

Controlled Growth of Zn-Polar ZnO Films on Al-Terminated α -Al₂O₃(0001) Surface by Using Wurtzite MgO Buffer *

YUAN Hong-Tao(袁洪涛)¹, LIU Yu-Zi(刘玉资)¹, WANG Xi-Na(王喜娜)¹, LI Han-Dong(李含冬)¹, WANG Yong(王勇)¹, ZENG Zhao-Quan(曾兆权)¹, MEI Zeng-Xia(梅增霞)¹, DU Xiao-Long(杜小龙)^{1**}, JIA Jin-Feng(贾金锋)², XUE Qi-Kun(薛其坤)^{2,1}, ZHANG Ze(张泽)³

¹Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080

²Department of Physics, Tsinghua University, Beijing 100084

³Beijing University of Technology, Beijing 100022

(Received 10 May 2007)

The controlled growth of Zn-polar ZnO films on Al-terminated α -Al₂O₃ (0001) substrates is investigated by the radio-frequency plasma-assisted molecular beam epitaxy method. Prior to the growth, α -Al₂O₃ (0001) surface is modified by an ultrathin MgO layer, which serves as a uniform template for epitaxy of Zn-polar ZnO films. The microstructures of ZnO/MgO/Al₂O₃ interface are investigated by *in-situ* reflection high-energy electron diffraction observations and *ex-situ* high-resolution transmission electron microscopy characterization. It is found that under Mg-rich condition, the achievement of the wurtzite MgO ultrathin layer plays a key role in the subsequent growth of Zn-polar ZnO. An interfacial atomic model is proposed to explain the mechanism of polarity selection of both MgO and ZnO films.

PACS: 81.15.Hi, 61.14.Hg, 61.14.Lj

As a wide band-gap (3.37 eV) semiconductor with a large exciton binding energy of 60 meV, ZnO has attracted much attention for its potential applications in high-efficiency optoelectronic devices, such as light emitting diodes, laser diodes and UV detectors.^[1,2] The lack of inversion symmetry along the *c* axis in wurtzite ZnO leads to the formation of two different surfaces: O-polar and Zn-polar. Different electric charge distributions on both the polar faces will cause different behaviour in optics,^[3,4] electronics,^[5,6] as well as doping and epitaxial growing processes.^[7,8] Because of the absence of suitable substrates with high quality and low cost, great effort has been concentrated on ZnO heteroepitaxy on α -Al₂O₃ (0001) substrates.^[2,5,7] When ZnO films are directly grown on highly mismatched Al₂O₃, mixed polarities and domain boundaries are often obtained in the films. Thus the crystal quality is degraded. Therefore, unipolar ZnO growth becomes an important issue for both high-quality film preparations and device fabrications.

Recently, the achievements of ZnO heteroepitaxy on sapphire have been made by interface engineering between the substrate and the epilayer.^[9-11] One good example is polarity-controlled growth of ZnO films by using MgO buffer layers with manipulated interface structures (rocksalt or wurtzite).^[5] Particularly, using an ultrathin wurtzite MgO buffer layer on O-terminated α -Al₂O₃ (0001) surface, Chen *et al.* obtained high quality O-polar ZnO films.^[12,13] In their

work, O-rich condition was applied to the growth of O-polar wurtzite MgO on the oxygen-plasma pretreated sapphire substrate. Similarly, it is of practical interest to prepare Mg-polar wurtzite MgO at the interface for Zn-polar ZnO growth. However, to our knowledge, no attempts have been reported on this issue yet. In this Letter, an interface engineering technique is developed to achieve the Mg-rich condition for the preparation of wurtzite MgO, and then for the controlled growth of Zn-polar ZnO films. High-resolution transmission electron microscopy (HRTEM) is carried out to gain a fundamental understanding of the interface microstructures. Based on the HRTEM results, an atomic model of the ZnO/MgO/Al₂O₃ interface is proposed to explain the mechanism governing the polarity selection of both wurtzite MgO and ZnO.

The growth was carried out on a radio frequency plasma-assisted molecular beam epitaxy system (OmniVac) with a background pressure better than 2.0×10^{-10} mbar. An SVT rf-plasma source was used to provide active oxygen radicals. Oxygen gas (over 5N grade) was further purified by using a gas purifier (SAES) before injected into the plasma source through a mass flow controller. Element zinc (6N grade), magnesium (5N grade) in effusion cells were used as solid sources for evaporation. High-quality Zn-polar ZnO samples were prepared on α -Al₂O₃(0001) substrates using wurtzite MgO ultrathin layer as the buffer layer under the Mg-rich condition. A distinct

* Supported by the National Natural Science Foundation of China under Grant No 60606023 and 50532090, the National Basic Research Programme of China under Grant No 2002CB613502, and Chinese Academy of Sciences.

