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Controlled growth of O-polar ZnO epitaxial film by oxygen radical preconditioning of sapphire substrate

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Oxygen radicals pregrowth treatment and surface nitridation were used to eliminate Zn-polar inversion domains and control the growth of single-domain O-polar ZnO film on sapphire (0001) substrate by rf plasma-assisted molecular beam epitaxy. We found that the formation of oxygen-terminated sapphire surface prior to nitridation is crucial for achieving the anion polarity in subsequent AlN and ZnO layers, as demonstrated by formation of the 3×3 surface reconstruction during ZnO growth and *ex situ* polarity determination. This method, in general, can be applied to growth of other polar films, such as II-VI oxides and III-V nitrides, on sapphire (0001) substrates.© © *2004 American Institute of Physics*. [DOI: 10.1063/1.1812362]

ZnO is an attractive wide-band gap (3.37 eV at room temperature) oxide semiconductor for its potential applications in short-wavelength optoelectronic devices, such as ultraviolet (UV) detectors and UV light emitters. ZnO has the same wurtzite structure as GaN. Compared to GaN, ZnO has a much larger exciton binding energy ($\sim$60 meV cf. $\sim$25 meV), which is favorable for fabricating low-threshold excitonic lasers. α-Al_2O_3 (0001) has been extensively adopted as a substrate in the growth of ZnO in terms of its high crystal quality, low cost, and hexagonal surface structure. Nevertheless, the strain induced by the large in-plane lattice mismatch (18.3%) between ZnO and sapphire, and particularly the formation of inversion domains (IDs) (the Zn-polar domains in an O-polar ZnO matrix, for instance), severely deteriorate the crystal quality of ZnO film.[1,2]

α-Al_2O_3 (0001) surface shows a complex structure and can be terminated with different layers, such as an Al monolayer, an Al bilayer, or an O monolayer, depending on surface treatment conditions.[3–5] One monolayer Al-terminated surface is nonpolar and most stable, whereas the other two surfaces are cation polar and anion polar, respectively.[6] When ZnO is directly grown on the Al monolayer-terminated surface, IDs are inevitably introduced to the ZnO epilayer due to the co-existence of Al sublattice and O sublattice on this surface. To accommodate in the different polarities of ZnO (0001) and α-Al_2O_3 (0001), the sapphire surface must have a defined polar wurtzite structure, either cation polar or anion polar, before ZnO growth. Du and co-workers reported a successful example to achieve a cation-polar sapphire surface by Ga pre-exposure process.[7–9] MgO buffer layer was adopted by Chen *et al.* to provide an anion-polar surface for O-polar ZnO growth.[10,11] Here we report another effective method, sapphire surface nitridation, to realize the unipolar ZnO epitaxy.

Surface nitridation has been widely employed in GaN growth on sapphire by molecular beam epitaxy (MBE) or metal-organic vapor phase epitaxy. A thin AlN layer with wurtzite structure formed on top of α-Al_2O_3 after nitridation is found to significantly improve the crystalline quality of GaN grown by MBE.[12] However, the structure of AlN is very sensitive to the nitridation conditions, such as substrate temperature, nature of the nitrogen source, gas flow rate, and is difficult to control.[13,14] The influence of polar sapphire surface, especially anion-polar surface, on the polarity selection of the AlN intervening layer and subsequent GaN or ZnO epilayers was also ignored theoretically and experimentally in previous work. Recently, we used two different methods to precondition the sapphire surface to control the sapphire polarity, and thus the polarity of subsequent AlN and ZnO layers. The different finding in this work is that the formation of a uniform O-terminated surface before nitridation is crucial for the formation of the N-polar AlN and suppression of the Zn-polar IDs to achieve uniform O-polar ZnO films, as established by our combined studies of reflection high-energy electron diffraction (RHEED), convergent beam electron diffraction (CBED) and transmission electron microscopy (TEM).

