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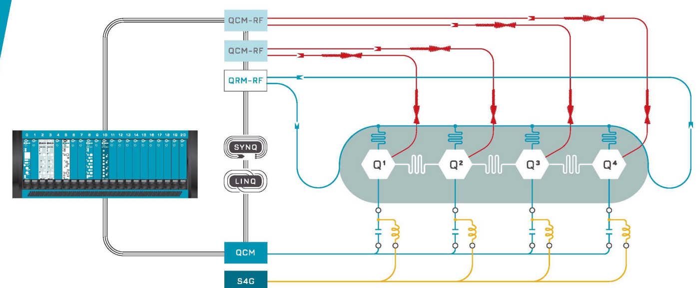

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Initial growth behavior and resulting microstructural properties of heteroepitaxial ZnO thin films on sapphire (0001) substrates

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The initial growth behavior and resulting microstructural properties of heteroepitaxial ZnO thin films prepared by pulsed laser deposition on sapphire (0001) substrates were investigated. High-resolution x-ray diffraction and transmission electron microscopy studies revealed that the initial growth behavior and the microstructure of the films were significantly dependent on the growth parameters employed. ZnO films grown at 700 °C with an O_2 partial pressure of 20 mTorr initiated in a columnar growth mode and contained two types of domains. These domains were in plane orientated either ZnO$[11\bar{2}0] \parallel$ $Al_2O_3[10\bar{1}0]$ or ZnO$[10\bar{1}0] \parallel$ $Al_2O_3[10\bar{1}0]$ and were surrounded by highly defective domain boundaries with threading dislocations. ZnO films grown at 800 °C with 1 mTorr O_2 showed a two-dimensional layered growth with only one in-plane epitaxial relationship, ZnO$[11\bar{2}0] \parallel$ $Al_2O_3[10\bar{1}0]$. Most of the defects in the layered grown films were basal plane stacking faults near the interface between the ZnO and the substrate. The mechanism of formation of the 30°-twisted domains with the in-plane orientation of ZnO$[10\bar{1}0] \parallel$ $Al_2O_3[10\bar{1}0]$ is discussed. *© 2007 American Institute of Physics*. [DOI: 10.1063/1.2428489]

Due to its superior excitonic properties, ZnO has attracted enormous research attention because of its applications in short wavelength light emitting diodes and exciton-based laser diodes.[1] ZnO thin films have mostly been grown on sapphire (Al_2O_3) (0001) substrate due to its hexagonal symmetry and low cost. The lattice strain relaxation and accompanying structural evolution in the initial growth stage directly affect crystalline quality and device properties.[2–4] Despite many x-ray diffraction (XRD) studies,[5–9] the initial growth behavior and the microstructures of heteroepitaxial ZnO thin films on sapphire are not very well understood, mainly due to the very large mismatch in lattice constants and thermal expansion coefficients between ZnO and sapphire. Different growth modes and microstructural properties of the ZnO films have been suggested based on XRD (0002) rocking curves. The ZnO films grown by radio-frequency (rf) sputtering have been proposed to follow the two dimension (2D)–three dimension (3D) transition mode in which 3D columnar grains are nucleated on a highly strained 2D epitaxial ZnO layer.[5,6] Conversely, ZnO films deposited by molecular beam epitaxy were reported to nucleate into 2D islands on the substrate[7] and to contain a high crystalline epitaxial layer on top of a highly defective thin interface layer.[7,8] These contradictions imply that structural properties and growth behavior are strongly dependent on the deposition conditions used. However, no real-space microstructural information was presented in these reports.

In this letter, we provide detailed information on such microstructural properties through high-resolution transmission electron microscopy (HRTEM) together with both out-of-plane and in-plane XRD analyses for the heteroepitaxial ZnO films. The findings demonstrate that the nucleation and strain relaxation behaviors during the initial growth stage of ZnO films on sapphire (0001) substrates can be greatly affected by the growth conditions.