** To whom correspondence should be addressed. Email: xldu@aphy.iphy.ac.cn

method was used to prepare wurtzite MgO as follows: (1) substrate degassing at high temperature (800°C) for 20 min to obtain Al-terminated surface; (2) Mg deposition for 5 min (about several nanometres) at low temperature (80°C) under ultra high vacuum (UHV) condition; (3) ramping to 260°C under UHV; (4) exposure to O-plasma at 260°C to obtain an ultrathin MgO wetting layer. On this MgO layer, ZnO film growth was performed by using the conventional two-step growth technique, i.e., low temperature growth of ZnO buffer was followed by high temperature epilayer growth at 650°C . The whole growth process was monitored by *in-situ* reflection high-energy electron diffraction (RHEED). The dark field images and the HRTEM observations were performed with a Philips CM-200FEG system operated at 200 kV. In addition, the polarities of ZnO films were analysed by convergent beam electron diffraction (CBED).

Figure 1 shows the evolution of RHEED patterns during ZnO growth, with incident azimuths along the $[11\bar{2}0]_{\text{ZnO}}$ and $[10\bar{1}0]_{\text{ZnO}}$ directions. Clear and streaky RHEED patterns of sapphire surface after thermal cleaning at 800°C are shown in Fig. 1(a). The atomic structure of $\alpha\text{-Al}_2\text{O}_3(0001)$ surface, which has been extensively studied,^[14–17] plays a key role in determination of the microstructures of subsequent overlayers. Depending on different pretreatment processes, sapphire surface can be Al-rich (terminated with an Al monolayer or an Al bilayer) or O-rich (terminated with an O monolayer). It has been ascertained from electrostatic aspect that the Al-monolayer-terminated surface of $\alpha\text{-Al}_2\text{O}_3(0001)$ is the most stable surface, especially after high-temperature degassing.^[16] Therefore, in our case, the Al-monolayer-terminated surface was expected after the degassing, on which a magnesium layer was deposited under UHV condition. The RHEED patterns after Mg deposition are shown in Fig. 1(b). From the RHEED pattern geometry, a single-crystal hexagonal Mg(0001) surface can be established. When we increased the substrate temperature, the Mg patterns gradually became dim (which corresponds to the re-vaporization of Mg layer from the substrate). When this surface was exposed to oxygen-plasma, MgO patterns came into being, as shown in Fig. 1(c). The wurtzite structure of the MgO wetting layer, evenly formed on sapphire surface, could be determined by the 2 mm symmetry of the diffraction geometry and the rectangular primitive unit cell of elongated diffraction spots in RHEED patterns. On this MgO template, ZnO buffer layer was grown without any 30° in-plane rotation domains, which could be confirmed with only one set of ZnO patterns, as shown in Fig. 1(d). Small spots became dominant, indicating a three-dimensional (3D) island growth mode of the ZnO buffer layer. Clear spotty patterns of ZnO epilayer in Fig. 1(e) imply a rough

surface but a high crystal quality.