ZnO samples were prepared on sapphire (0001) substrates using a rf plasma-assisted MBE system (OmniVac). The base pressure in the growth chamber was $\sim$1 $\times 10^{-10}$ Torr. Zn with a purity of 99.9999% was evaporated from a commercial Knudsen cell (CreaTech). Active oxygen and nitrogen radicals were produced by two rf-plasma systems (SVTA), respectively. The flow rate of oxygen/nitrogen gas was controlled by a mass flow controller (ROD-4, Aera). After degreased in trichloroethylene and acetone, the sapphire substrates were chemically etched for 30 min in a

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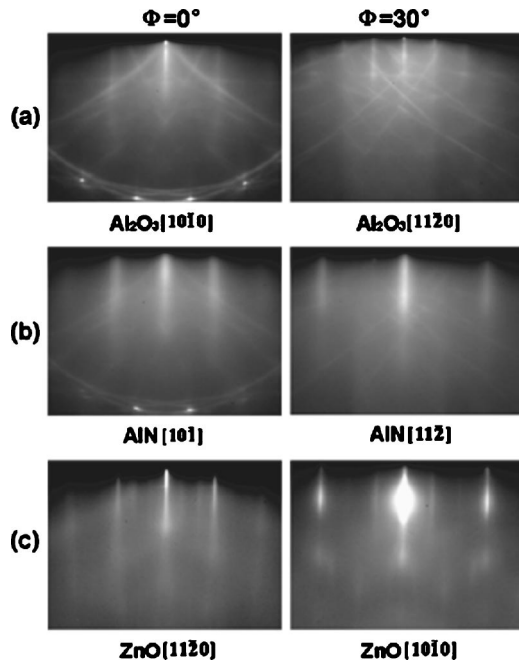
FIG. 1. RHEED patterns along $[10\bar{1}0]$ and $[11\bar{2}0]$ electron beam azimuths observed during growth. (a) Before sapphire nitridation; (b) after sapphire nitridation, and (c) ZnO epilayer after annealing.
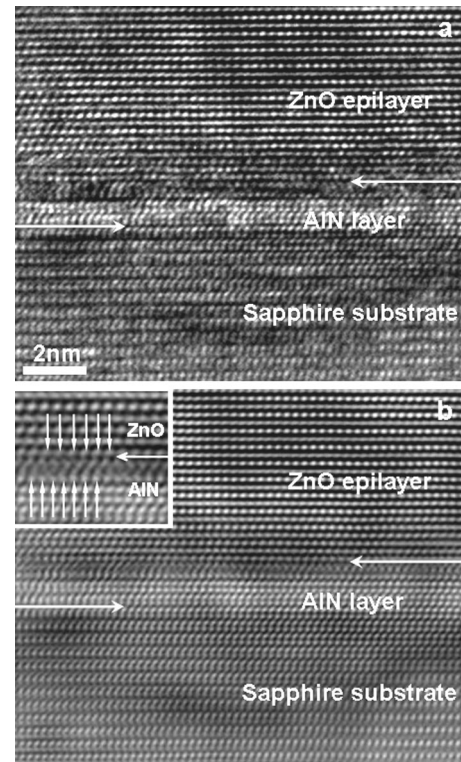

FIG. 2. (a) HRTEM image and (b) Fourier-filtered image along $[10\bar{1}0]_{sapph}$ of the nitridation layer. The inset shows the domain-matching epitaxial relationship between ZnO and AlN.

hot solution of $H_2SO_4:H_3PO_4=3:1$ at $110\,^\circ C$ and then rinsed with de-ionized water. In an ultrahigh vacuum chamber, the substrates were exposed to oxygen radicals for 30 min at $180\,^\circ C$ with a rf power of 350 W and an oxygen flux of 2.5 standard cubic centimeters per minute (sccm), followed by nitridation at $180\,^\circ C$ for 1 h with a rf power of 480 W and a nitrogen flux of 3.0 sccm. Oxygen-terminated sapphire surface was expected to form before nitridation. A conventional two-step growth of ZnO, i.e., a low-temperature buffer layer growth at $400\,^\circ C$ and a high-temperature growth at $650\,^\circ C$, was performed after nitridation. The in-plane epitaxial relationship, surface morphology evolution, and crystallinity were monitored *in-situ* by RHEED. A Philips CM200 field-emission gun TEM equipped with a Gatan image filtering system, operating at 200 KV, was used to carry out the cross-sectional transmission electron microscopy experiments.

