Microstructure and crystal defects in epitaxial ZnO film grown on Ga modified (0001) sapphire surface

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Surface modification of sapphire (0001) by Ga can eliminate multiple rotation domains in ZnO films. The existence of Ga at ZnO/sapphire interface was confirmed by x-ray energy dispersive spectroscopy in a transmission electron microscope. Atomic detail of mismatch dislocations at interface was imaged by high resolution transmission electron microscopy. Inside the ZnO film, there is a high density of stacking fault. Both pure gliding of ZnO (0001) plane and condensation of vacancies or interstatials are possible mechanisms to generate the stacking fault. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1811393]

Wurtzite ZnO is a wide band gap (3.27 eV) II–VI compound semiconductor with promising applications to UV light emitters, spin functional devices, gas sensors, and transparent electronic devices. ZnO can be grown on cheap substrates such as glass at relatively low temperatures and it has several potential advantages over GaN for some of these applications because of a larger exciton binding energy (~60 meV).[1] Optically pumped excitonic lasing of ZnO thin films at room temperature has been observed.[2,3] Recently, lasing effect of ZnO nanowire arrays was also demonstrated.[4] Epitaxial growth of ZnO has been carried out on Si[5,6] and mainly on sapphire[7–11] using various techniques. Efforts are also made to obtain ZnO film with controlled electronic and optical properties, such as *p*-type ZnO by N doping[12] and magnetic ZnO by Mn doping.[5]

It was found that ZnO film was grown via island nucleation and then lateral extension on a substrate surface,[2,13] which is particularly true for substrate with large lattice mismatch. This growth mode will produce a film with a columnar structure and incoherent grain boundaries, and introduce high density of threading dislocations in the film.[14,15] Stacking fault is another type of defect frequently observed in ZnO films.[16,17] Multiangle rotation domains can form when ZnO is grown on sapphire (0001) surface (c-face), but pretreatment of the sapphire (0001) surface by Ga predeposition can eliminate these rotation domains.[7,8] This pretreatment can also be used to suppress inversion domains which often appear in ZnO films,[18] and sole Zn polarity film was obtained.[19] In this letter, we report a transmission electron microsocpy (TEM) study of the microstructure, interfacial dislocations and antiphase boundaries in ZnO layers grown on the Ga pretreated sapphire (0001) surface.

The ZnO films were prepared by using rf-plasma assisted molecular beam epitaxy. Substrate pretreatments were performed in a sequence of chemical etching, annealing, atomic hydrogen radiation, plasma-excited oxygen cleaning, and finally Ga exposure for 22 s. A ZnO buffer layer was then deposited at 400 °C and annealed at 650 °C for 5 min. Finally a ZnO epilayer was grown at 650 °C for 3 h. More experimental details were described elsewhere.[7,19] Cross-sectional TEM samples were prepared by gluing the film with Si, cutting to slices followed by mechanical polishing, dimpling and ion-milling (Gatan PIPS™, Model 691, Pleasanton, CA). The sample was cut along the sapphire $(10\bar{1}0)$ prismatic face, so the electron beam in TEM is looking down the sapphire $[10\bar{1}0]$ direction. A JEOL 2010F TEM was used to investigate the morphology, crystal structure, interface, and chemistry of the samples.

Dense single crystal ZnO film was obtained for the Ga-pretreated sample, as shown in Fig. 1(a). Some vertical straight dark fringes in the film show the existence of stacking faults, inversion boundaries, and/or threading dislocations. The inset in Fig. 1(a) is a selected area electron diffraction pattern from a region including both the ZnO film and the sapphire substrate. It shows the orientation relationship between the film and the substrate: ZnO$(0001)[2\bar{1}\bar{1}0] \parallel$ sapphire $(0001)(10\bar{1}0)$. This orientation relationship is called the main domain as illustrated in Fig. 1(b). Corresponding atomic arrangement can be found in Refs. 19 and 20. No 30°