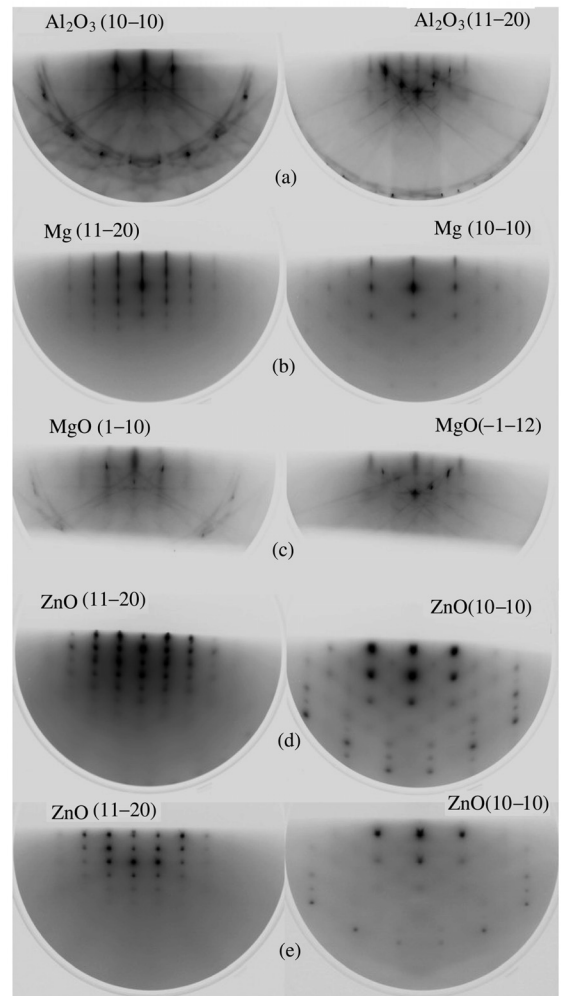


Fig. 1. Evolution of RHEED patterns during ZnO growth using an ultrathin wurtzite MgO layer formed on an Al-terminated $\alpha\text{-Al}_2\text{O}_3(0001)$ substrate under Mg-rich condition, with incident azimuths along the $[11\bar{2}0]$ and $[10\bar{1}0]$ directions, respectively.

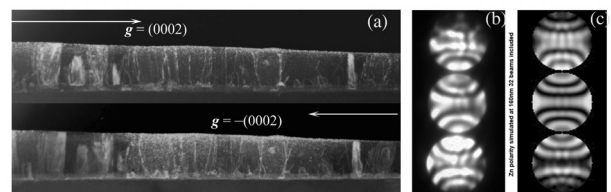


Fig. 2. (a) Dark field TEM images of $g = \pm(0002)$ with the primary beam parallel to the $[11\bar{2}0]$ direction. (b) Experimental CBED patterns of the ZnO film in comparison with (c) the simulated CBED patterns.

In order to figure out the role of the MgO layer in ZnO epitaxial growth, TEM studies were carried out. The dark field images of $g = \pm(0002)$ with the primary beam parallel to the $[11\bar{2}0]$ zone axis are shown in Fig. 2(a). By comparison of these two images, it can be deduced that there is no inversion domain in ZnO film, suggesting that ZnO inversion domains were

completely suppressed by using this ultrathin MgO layer.

Furthermore, polarities of these ZnO films were determined by comparing the experimental convergent beam electron diffraction (CBED) patterns of the ZnO films together with the simulated ones for ZnO with thicknesses between 120–180 nm. The experimental patterns were taken along the $[10\bar{1}0]$ zone axis, and the calculated ones were simulated in the same direction. The CBED patterns of the ZnO film [Fig. 2(b)] agree well with the simulated ones for the 160-nm-thick ZnO sample [Fig. 2(c)], implying that the ZnO film has the Zn-terminated $[0001]$ orientation (Zn-polar).

To further clarify the polarity selection mechanism, the interface microstructure and the crystal orientation of the ZnO/MgO/ α -Al₂O₃ system were investigated in detail by HRTEM. As shown in Fig. 3, the HRTEM image of Zn-polar ZnO film on MgO ultrathin layer was taken along $[10\bar{1}0]_{\text{sapphire}}$. There is an obvious MgO interlayer with a thickness less than 1 nm between ZnO and α -Al₂O₃ substrate, as indicated by the white arrows. In order to reduce the noise and minimize blurring, the Fourier-filtered images were processed by the software Digital Micrograph.^[18] The inset of Fig. 3 shows the fast Fourier transform image of one region in MgO interlayer. It shows a typical ABAB stacking sequence along the c -axis, which is an essential character of the wurtzite structure. Combined the TEM results with the RHEED observations, the MgO interlayer was established as wurtzite structure and the epitaxial orientation between ZnO and α -Al₂O₃ substrate was determined to be ZnO $[11\bar{2}0]//$ MgO $[11\bar{2}0]//$ Al₂O₃ $[10\bar{1}0]$, ZnO $[10\bar{1}0]//$ MgO $[10\bar{1}0]//$ Al₂O₃ $[11\bar{2}0]$, and ZnO $[0001]//$ MgO $[0001]//$ Al₂O₃ $[0001]$.