Figures 1(a)–1(c) show the RHEED patterns recorded from the sapphire surface before and after nitridation and after annealing of the ZnO epilayer. After nitridation, a thin AlN layer forms with a 30° in-plane rotation of its lattice with respect to the substrate, and the sharp streaky pattern becomes diffuse [Figs. 1(a) and 1(b)]. The RHEED signal from sapphire still exists after nitridation, which indicates that the thickness of the AlN layer is very small (~ 2 nm). This thickness was confirmed by our high-resolution transmission electron microscopy (HRTEM) observation. In addition, the diffuse RHEED patterns [Fig. 1(b)] suggest that the strain between AlN and sapphire is not relaxed. The structure of this AlN layer is zincblende with stacking faults parallel to the AlN/Al_2O_3 interface, which will be discussed later.

After annealing of the as-grown ZnO epilayer at $750\,^\circ C$, an intense RHEED specular spot appears and the 3×3 reconstruction is observed [Fig. 1(c)]. Since 3×3 is a typical

surface reconstruction for the O-polar ZnO films,[10,11,15] these observations suggest that single-domain uniform O-polar ZnO film is formed.

A cross-sectional HRTEM study was carried out to determine the interface microstructure between the nitridation intermediate layer and sapphire substrate. Figure 2(a) shows a micrograph taken along $[10\bar{1}0]_{sapph}$, which demonstrates the formation of a continuous crystalline film of $5\sim 6$ atomic layers thick. The interface is smooth and sharp without any indication of interdiffusion. In order to reduce the noise and minimize blurring, a Fourier-filtered image [Fig. 2(b)] of Fig. 2(a) has been obtained.[16] It reveals that the AlN layer has a zincblende structure. The epitaxial relationships are verified to be $[111]AlN//[0001]Al_2O_3$ and $[11\bar{2}]AlN//[11\bar{2}0]\,Al_2O_3$. It should be noted that a continuous cubic AlN is formed after sapphire nitridaiton. The influence of sapphire substrate pretreatment and nitridation on the AlN film structure has been studied systemically and will be published elsewhere.

From Fig. 2(b), no misfit dislocations are found at the $AlN/\alpha\text{-}Al_2O_3$ interface, which illustrates that the AlN layer is not relaxed. This is different from previous observation.[17] Thus formation of the AlN layer does not reduce the lattice mismatch between ZnO and sapphire (18.3%). The inset shows the detail of the interface structure featured with misfit dislocations between AlN and ZnO. It indicates that the large lattice mismatch is effectively accommodated by the formation of the so-called coincidence lattices, where seven $[10\bar{1}]_{AlN}$ planes match six $[11\bar{2}0]_{ZnO}$ planes, similar to the case of ZnO/GaN epitaxy directly on sapphire.[18]
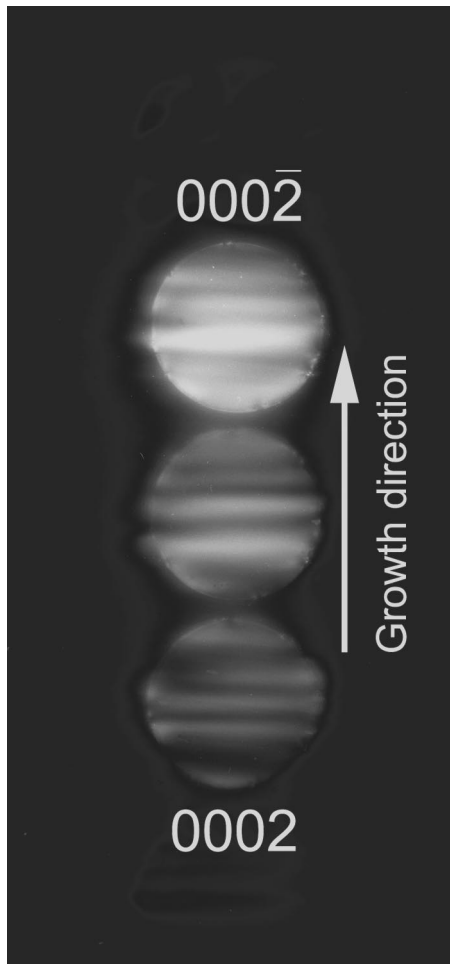
FIG. 3. CBED pattern of ZnO thin film grown on nitridated sapphire.

FIG. 4. Structure of the interface between sapphire and AlN projected along $[10\bar{1}0]_{sapph}$.