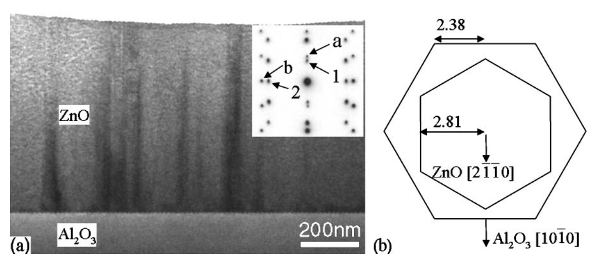

FIG. 1. (a) Cross-sectional TEM image showing the morphology of a ZnO film grown on the (0001) sapphire. The inset is a corresponding selected area electron diffraction pattern with electron beam parallel to the $[2\bar{1}\bar{1}0]$ zone axis of ZnO, in which 1 and 2 are ZnO(0001) and $(01\bar{1}0)$ reflections, and *a* and *b* are reflections of sapphire (0003) and $(1\bar{2}10)$. (b) Illustration of the main domain orientation relationship of ZnO on sapphire.

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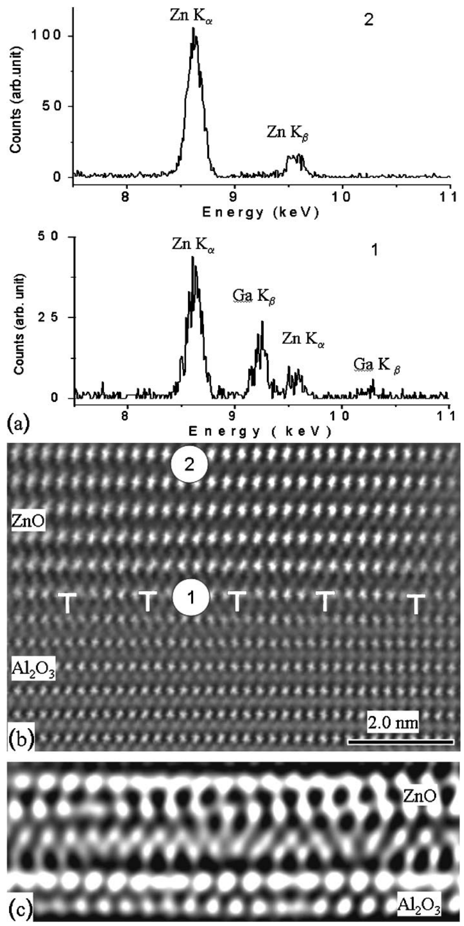

FIG. 2. (a) EDS spectra 1 and 2 are collected from the ZnO/sapphire interface [spot 1 marked in (b)] and the ZnO film [spot 2 in (b)], respectively, using 1.0 nm beam size. (b) High resolution TEM image showing the periodic distribution of misfit dislocations along ZnO/sapphire interface. (c) Fourier filtered image shows lattice distortion around dislocation cores.

rotation domain, i.e. ZnO(0001)$[2\bar{1}\bar{1}0] \parallel$ sapphire (0001) ZnO(0001)$[2\bar{1}\bar{1}0]$, was found in the films. This reveals that ZnO film with only one domain orientation can be obtained by surface modification of the substrate with Ga.

The Ga–O bond at the substrate surface is believed to play a key role in eliminating other rotation domains. X-ray energy dispersion spectroscopy (EDS) [Fig. 2(a)] shows the existence of Ga at the interface. Line-profile analysis by EDS across the film/substrate interface shows that the Ga distribution is limited to the first few atomic layers at the interface. More detailed mechanism of formation of bonding at the interface and how surface modification changes the nucleation behavior of ZnO are interesting topics for future study.

Lattice mismatch between the ZnO film and the sapphire substrate for the main domain orientation is about 18%, which results in a high density of misfit dislocation at the interface. The misfit dislocations can be observed by high resolution transmission electron microscopy (HRTEM) imaging. Dislocation cores with an average spacing about 2 nm are indicated in Fig. 2(b). Around the dislocation cores, the atom positions in ZnO as well as in sapphire are highly displaced as shown in Fig. 2(c), suggesting the existence of a high strain in the film.

