

Interface engineering for lattice-matched epitaxy of ZnO on (La,Sr)(Al,Ta)O₃(111) substrate

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ZnO/(La,Sr)(Al,Ta)O₃(LSAT) heterointerface is engineered to control the crystallographic orientation of ZnO films grown by plasmas-assisted molecular beam epitaxy. Lattice-matched in-plane alignment of $[11\bar{2}0]_{\text{ZnO}} \parallel [11\bar{2}]_{\text{LSAT}}$ has been realized using Mg modification of the substrate surface, which is confirmed with *in situ* reflection high-energy electron diffraction observation, and *ex situ* characterization of x-ray diffraction and transmission electron microscopy. The low-temperature deposition and high-temperature treatment of the Mg layer on the oxygen-terminated LSAT(111) surface results in selective nucleation of a MgO interface layer which serves as a template for single-domain epitaxy of ZnO. Oxygen-polar ZnO film with an atomically smooth surface has been obtained, which is favorable for metal-ZnO Schottky contact with high barrier height. © 2005 American Institute of Physics. [DOI: 10.1063/1.2130523]

As a promising material for the application in ultraviolet optoelectronic devices, epitaxial ZnO film has attracted much attention in terms of its wide band gap of 3.37 eV and a large exciton binding energy of 60 meV at room temperature.^{1,2} Although bulk ZnO substrate has been commercially available,³ due to its high price, heterogeneous substrates, such as sapphire (α -Al₂O₃) and Si, have been employed extensively for the growth of ZnO films.^{4,5} However, the crystal quality of ZnO deposited directly on sapphire(0001) or Si(111) is usually poor due to the large lattice mismatch between the substrate and the epitaxial film, which results in extremely high defect density and is a limiting factor for quality improvement of the films. By introducing a MgO buffer layer, the crystal quality of ZnO epitaxial films deposited on sapphire has been greatly improved.⁶ High-quality ZnO films have also been realized on lattice-matched substrate of ScAlMgO₄, which is the precondition for the realization of *p*-type ZnO.⁷ Therefore, the search for other lattice-matched substrate is a very important issue.

(La,Sr)(Al,Ta)O₃(LSAT) is an excellent newly developed crystal and has been already used as substrate for high T_c superconductivity film growth.^{8,9} It has a mixed perovskite structure and its (111) plane has the same sixfold symmetry as the (0001) plane of ZnO.^{10,11} LSAT(111) was once considered as a promising substrate for GaN film, because theoretically, with the epitaxial relationship of $[0001]_{\text{GaN}} \parallel [111]_{\text{LSAT}}$ and $[11\bar{2}0]_{\text{GaN}} \parallel [11\bar{2}]_{\text{LSAT}}$, the lattice mismatch between GaN and LSAT(111) is less than 1%.¹² However, experimental results showed that the actual crystallographic orientation for epitaxial GaN or AlN film on LSAT was rotated in-plane by 30° against the theoretical one, resulting in a much larger lattice mismatch than

expected.^{12,13} A similar problem exists for ZnO epitaxy on LSAT(111). With the ideal in-plane alignment of $[11\bar{2}0]_{\text{ZnO}} \parallel [11\bar{2}]_{\text{LSAT}}$, the lattice mismatch between ZnO and LSAT is only ~2.9% compared to 18.9% for the $[10\bar{1}0]_{\text{ZnO}} \parallel [11\bar{2}]_{\text{LSAT}}$ alignment.

In this paper, lattice-matched ZnO epitaxy with the in-plane $[11\bar{2}0]_{\text{ZnO}} \parallel [11\bar{2}]_{\text{LSAT}}$ alignment has been realized on LSAT(111) by using Mg modification of the substrate surface. The epitaxial relationship is confirmed by *in situ* reflection high-energy electron diffraction (RHEED) and *ex situ* x-ray diffraction (XRD) and transmission electron microscope (TEM).

