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Initial formation mechanisms of the supersaturation region and the columnar structure in ZnO thin films grown on *n*-Si (001) substrates

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ZnO thin films were grown on *n*-Si (001) substrates by using plasma-assisted molecular beam epitaxy. A cross-sectional bright-field transmission electron microscopy (TEM) image showed that small ZnO columnar grains were embedded into large columnar grains, and a selected-area electron diffraction pattern, and an x-ray diffraction pattern showed that the ZnO thin film were nearly *c*-axis oriented. The evolution of the ZnO columnar structure was analyzed by using the evolution of the strain due to the interaction of the columnar grains, as observed by using high-resolution TEM. The initial formation mechanisms of the supersaturation region and the columnar grains are described. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2432223]

ZnO thin films are of current interest because of their potential applications in optoelectronic devices, such as transparent conducting electrodes, gas sensors, varistors, solar cells, light-emitting diodes, and laser diodes,[1–3] because they are large band-gap semiconductors with physical properties of low dielectric constants, large exiton binding energies, and excellent chemical stabilities.[4–9] ZnO/Si heterostructures are of particular interest in the integration of optoelectronic devices[10–13] due to the large excitonic binding energy of the ZnO thin film and the cheapness and the large size of the Si substrate. Potential applications of ZnO thin films in high-efficiency optoelectronic devices operating in the blue region of the spectrum have driven extensive efforts to grow high-quality ZnO thin films on Si substrates. However, the achievement of high-quality ZnO epilayers on Si substrates is very difficult due to the differences in the lattice constants and the thermal expansion coefficients of ZnO and Si, which deteriorate the crystal quality of the ZnO thin film and the performance of optoelectronic devices fabricated utilizing the ZnO layer. Since the optical properties of ZnO thin films are strongly affected by the microstructural properties of ZnO thin films and of ZnO/Si heterostructures, studies of such properties are necessary for fabricating high-quality optoelectronic devices utilizing ZnO/Si heterostructures. Even though some works concerning the surface and the microstructural properties related to the columnar structures in ZnO thin films have been performed,[14–16] the initial formation mechanisms of the supersaturation region and the columnar structures in ZnO thin films grown on *n*-Si (001) substrates are not yet known.

This letter reports data on the initial formation mechanisms of the supersaturation region and the columnar structures in ZnO thin films grown on *n*-Si (001) substrates by using plasma-assisted molecular beam epitaxy (PA-MBE). Transmission electron microscopy (TEM), selected-area electron diffraction (SAED), and x-ray diffraction (XRD) measurements were carried out in order to investigate the microstructural properties of the ZnO/*n*-Si (001) heterostructures. The initial formation mechanisms of the supersaturation region and the columnar structures in ZnO thin films grown on *n*-Si (001) substrates are described on the basis of those measurements.

The ZnO thin films used in this work were grown on *n*-Si (001) substrates by using PA-MBE. The carrier concentration of the *P*-doped *n*-Si substrates with (001) orientations 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 molybdenum susceptor in a growth chamber. After the chamber had been evacuated to 1×10^{-9} Torr, the depositions were done at a substrate temperature of 27 °C. Metal Zn grains with a purity of 99.9999% were used as the Zn source, and chemically active oxygen atoms were supplied by using a rf discharge at 450 W. The temperature of the Zn source for the ZnO thin films was 335 °C. The deposition of the ZnO layer was done at a system pressure of approximately 1×10^{-5} Torr. The detail growth procedure for ZnO thin films is described elsewhere.[17]

Figure 1 shows a cross-sectional bright-field TEM image, SAED pattern, and XRD pattern of a ZnO thin film grown on a *n*-Si (001) substrate. Minimization of the strain and the surface energy and the anisotropy of the growth velocity can cause the crystallographic texture of the columnar grains at the film's cross section to evolve as columnar grains with high energy or a low growth velocity is eliminated or

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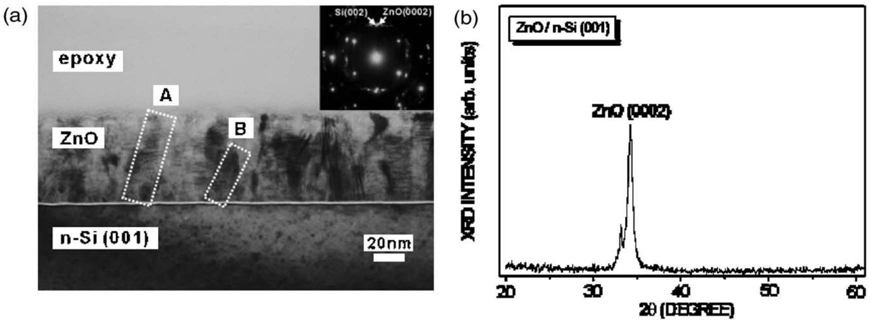