To confirm the polarity of ZnO film, we carried out a CBED experiment. The CBED pattern was taken near to $[10\bar{1}0]$ zone axis, with a small angle away from the axis toward the $[11\bar{2}0]$ direction. Since the $(0002)_{Zn}$ face can reflect the electron beam much more strongly than the $(000\bar{2})_O$ face, the center fringes at (0002) an $(000\bar{2})$ disks should be bright and dark, respectively.[19,20] From the tokens in the CBED pattern (Fig. 3), the ZnO film is determined to have $[000\bar{1}]$ polarity. The formation of N-polar AlN on O-terminated sapphire surface upon nitridation can be thus inferred from this fact. The analysis of dark field imaging further shows clearly that IDs with Zn polarity have been effectively suppressed and single-domain O-polar ZnO film was formed.

It has been well established that nitridation involves the diffusion of nitrogen atoms into sapphire and substitution for oxygen, and AlN thin layer is formed as a result of the atom substitution. This is observed by the in-plane 30° rotation of AlN lattice relative to sapphire in the RHEED pattern. However, the underlying Al–N bonding sequence on different sapphire surface configurations, which is the key for the polarity selection of AlN layer, has not been discussed in previous work. Before nitridation, if the substrates were treated with the oxygen radical pretreatment at higher temperature (300~500 °C), IDs, probably due to oxygen desorption (the
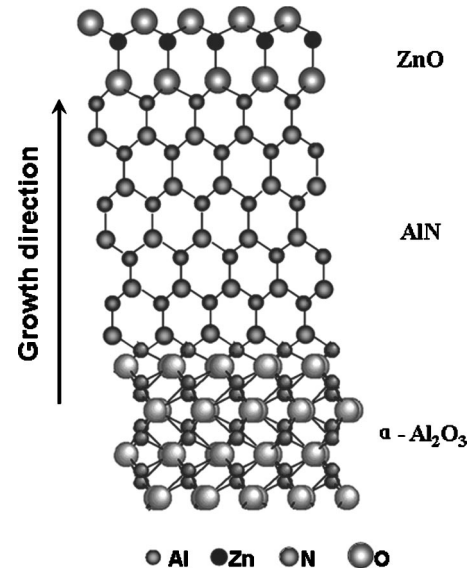
surface might be partially terminated by Al), were observed in the cross-sectional TEM images (not shown here). This indicates that the pretreatment conditions must be delicately controlled to achieve the unipolar films.

According to the above discussion, oxygen termination will result in anion-polar film while aluminum termination the cation polarity. It is the coordination of Al atoms at the interface that makes the difference. In the case of oxygen termination, Al atoms at the interface will occupy *octahedral* sites, i.e., binding to three oxygen atoms in topmost layer and another three in the second oxygen layer beneath, as in the bulk. When nitridation was initiated, the substitution of nitrogen for oxygen will take place, and the AlN layer formed at the interface will be sequenced as Al (octahedral)-N (tetrahedral)-Al (tetrahedral) and thus N polar (Fig. 4). Those Al atoms in the Al-terminated area, however, will adopt a *tetrahedral* environment, i.e., binding to three oxygen atoms in the layer below and leaving one dangling bond on the top. Nitridation of this kind of regions will lead to a direct bonding of N–Al and a stacking sequence of Al (tetrahedral)-N (tetrahedral)-Al (tetrahedral) at the interface, the Al-polar AlN will form. Therefore, to ensure the uniform O-polar ZnO films, the surface has to be processed in such a way that the whole surface of the sapphire could be covered by one monolayer oxygen. Otherwise, deficiency in oxygen will induce nucleation of Zn-polar regions and formation of IDs. When nitridation was performed on thermally cleaned sapphire surface at 800 °C for 1 h, we did obtain the Zn-polar ZnO films due to the ideal Al termination, which further justifies the atomistic view for polarity selection. Clearly, this kind of argument should be applied to other oxides and nitrides as long as the involved crystal structures are similar.

In summary, the role of pretreatments of the sapphire substrate in the polarity selection of ZnO films was systematically examined by RHEED, TEM, and CBED. Oxygen plasma pretreatment before surface nitridation was intro-

duced and applied to obtain unipolar single-domain ZnO films of high quality. An atomistic model was proposed to understand the polarity control process.

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