Stacking faults in the (0001) plane were also observed in the epitaxial ZnO film. As shown in Fig. 3(a), the density of

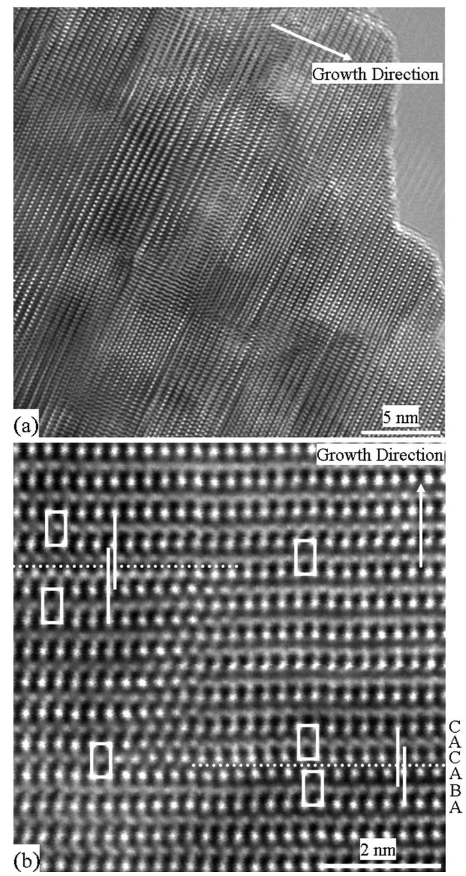

FIG. 3. (a) High resolution TEM image showing a high density of stacking fault. (b) High resolution image of stacking faults with Burger vector lying in the (0001) plane.

stacking faults in the ZnO film is fairly high. Stacking faults can easily be recognized because of a change in the stacking sequence of the (0001) planes along the [0001] growth direction, as shown in Fig. 3(b), where the stacking faults are indicated by dashed lines. These stacking faults consist of a relative displacement of $a/\sqrt{3}$ along the $\langle\bar{1}100\rangle$ directions in the (0001) plane. The displacement does not have a vertical component along the [0001] direction, as illustrated by AD in Fig. 4(b). Such stacking faults may originate from incoherent boundaries between adjacent columnar grains during the growth.

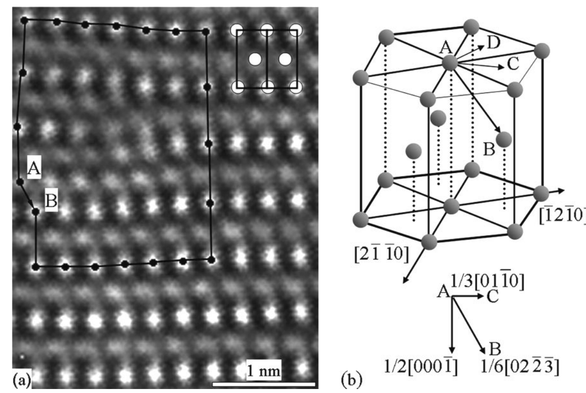

FIG. 4. (a) High resolution TEM image of a partial dislocation around a stacking fault in ZnO with the Burger vector $\mathbf{b}=\mathbf{AB}=1/6[02\bar{2}\bar{3}]$. (b) Illustration of possible Burger vector **AB** and **AD** in ZnO.

Another way to form a stacking fault is by condensation of vacancies or interstitials, so that a missing or an extra (0001) plane will be introduced into the lattice. This type of SF is bounded by partial dislocations with Burgers vector $\mathbf{b}=1/6\langle 02\bar{2}3\rangle$, as shown in Fig. 4. A more detailed discussion of this type of stacking fault can be found in a recent paper by Gerthsen *et al.*,[16] in which they attribute the formation of stacking faults to the precipitation and condensation of Zn interstitials. In this case, the density of stacking fault is growth-condition related and oxygen vacancies have to be generated in the film. Distribution of oxygen vacancies in the ZnO layer has not been very well studied yet. Vacancy clustering and ordering is likely to occur in this hexagonal material, and may affect the film properties.

In conclusion, our TEM observations show that the ZnO thin film grows epitaxially on the (0001) sapphire substrates by molecular beam epitaxy with a Ga pretreatment, which is free of 30° in-plane rotation domains. Local bonding configuration at the ZnO/sapphire interface with the existence of Ga determines the nucleation mechanism and hence the domain structure of the ZnO layer. HRTEM image reveals a detailed structure of misfit dislocation cores at the interface. In the ZnO film there is a high density of stacking faults which are introduced either by a translation of the crystal lattice along three equivalent close-packing directions in the (0001) plane or by condensation of vacancies or interstitials to form dislocation loop accompanied with partial dislocations. More efforts are needed to control the formation of stacking fault and to understand its effect on the properties of the ZnO layer.

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