C and (b) a SADP of the top region shown in (a).

200 °C receives a tensile stress along the *c* axis, which is in reasonable agreement with the XRD result. Since the interplanar spacing distance of the $(01\bar{1}0)_{ZnO}$ for the middle region in the ZnO film is 0.2778 nm, the ZnO thin film grown on the *p*-Si substrate at 200 °C receives a compressive strain along the *a* axis. Therefore, the growth process of the competing columns induces an in-plane compressive stress, resulting in an increase in the lattice constant along the growth direction. Consequently, the ZnO film receives a tensile stress along the *c* axis and a compressive stress along the *a* axis. The tensile strain along the *c* axis for the ZnO film grown on the *p*-Si substrate at 200 °C, which is observed in the XRD result, exists in the middle or lower region. While stress relaxation does occur in the upper region of the ZnO thin film grown at high temperature, no such relaxation occurs in any region of the ZnO thin film grown at low temperature.

Figure 4 shows cross-sectional bright-field TEM images with high magnification of the ZnO thin films grown on *p*-Si (100) substrates at (a) 27, (c) 200, and (d) 600 °C and (b) a SADP of the top region shown in Fig. 4(a). A facet plane, which is a high-order-indexed unstable plane in the ZnO film, is observed in the upper region of the ZnO thin film grown on a *p*-Si substrate at 27 °C because the diffusion rate of the atoms on the ZnO surface during the column growth is smaller than its deposition rate. As a result, since the ZnO surface maintains a convex shape caused by crystallite coalescence, the growth is competitive.[21] When the high-order-indexed unstable plane is changed into a more stable plane to minimize the boundary curvature with increasing growth temperature, it approaches the (0001) plane because the diffusion rate of the atoms on the ZnO surface during the growth of the column at high temperatures is larger than their deposition rate. Therefore, the top region of the ZnO film grown on *p*-Si substrate becomes flat with increasing growth temperature.

Even though the Zn and the O_2 sources contribute to a probably quite complicated morphological evolution of the columnar structures in the ZnO thin film, a qualitative idea of their morphological evolution can be suggested on the basis of the TEM results. The stability of the columnar structures and the surface morphology of the ZnO thin film is improved with increasing growth temperature. The columnar structure of the ZnO thin film is typically formed due to nucleation on the surface of the *p*-Si substrate. A nuclei growth process leads to impingement and coalescence of ZnO islands, resulting in the columnar structure of the ZnO thin film. Since the initial formation stage of the columnar structure resulting from impingement and coalescence of ZnO islands is in a nonequilibrium state, the surface of the ZnO thin film has a convex shape.[20] The stress of the ZnO thin film becomes relaxed from the upper region with increasing growth temperature, and the surface becomes smooth and that the evolution process of the columnar structure in the ZnO thin films is significantly affected by the growth temperature, which affects the atomic mobility.

In summary, XRD analyses revealed that the ZnO thin films grown on Si substrates had a preferential [0001]direction, and the TEM images showed that columnar structures occurred in those ZnO thin films. The columnar structure and the surface morphology of the ZnO thin films grown on Si substrates were significantly affected by the growth temperature. The morphological evolution of the columnar structures in ZnO thin films temperature and were described on the basis of the experimental results.

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