A radio-frequency (rf) plasma-assisted molecular beam epitaxy (MBE) system (OmniVac)^{14,15} was used to grow ZnO films on LSAT(111) substrates. The substrates were degreased in trichloroethylene and acetone and rinsed with deionized water before introduced into the load-lock. Proper substrate preconditioning with oxygen radicals has been carried out for the three samples we studied in this paper. Oxygen-terminated LSAT(111) surfaces were expected after this pre-growth treatment. For sample A, Mg was deposited on this surface at 170 °C after the MBE chamber was vacuumized. The extra Mg was re-evaporated by annealing at 550 °C after an MgO layer was formed. Then, a conventional two-step growth of ZnO, i.e., a low temperature buffer layer growth at 550 °C and a high temperature epilayer at 620 °C, was performed. For comparison, for sample B and C the ZnO films were deposited directly on LAST, and no intentional control of the ZnO-LSAT interface was done. Sample B was prepared by a low temperature ZnO buffer layer growth at 500 °C and a high temperature epilayer growth at 620 °C while the buffer layer growth temperature was lowered to 380 °C for sample C.

Figure 1 shows the RHEED patterns at different growth stages of sample A. Figure 1(a) are for the substrate right after the pretreatment with oxygen radicals. When Mg depo-

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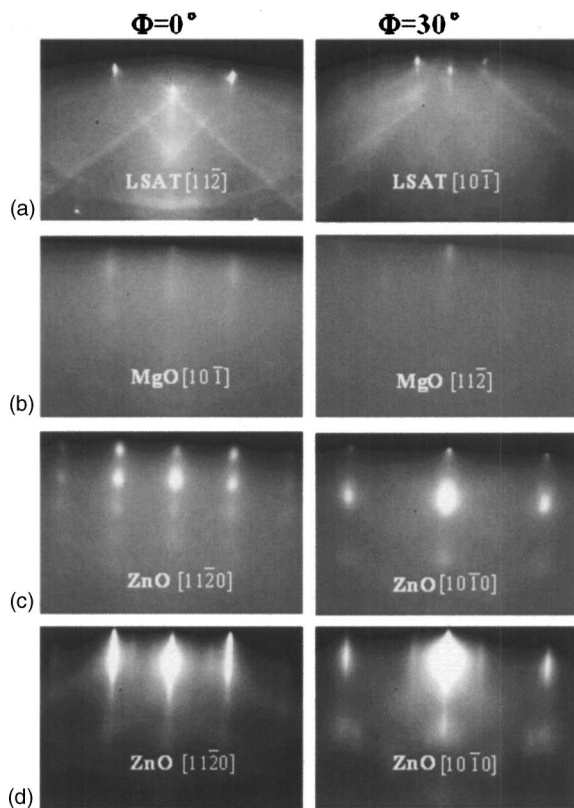


FIG. 1. RHEED patterns along $[11\bar{2}]_{\text{LSAT}}$ and $[10\bar{1}]_{\text{LSAT}}$ electron-beam azimuths obtained from (a) LSAT substrate, (b) MgO interface layer, (c) as-grown ZnO buffer layer, (d) ZnO epilayer. A well-defined 3×3 reconstruction pattern is observed in (d).

sition begins, a thin Mg wetting layer is formed on this oxygen-terminated surface, and streaky patterns for Mg appear on top of the substrate ones. During the temperature ramping to and annealing at 550°C , migration and re-evaporation of Mg atoms take place, leaving an ultra-thin MgO film due to the residual oxygen in the chamber and the oxygen from the substrate. Figure 1(b) shows the RHEED patterns of this MgO layer. It is clear that the MgO layer has a 30° in-plane rotation of its lattice with respect to the substrate. In addition, the RHEED signals from the substrate still exist, indicating a very small thickness (~ 1 nm) of MgO layer, which was further confirmed by the high-resolution TEM (HRTEM). We will discuss this later.

When the ZnO buffer layer deposition begins, the diffuse MgO patterns disappear and spotty patterns from ZnO appear, which are superimposed on the patterns from MgO. The spotty patterns maintain during the buffer layer growth [Fig. 1(c)], and become streaky gradually when the substrate temperature ramps to 620°C . After the epilayer growth at this temperature for 3 h, the sample surface appears very flat, as indicated by the sharp streaky RHEED patterns and the intense specular spots in Fig. 1(d). Also clearly seen is the 3×3 surface reconstruction, suggesting the formation of single-domain ZnO with anion polarity.^{4,15} Based on the RHEED observation, the epitaxial relationship between ZnO and LSAT is $[10\bar{1}]_{\text{ZnO}} \parallel [10\bar{1}]_{\text{LSAT}}$ and $[11\bar{2}]_{\text{ZnO}} \parallel [11\bar{2}]_{\text{LSAT}}$. The lattice mismatch with this in-plane alignment is 2.9%.