FIG. 1. (a) Cross-sectional bright-field transmission electron microscopy image and (b) x-ray diffraction pattern of a ZnO thin film grown on a *n*-Si (001) substrate. A and B indicate a large columnar grain and a small columnar grain, respectively. The inset is a selected-area electron diffraction pattern.

occluded with increasing thickness. In this case, the as-grown ZnO thin film consisted of a large number of large columnar grains and a small number of small columnar grains, denoted by "A" and "B" in Fig. 1(a) and most ZnO columnar grains had a nearly preferential *c*-axis orientation, as shown in the SAED pattern shown in the inset of the Fig. 1(a) and the XRD pattern shown in Fig. 1(b). This behavior frequently occurs during the formation of polycrystalline thin films at a relatively low substrate temperature of 27 °C.[18]

In order to identify the lattice parameters of the A and B columnar grains, we performed high-resolution TEM (HRTEM) measurements. Figure 2(a) shows a cross-sectional HRTEM image of a large columnar grain, denoted by A in Fig. 1(a), in a ZnO thin film grown on a *n*-Si (001) substrate. A magnified image taken from the HRTEM image is shown in the inset of the Fig. 2(a). The distances between the lattice planes along $[0001]$ and $[10\bar{1}0]$ directions in the lower regions of the large columnar grains are 0.520 and 0.280 nm, respectively, which are in reasonable agreement with the standard PDF values (No. 36-1451) of 0.520 and 0.281 nm. Because as-grown ZnO thin films grown at 25 °C have a uniform tensile stress parallel to the *c* axis,[14] the slight decrease in the distance between the ZnO lattice planes along the $[10\bar{1}0]$ direction indicates that the bottom region of the large columnar grain receives a small compressive stress along the $[10\bar{1}0]$ direction. The distances between the lattice planes along $[0001]$ and $[10\bar{1}0]$ directions in the upper region of the large columnar grain are 0.536 and 0.276 nm, which indicates that the ZnO thin film receives a strongly compressive stress along the $[10\bar{1}0]$ direction. When the number of diffused atoms existing on the surface of the growing columnar grains is smaller than the number of atoms arriving from the vapor, the strain of the epitaxial grains is enhanced in the upper region because the atoms that have just arrived at the strained columnar grains are covered with the newly arriving adatoms before the former can diffuse to more stable states, which would have relaxed the strain. Therefore, the stress generated at the coalescing grains is not relaxed, resulting in an increase in the strain in the upper region of the columnar grain.

Figure 2(b) shows a corresponding cross-sectional HRTEM image of a small columnar grain, denoted by B in Fig. 1(a), in a ZnO thin film on a *n*-Si (001) substrate. The inset of Fig. 2(b) is a magnified HRTEM image. The distances between the lattice planes along $[0001]$ and $[10\bar{1}0]$ directions of a small columnar grain are 0.501 and 0.275 nm, respectively. The spacing distances along $[0001]$ and $[10\bar{1}0]$ directions of the small columnar grain in the ZnO thin film are smaller than those of ZnO powders, which indicates that the columnar grain receives a compressive stress along $[0001]$ and $[10\bar{1}0]$ directions. The decreases in the distances along ZnO $[0001]$ and ZnO $[10\bar{1}0]$ directions due to the compressive stress result in an increase in the number of atoms per unit area in the small columnar grain in comparison with that in the large columnar grain. Therefore, the supersaturation region originates from the biaxially compressive stress existing in the small columnar grain, which is attributed to the existence of the many voids in the ZnO thin film.[19]

Because the *c*-axis preferentially oriented ZnO thin film is grown on the amorphous interfacial layer, the orientation relationship between ZnO $[0001]$ and *n*-Si $[001]$ directions is very important for determining the size of the columnar grains. The deviation angle in the crystallographic orientation of the large columnar grain in the ZnO thin film along the $[0001]$ direction is about 26° with respect to the *n*-Si $[001]$ direction, as shown in Fig. 3(a) and the corresponding deviation angle of the small columnar grain is about 31°, as shown in Fig. 3(b). The deviation angles of the large and the

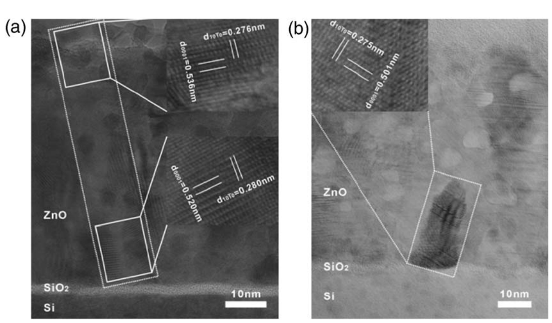

FIG. 2. Cross-sectional high-resolution transmission electron microscopy images of (a) a large columnar grain and (b) a small columnar grain in a ZnO thin film grown on a *n*-Si (001) substrate. The insets are magnified images.