ZnO thin films were deposited on sapphire (0001) substrates by ablating a ceramic ZnO target (99.999% pure). The sapphire substrates were annealed in a furnace at 1100 °C for 1 h in an air ambient to obtain atomically flat surface. A KrF excimer laser with a wavelength of 248 nm was used, and the fluence and repetition rate were about 3 J/cm^2 and 3 Hz, respectively. Two deposition conditions, (a) 700 °C with an O_2 partial pressure of 20 mTorr and (b) 800 °C with an O_2 partial pressurse of 1 mTorr, were used to investigate the initial growth behaviors, because films grown at these two conditions showed typical XRD (0002) ω-rocking curve profiles as previously reported.[5,7] Films with various thicknesses were prepared at both of the above growth conditions to investigate the initial structural evolution of heteroepitaxial ZnO films. High-resolution XRD was measured with a laboratory source (Bruker D8 Discover) and a synchrotron radiation source (Beamline 10C1, Pohang Light Source, Ko-

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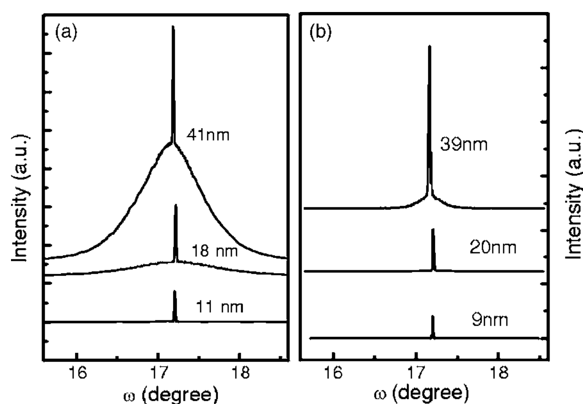

FIG. 1. (0002) ω-rocking curves of ZnO films grown at (a) 700 °C and 20 mTorr O_2 and (b) 800 °C and 1 mTorr O_2.

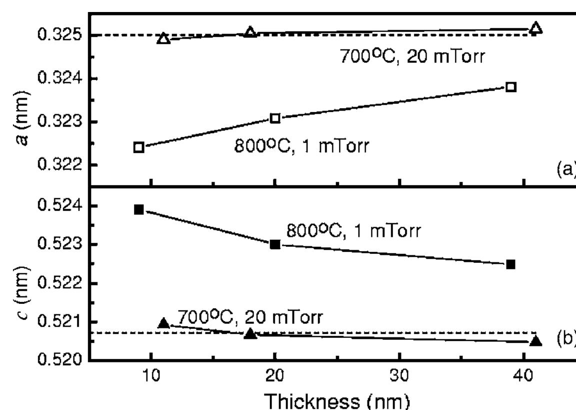

FIG. 3. Dependence of (a) a-axis and (b) c-axis lattice constants on film thickness. The dashed lines in (a) and (b) show the value of the a-axis and c-axis lattice constants, respectively, in bulk ZnO. The solid line connecting the points is a visual guide.

rea). TEM observations were made using a 002B Topcon high-resolution microscope operated at 200 kV.

XRD (0002) ω-rocking curves from ZnO films grown at the two conditions show an obvious different dependence on film thickness. In Fig. 1(a), the 11-nm-thick ZnO film, grown at 700 °C/20 mTorr, shows only a sharp peak with a full width at half maximum (FWHM) of about 0.02°. When the film thickness increases to 18 nm, a weak and broad background peak appears below the sharp peak. A further increase in film thickness to 41 nm results in a significant increase in the intensity of the broad background peak. The sharp peak is due to the crystalline grains with their c axes well aligned with $Al_2O_3[0001]$, while the broad peak arises from the crystalline grains with their c axes slightly misaligned with $Al_2O_3[0001]$. The ZnO films grown at 800 °C/1 mTorr show a much improved out-of-plane alignment, as indicated by the strong and sharp peak in Fig. 1(b). When the film thickness is 39 nm, only weak Lorentzian tails appear on both sides of the sharp central peak. Overall, the broad component in the rocking curve decreases with increasing growth temperature and decreasing O_2 partial pressure (data not shown here).