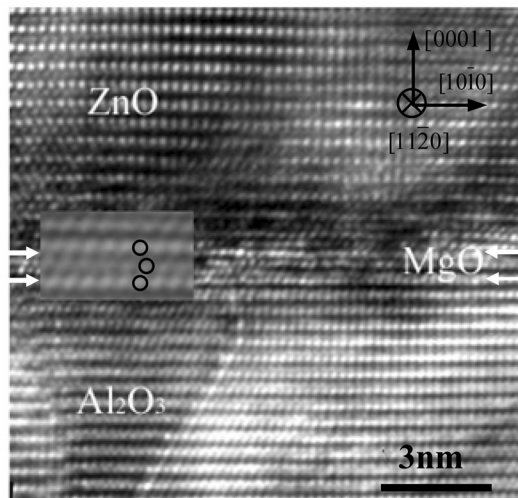


Fig. 3. Cross sectional HRTEM images near the interface with the wurtzite MgO ultrathin layer. Inset: a part of Fourier filtered image showing the clear ABAB stacking sequence of the MgO layer.

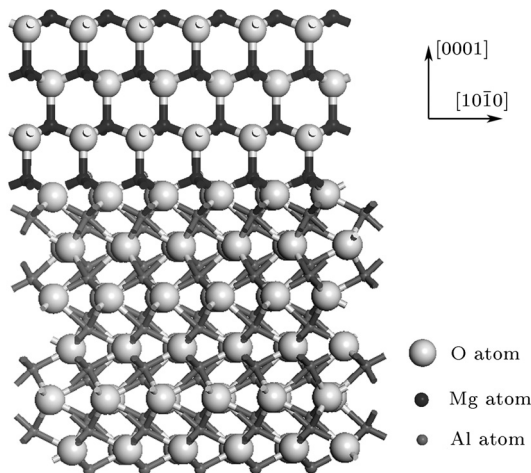


Fig. 4. Atomic model proposed for the interface structure of the Al₂O₃ substrate and wurtzite MgO.

Some groups have reported that under an oxygen rich condition, an O-polar wurtzite MgO buffer layer on O-terminated sapphire could be achieved, which eventually resulted in the formation of O-polar ZnO.^[5,12,13] In our case, Mg(0001) layer was deposited on Al-terminated α -Al₂O₃(0001) and the wurtzite MgO ultrathin layer was achieved under the Mg-rich condition. By this interface engineering, Mg-polar wurtzite MgO is speculated to be formed and finally served as the template for Zn-polar ZnO growth. Figure 4 shows a schematic atomic model of the interface between the substrate and MgO layer based on our studies. Considering that the monolayer-Al-terminated α -Al₂O₃ surface is most stable under UHV,^[16] the dangling bond numbers on this surface should be as less as possible. Thus, when Mg/ α -Al₂O₃ was exposed to oxygen atoms and MgO/ α -Al₂O₃ interface was formed under Mg-rich condition, the following bonding configuration can be deduced: each outmost Al atom forms one bond upwards with one oxygen atom. In this way, the outmost Al-terminated surface has the least bonding numbers. Meanwhile, each new-deposited O atom forms one bond with one Al atom below and three bonds with three Mg atoms above. As a result, the wurtzite MgO with Mg-polar is formed, which leads to formation of the Zn-polar ZnO film. Previous results, on the other hand, demonstrated a different bonding configuration of oxygen atoms in the wurtzite MgO structure on O-terminated α -Al₂O₃(0001) surface under the O-rich condition. For the oxygen atoms, three bonds downward on three Al atoms and one bond upward on one Mg atom will lead to O-polar wurtzite MgO. When the polar MgO is formed, it serves as a template for subsequent growth of ZnO film. The bonding configuration of ZnO will inherit that of the underlying MgO layer. Therefore, in our case, Mg-rich condition on Al-terminated α -Al₂O₃(0001) surface is essential for the formation of

Mg-polar wurtzite MgO, which finally results in the subsequent epitaxy of Zn-polar ZnO films.

In summary, by using a Mg-polar wurtzite MgO ultrathin layer formed on an Al-terminated α -Al₂O₃(0001) substrate under Mg-rich condition, high-quality ZnO film is achieved with the Zn-polarity. The *in-situ* RHEED observations and *ex-situ* TEM characterization demonstrate that under the Mg-rich situation, the bonding configuration at the MgO/ α -Al₂O₃ interface determines the polarity of wurtzite MgO layer. The Mg-polar wurtzite MgO structure is speculated to be formed and finally served as the template for Zn-polar ZnO growth. Therefore, the surface structure of substrate as well as the formation condition of MgO should be delicately controlled to obtain a uniform template for epitaxy of a single-domain ZnO film.

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