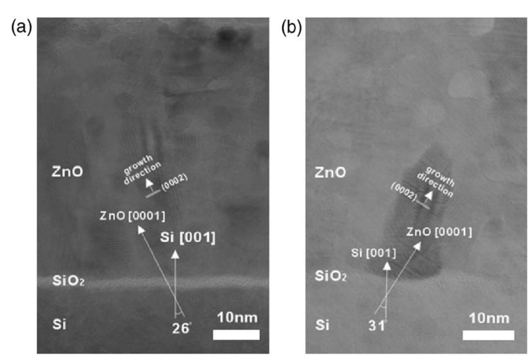

FIG. 3. Cross-sectional high-resolution transmission electron microscopy images of (a) a low tilted columnar grain and (b) a high tilted columnar grain in a ZnO thin film grown on a *n*-Si (001) substrate.

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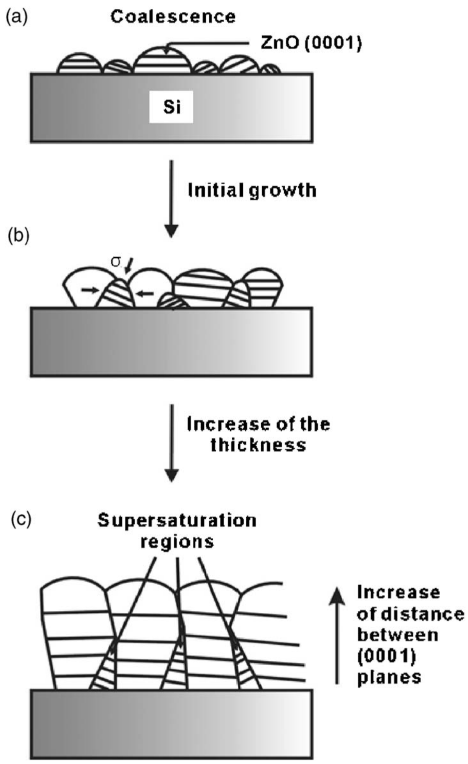

FIG. 4. Schematic cross-sectional diagrams with different stages of the supersaturation region and the columnar structure in the ZnO thin film grown on the n-Si (001) substrate.

small columnar grains in the ZnO thin film are those of the $[10\bar{1}4]$ and the $[10\bar{1}3]$ directions relative to the [0001] direction. Therefore, while the ZnO $\{10\bar{1}4\}$ planes in a large columnar grain are on the surface of the n-Si (001) plane, the ZnO $\{10\bar{1}3\}$ planes in the small ZnO columnar grain are on the surface of the n-Si (001) plane. Because the growth velocity of the ZnO [0001] epilayer under a hydrothermal condition is the fastest among all directions,[20,21] the high tilted columnar grains collide with the low tilted columnar grains during an increase in the thickness of the ZnO thin film. Therefore, while the low tilted columnar grains are transformed into large columnar grains with increasing thickness, the high tilted columnar grains are transformed into the small columnar grains. The deviation angle between the ZnO [0001] and the n-Si [001] direction at an initial growth stage of the ZnO thin film significantly affects the size of the columnar grains in a ZnO thin film with a uniform thickness.

Figure 4 shows schematic diagrams of possible stages in the formation of the supersaturation region and the columnar structure in a ZnO thin film grown on a n-Si (001) substrate on the basis of TEM and HRTEM images. First, the nucleation frequencies in most physical vapor deposition processes are so high that the nuclear spacings are very small,[22] and the initial grain size at the base of a ZnO c-axis film is very small, as shown in Fig. 4(a). As the deposition proceeds, because high tilted columnar grains are embedded in the low tilted columnar grains, as shown in Fig. 4(b), the high tilted columnar grains in the ZnO thin film are biaxially stressed with increasing thickness. Then, due to growth competition at the grain boundaries resulting from surface energy differences[23,24] or from growth velocity anisotropies,[25,26] supersaturation regions are formed, as shown in Fig. 4(c).