The evolution of the in-plane lattice alignment in the ZnO films also shows a strong dependence on growth conditions. Figure 2(a) shows the ϕ scans along the azimuthal circle of the ZnO $\{10\bar{1}1\}$ reflection from ZnO films grown at 700 °C/20 mTorr. There are two sets of peaks with an angle difference of 30°. One set of peaks is from aligned ZnO domains with an in-plane epitaxial orientation of $ZnO[11\bar{2}0] \| Al_2O_3[10\bar{1}0]$, which is typically observed in heteroepitaxial ZnO thin films on sapphire (0001) substrates. The other set of peaks is assigned to 30°-twisted ZnO domains with an in-plane orientation of $ZnO[10\bar{1}0] \| Al_2O_3[10\bar{1}0]$. As the film thickness increases from 11 to 41 nm, the relative peak intensity from the 30°-twisted domains decreases and becomes very weak, while the peaks from the aligned domains become stronger and sharper. This indicates that the 30°-twisted domains formed at the beginning of the growth are metastable due to the large lattice mismatch (32%) with the substrate. On the other hand, ϕ scans for the ZnO thin films grown at 800 °C/1 mTorr show sharp peaks only from aligned domains [Fig. 2(b)]. The FWHM of the peaks from a 39-nm-thick film is about 0.9°, much smaller than that of the aligned peaks from the 41-nm-thick ZnO film (about 2°) in Fig. 2(a). Therefore, heteroepitaxial ZnO films grown at higher temperature with a lower O_2 partial pressure have a better in-plane lattice alignment with only one in-plane orientation of $ZnO[11\bar{2}0] \| Al_2O_3[10\bar{1}0]$.

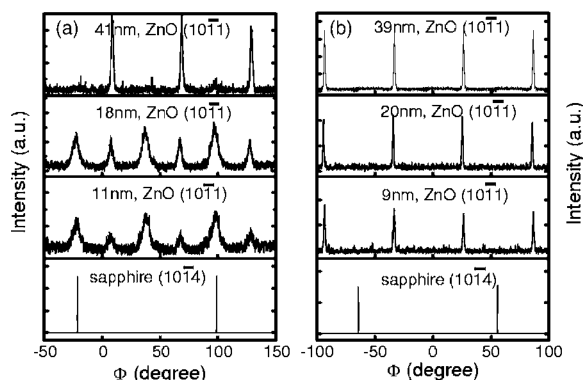

FIG. 2. ϕ scans for the $\{10\bar{1}1\}$ reflection of ZnO films grown at (a) 700 °C and 20 mTorr O_2 and (b) 800 °C and 1 mTorr O_2.

To investigate the strain status of the films, the a- and c-lattice constants of the ZnO films were measured by XRD θ-2θ scans of (0002) and K scans of $(10\bar{1}2)$ reflections, respectively. Figure 3(a) shows that ZnO films grown at 700 °C/20 mTorr are almost relaxed, while the films grown at 800 °C/1 mTorr are compressively in plane strained, which is further supported by the consistent evolution of c-lattice constants with film thickness shown in Fig. 3(b). This indicates that the strain is compensated in the ZnO thin films grown at 700 °C/20 mTorr. We found that strain relaxation in ZnO films is closely correlated to their microstructure, as discussed below.

The HRTEM image in Fig. 4(a) shows that the ZnO film grown at 700 °C/20 mTorr has a columnar structure formed by two types of domains. The dark areas, marked "1," correspond to aligned domains with a $ZnO[11\bar{2}0] \| Al_2O_3[10\bar{1}0]$ orientation. $ABAB\cdots$ stacking in the hexagonal close packing along the [0001] direction can be seen in the magnified image shown in Fig. 4(c). The bright areas, marked "2," correspond to the 30°-twisted domains with a $ZnO[10\bar{1}0] \| Al_2O_3[10\bar{1}0]$ orientation. Only the 0002 fringes are observed from these domains. The selected area diffraction pattern, presented in Fig. 4(b), also shows two sets of domains with different in-plane orientations. In contrast,