Ex situ atomic force microscope (AFM) measurement also confirms the flat nature of the surface morphology of sample A. The root-mean-square (RMS) roughness in a $2 \times 2 \mu\text{m}^2$ area is only 0.79 nm. Therefore, a high-quality

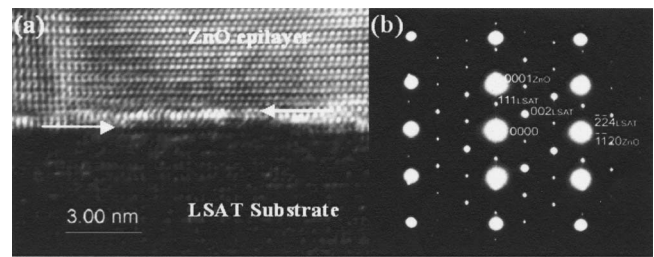


FIG. 2. Cross-sectional HRTEM image (a) and corresponding SADP (b) near the interface region of ZnO/MgO/LSAT, taken along $[11\bar{2}]_{\text{ZnO}}$ zone axis of ZnO. A thin MgO layer, depicted by the arrows, is formed near the ZnO/LSAT interface.

oxygen-polar ZnO film is obtained with an atomically smooth surface, which is favorable for fabrication of ZnO-based optoelectronic devices, especially for the metal-semiconductor-metal UV detectors. It has been reported that Schottky contacts with barrier height as big as 0.83 eV have been formed by electron beam evaporation of Pd on the ZnO(00 $\bar{1}$)-face.¹⁶

To determine the microstructure near the ZnO–MgO–LSAT interface, a cross-sectional HRTEM study was carried out. Figure 2(a) shows the HRTEM micrograph taken along $[11\bar{2}]_{\text{ZnO}}$, which demonstrates clearly the formation of a continuous crystalline interface between ZnO and LSAT with 2 to 3 atomic layers thick. The continuous crystalline feature of this interface layer suggests that a two-dimensional (2D) MgO wetting layer is formed, which is consistent with the streaky RHEED patterns in Fig. 1(b).

Figure 2(b) shows the corresponding selected area diffraction pattern (SADP) near the interface region of sample A. No diffraction spots from the MgO layer were observed because its thickness is too small. The crystallographic orientation of ZnO on LSAT is revealed as $[11\bar{2}]_{\text{ZnO}} \parallel [11\bar{2}]_{\text{LSAT}}$, consistent with the RHEED observation. Also it should be noticed that the diffraction spot of $(\bar{1}120)_{\text{ZnO}}$ is almost superposed on that for $(2\bar{2}4)_{\text{LSAT}}$, suggesting a very small lattice mismatch between the grown film and the substrate. By comparing the distance between the scattering and transmitted spots of ZnO and LSAT, the misfit is estimated to be about 3%, very close to the theoretical value of 2.9% for the ideal aligned ZnO/LSAT epitaxial system.

We found that this interface control technique, i.e., deposition and proper treatment of the Mg layer on the oxygen-terminated LSAT(111), is essential for single-domain lattice-matched ZnO growth. In contrast, direct deposition of a thin MgO buffer layer between ZnO and LSAT results in formation of rotation domains in MgO and consequently in ZnO. We speculate that the suppression of rotation domains is due to the long time evaporation process, which allows the Mg atoms migrate enough to find suitable nucleation sites at the substrate surface. This assumption is confirmed by the fact that the small fraction of rotation domains in the Mg layer, which were observed by RHEED at low temperature, disappeared completely during the high temperature annealing process and the Mg layer was finally replaced by a thin single-domain MgO wetting layer.