In summary, the initial formation mechanisms of the supersaturation region and the columnar structures in ZnO thin films grown on n-Si (001) substrates by using PA-MBE were investigated by means of TEM and HRTEM measurements. TEM and HRTEM images showed that the ZnO thin films consisted of large columnar grains with a small deviation angle and of small columnar grains with a large deviation angle along the ZnO [0001] direction with respect to the n-Si [001] direction. Because the number of atoms per unit area in a small columnar grain was larger than that in a large columnar grain due to the existence of a biaxial stress generated by the nearest neighbor columnar grains, the supersaturation regions were formed in the small columnar grains. The stress generated at the coalescing ZnO epilayer did not relax, resulting in the strain increasing from the lower regions of the columnar grains to the upper regions of the columnar grains; in addition, the distance between the ZnO (0001) planes increased along the [0001] direction in the ZnO columnar grains.

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[1]W. W. Wenas, A. Yamada, and K. Takahashi, J. Appl. Phys. **70**, 7119 (1991).
[2]H. Ohta, K. Kawamura, M. Orita, M. Orita, M. Hirano, N. Sarukura, and H. Hosono, Appl. Phys. Lett. **77**, 475 (2000).
[3]S. A. Studenikin, M. Cocivera, W. Kellner, and H. Pascher, J. Lumin. **91**, 223 (2000).
[4]T. Soki, Y. Hatanaka, and D. C. Look, Appl. Phys. Lett. **76**, 3257 (2000).
[5]R. F. Service, Science **276**, 895 (1997).
[6]Z. K. Tang, G. K. L. Wong, P. Tu, M. Kawasaki, A. Ohtomo, H. Koinuma, and Y. Segawa, Appl. Phys. Lett. **72**, 3270 (1998).
[7]Y. Chen, D. M. Bagnall, Z. Zhu, T. Sekiuchk, K. Park, K. Hiraga, T. Yao, S. Koyama, M. T. Shen, and T. Goto, J. Cryst. Growth **181**, 2230 (1997).
[8]D. M. Bagnall, Y. Chen, Z. Zhu, T. Yao, S. Koyama, M. Y. Shen, and T. Goto, Appl. Phys. Lett. **70**, 2230 (1997).
[9]Y. Segawa, A. Ohtomo, M. Kawasaki, H. Koinuma, A. K. Tang, P. Yu, and G. K. L. Wong, Phys. Status Solidi B **202**, 2 (1997).
[10]K. Iwata, P. Fons, S. Niki, A. Yamada, K. Matsubara, T. Tanabe, and H. Takasu, J. Cryst. Growth **214/215**, 50 (2000).
[11]M. Joseph, H. Tabata, and T. Kawai, Appl. Phys. Lett. **74**, 2543 (1999).
[12]Z. X. Fu, B. X. Lin, G. H. Liao, and Z. Q. Wu, J. Cryst. Growth **193**, 316 (1998).
[13]E. T. Soki, Y. Hatanaka, and D. C. Look, Appl. Phys. Lett. **76**, 3257 (2000).
[14]V. Gupta and A. Mansingh, J. Appl. Phys. **80**, 1063 (1996).
[15]M. Chen, Z. L. Pei, C. Sun, L. S. Wen, and Z. Wang, J. Cryst. Growth **220**, 254 (2000).
[16]S. S. Lin, J. L. Huang, and D. F. Lii, Mater. Chem. Phys. **90**, 22 (2005).
[17]Y. S. Jung, O. Kononenko, J. S. Kim, and W. K. Choi, J. Cryst. Growth **274**, 418 (2005).
[18]C. V. Thompson, Annu. Rev. Mater. Sci. **30**, 159 (2000).
[19]L. V. Azaroff, *Introduction to Solids* (McGraw-Hill, New York, 1960), pp. 371–372.
[20]W.-J. Li, E.-W. Shi, W.-Z. Zhong, and Z.-W. Yin, J. Cryst. Growth **203**, 186 (1999).
[21]R. A. Laudise and A. A. Ballman, J. Phys. Chem. **64**, 688 (1960).
[22]C. V. Thompson and R. Carel, Mater. Sci. Eng., B **32**, 211 (1995).
[23]G. Kyunt, C. Quaeyhaegens, J. D'Haen, and L. M. Stals, Phys. Status Solidi B **159**, 179 (1996).
[24]D. J. Srolovitz, A. Mazor, and B. G. Bukiet, J. Vac. Sci. Technol. A **6**, 2371 (1988).
[25]A. van der Drift, Philips Res. Rep. **22**, 267 (1967).
[26]J. M. Thijssen, Phys. Rev. B **51**, 1985 (1995).

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