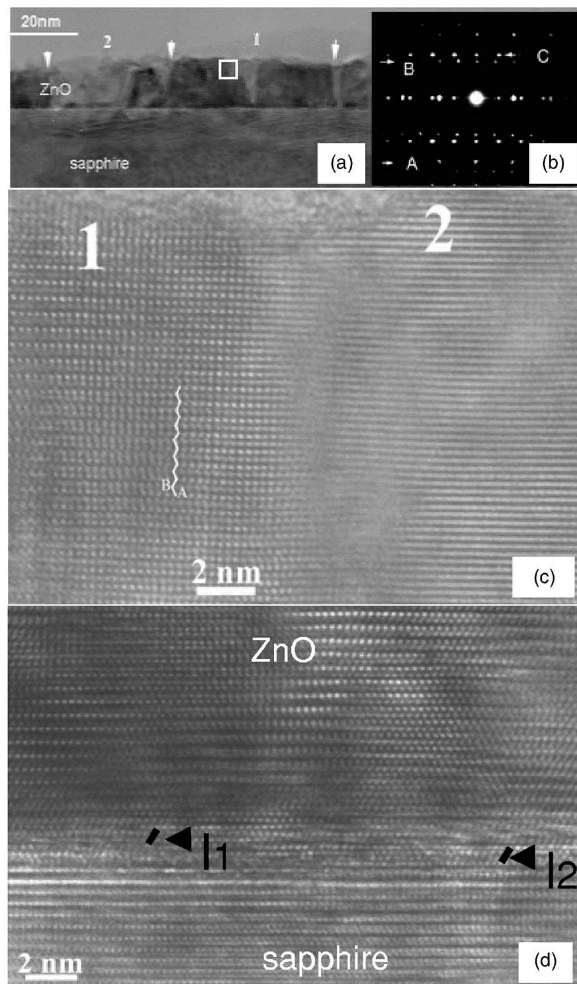

FIG. 4. (a) High-resolution cross-sectional TEM image of an 18-nm-thick ZnO film grown at 700 °C/20 mTorr. The areas labeled "1" and "2" represent domains with ZnO$[11\bar{2}0]\|$Al$_2$O$_3$ $[10\bar{1}0]$ and ZnO$[10\bar{1}0]\|$Al$_2$O$_3$$[10\bar{1}0]$ orientations, respectively. The white arrows indicate the domain boundaries. (b) Selected area diffraction pattern from the corresponding crystallites. The spot lines labeled A and B belong to the ZnO$[11\bar{2}0]$ and ZnO$[10\bar{1}0]$ zone axes, respectively. The Al$_2$O$_3$ $[10\bar{1}0]$ axis is labeled C. (c) Magnified TEM image of the rectangular area shown in (b). ABAB⋯ stacking is indicated in the image. (d) HRTEM image of a ZnO film grown at 800 °C/1 mTorr. Two stacking faults are underlined (arrows).

Fig. 4(d) shows that in a ZnO film deposited at 800 °C/1 mTorr most of the defects are stacking faults lying in the (0001) basal plane near the interface between ZnO and the substrate, some of which are marked with arrows. Further from the interface, the TEM image shows a layered atomic stacking with only one in-plane epitaxial orientation relationship of ZnO$[11\bar{2}0]\|$Al$_2$O$_3$$[10\bar{1}0]$.

The microstructural properties revealed by the TEM study provide a reasonable explanation for the evolution features of the ω-rocking curves (Fig. 1) and for the different strain states (Fig. 3). The ZnO films grown at 700 °C/20 mTorr have smaller domain size and higher density of domain boundaries due to the mixed in-plane orientations. The lattice mismatch between the substrate and ZnO film resulted in the generation of misfit dislocations at the interface, and threading dislocations, which easily form and propagate at the domain boundaries.[10] The high density of such defects may then provide a route to fast strain relaxation, as seen in Fig. 3. The occurrence of the broad components in the ω-scan profiles (Fig. 1) attributed to coalescence processes of adjacent columns. Although the features of the out-of-plane rocking curve and its evolution with film thickness [Fig. 1(a)] appear to be similar to those for the rf sputtered films,[5] the columnar structure shown in Fig. 4(a) indicates that our pulsed laser deposition (PLD)-grown ZnO films did not follow the 2D to 3D transition mode.

Since both aligned and 30°-twisted domains in Fig. 4(a) start directly from the substrate, the formation of the twisted domains can be attributed to competition between the local interface energy and epitaxial strain energy.[11,12] At lower growth temperature and higher O$_2$ pressure the diffusion energy of the adatoms may be not sufficient to overcome the local interface energy barrier. Therefore, twisted domains are formed at the beginning of the growth process. With increasing thickness, the aligned domains, which have smaller lattice mismatch with the substrate, become dominant, thus reducing the strain energy. At higher growth temperature and lower O$_2$ pressure, the adatoms have sufficient energy to diffuse to appropriate adsorption sites. Only the aligned domains are formed in this case because they are thermodymically stable, as shown in Fig. 4(d). In the case of rf sputtered ZnO films, it has been reported that the twisted domains are located far from the interface and make up a very small volume fraction.[9] Therefore, the mechanism of formation of the 30°-twisted domains in our PLD-grown films is quite different from that in rf sputtered films.

In summary, the initial growth behavior and the microstructures of heteroepitaxial ZnO thin films on sapphire (0001) were investigated. Through TEM measurements and detailed XRD analyses of the structure evolution with thickness, we showed that ZnO films could initiate with columnar or layered growth modes, depending on the growth conditions. Metastable 30°-twisted domains could form during the nucleation stage due to local interface energy, and they had a significant effect on the growth mode and strain relaxation process.

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