To further clarify the role of this interface engineering technique on the selection of in-plane orientations of ZnO on LSAT, the XRD ϕ -scans of ZnO (10 $\bar{1}2$) plane for samples A,

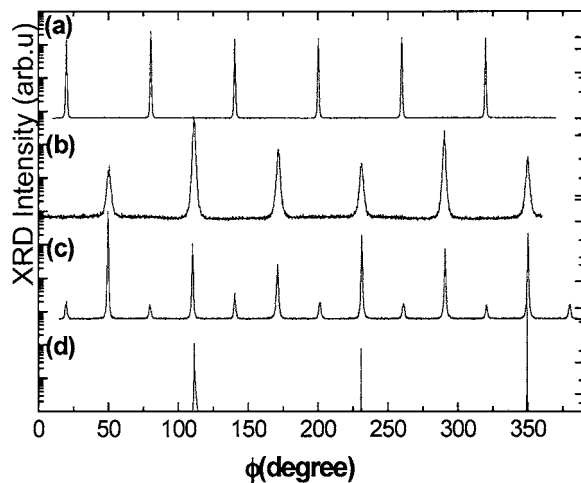


FIG. 3. The XRD ϕ -scans of ZnO (10 $\bar{1}2$) planes for (a) sample A, (b) sample B, and (c) sample C. For comparison, the ϕ -scan result of LSAT (220) is also given in (d).

B, and C were carried out and are shown in Fig. 3. Only six narrow peaks are observed in the scan range of 0°–360° for sample A [Fig. 3(a)], indicating a single-domain ZnO. The ZnO film has a 30° in-plane rotation with respect to the substrate, as seen from the ϕ -scan peaks of LSAT(220) [Fig. 3(d)]. This is consistent with the epitaxial orientation of the lattice-matched ZnO on LSAT(111).

Six broad peaks are observed for sample B, as shown in Fig. 3(b). The in-plane orientation between ZnO and LSAT is revealed as $[11\bar{2}0]_{\text{ZnO}} \parallel [10\bar{1}]_{\text{LSAT}}$, resulting in a lattice mismatch of 18.9%. The defect density in sample B is very high because of the large lattice mismatch, as indicated by the broad ZnO (10 $\bar{1}2$) ϕ -scan peaks shown in Fig. 3(b).

In the case of sample C, six weak peaks and six strong peaks are observed [Fig. 3(c)], indicating that two kinds of domains coexist in the ZnO epilayer. Between these two kinds of domains, there is a 30° rotation along the [111] LSAT axis. The role of growth temperature on the suppression of rotation domains for ZnO epitaxy deposited directly on LSAT has been discussed elsewhere.¹⁷

It is well known that the highly covalent materials favor the fourfold coordination structure whereas the highly ionic materials favor the sixfold and higher coordination structure. The realization of the lattice-matched ZnO epitaxy on LSAT(111) by using Mg modification of the substrate surface may originate from the different Mg–O and Zn–O bonding structures, i.e., rocksalt versus wurtzite. In our experiment, after oxygen radicals pretreatment, an oxygen terminated LSAT(111) surface with one dangling bond for each O is expected. When ZnO deposits directly on this surface, the Zn atoms of the first Zn–O bilayer tend to form bond on the top position of the O atom, leading to tetrahedrally bonded ZnO that is crystallographically aligned with respect to the substrate. For Mg deposition on this surface, however, the Mg atom is inclined to form bonds with three O atoms, because rocksalt MgO is most stable in all MgO structures. It is also possible for Mg and O to form a fourfold coordination structure.^{18,19} This is consistent with the 30° rotation domains we observed during the low temperature deposition of Mg or direct deposition of MgO on the oxygen-terminated LSAT(111), which may come from this kind of in-plane alignment. However, by using the Mg modification process

developed here, this small fraction of rotation domains could be completely removed because of the metastable property of the tetrahedrally bonded MgO structure.

In addition to the octahedral bonding feature with O, the excellent wetting property of Mg on oxygen-terminated LSAT(111) and the proper vapor pressure of Mg metal insures that the residual Mg can be easily re-evaporated before ZnO growth, forming a uniform MgO wetting layer on LSAT(111). Consequently, the resulting MgO layer serves as a template for single-domain lattice-matched ZnO epitaxy.

In summary, by control of the heterointerface using Mg modification of the substrate surface, lattice-matched ZnO epitaxy has been realized on LSAT(111), which has been confirmed by combined studies of RHEED, XRD and TEM. High quality ZnO with atomically flat surface has been obtained. This special interface control technique, i.e., to form a single-domain ultra-thin MgO wetting layer by Mg deposition and proper treatment process, has also been successfully applied to other ZnO epitaxy systems, which will be published elsewhere.²⁰

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