Controlled growth of Zn-polar ZnO epitaxial film by nitridation of sapphire substrate

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(Received 22 November 2004; accepted 26 January 2005; published online 9 March 2005)

Surface nitridation is used to eliminate O-polar inversion domains and control the growth of single-domain Zn-polar ZnO film on sapphire (0001) substrate by rf-plasma-assisted molecular-beam epitaxy. It is found that the nitridation temperature is crucial for achieving quality AlN buffer layers and ZnO films with cation polarity, as demonstrated by ex situ transmission electron microscopy. Under optimal growth conditions, a 4 × 4 surface reconstruction was observed, which is confirmed to be a characteristic surface structure of the Zn-polar films, and can be used as a fingerprint to optimize the ZnO growth. © 2005 American Institute of Physics.

As a wide-band-gap oxide semiconductor, ZnO has enormous potential applications in short-wavelength optoelectronic devices. Many achievements have been made due to the fact that high-quality epitaxial layers are available by various methods.1-9 Polarity control is one of the most important issues for obtaining good crystalline quality, because the formation of inversion domains (IDs) in polar ZnO will severely deteriorate the material.10,11 In addition, recent studies demonstrate much higher p-type doping efficiency in Zn-polar films compared to O-polar ones.1,12 Although the origin of p-type conduction in Zn-polar ZnO films is not clear at present, it is very important to achieve controllable growth of Zn-polar ZnO films for light-emitting diode and laser diode applications.

Bulk ZnO is commercially available and Zn-polar ZnO homoepitaxy has been reported recently.13,14 Due to the high cost, rough surface morphology, and poor crystal quality of the ZnO substrate, however, α-Al2O3 (0001) is still the more favorable substrate currently used. The problem with sapphire is the formation of O-polar IDs. The pregrowth surface nitridation at low temperature was employed to obtain uniform O-polar ZnO growth on sapphire by molecular-beam epitaxy (MBE) in our previous work.15 A thin AlN layer formed on α-Al2O3 is found to effectively suppress Zn-polar IDs and promote O-polar film growth. In this work, we use this method to control the polarity of AlN and ZnO layers. Our finding is that uniform Zn-polar ZnO films could be controllably obtained by nitridation at a higher temperature (400–550 ºC), as substantiated consistently by reflection high-energy electron diffraction (RHEED), convergent beam electron diffraction (CBED), and transmission electron microscopy (TEM) studies. This makes the films of this type very promising for high concentration p doping.1,12

Our ZnO samples were prepared on sapphire (0001) substrates using an rf-plasma-assisted MBE system (OmniVac). The base pressure in the growth chamber was ~1 × 10−10 Torr. Zn was supplied by evaporating 6N elemental Zn 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 degreasing in trichloroethylene and acetone, the sapphire substrates were chemically etched for 30 min in a hot solution of H2SO4:H3PO4=3:1 at 110 ºC and then rinsed with deionized water. Before growth, the substrates were thermally cleaned at 800 ºC for 1 h, followed by nitridation at 400–550 ºC for 1 h with an rf power of 480 W and a nitrogen flux of 3.0 sccm. Nitridation at either lower or higher temperatures was also investigated, but neither of them could lead to good-quality Zn-polar films. Then, conventional two-step growth of ZnO, i.e., a low-temperature (LT) buffer layer growth at 400 ºC and a high-temperature growth at 650 ºC, was performed. The in-plane epitaxial relationship, surface morphology evolution, and crystallinity were monitored in situ by RHEED. A Philips CM200 field emission gun transmission electron microscope, operating at 200 kV, was used for polarity determination and cross-sectional microstructure characterization.

We first describe the detailed growth processes of the ZnO epilayers based on in situ RHEED observation. Figures 1(a) and 1(b) show the RHEED patterns recorded before and after nitridation, respectively. A thin AlN layer forms with a 30º in-plane rotation of its lattice with respect to the substrate after nitridation, and the sharp streaky patterns become diffuse. The RHEED signal from sapphire still exists, which indicates a very small thickness (~2 nm) of the AlN layer.
This thickness was further confirmed by the high-resolution TEM (HRTEM) observation. In addition, the diffuse RHEED patterns [Fig. 1(b)] suggest that the strain between AlN and sapphire is not relaxed. Similar to the case of O-polar ZnO, the AlN layer has a zincblende structure with stacking faults parallel to the AlN/Al$_2$O$_3$ interface. The diffuse patterns disappear once the LT ZnO buffer growth is initiated, and become spotty a few minutes later, with an in-plane epitaxial relationship of ZnO [1120] //AlN[101] and ZnO[1010]//AlN[112]. During the LT buffer layer growth, the spotty patterns remain [Fig. 1(c)].

When the temperature ramps up to 650 °C, the RHEED patterns become streaky gradually. This situation could be dramatically promoted by interrupting the deposition and annealing at 750 °C. 10 min of annealing leads to very sharp streaky RHEED patterns, and more importantly, a well-defined 4×4 reconstruction is observed [Fig. 1(d)], which maintains for the entire deposition process. Previously, only two reconstructions (1×1 and 3×3) were observed. 3×3 reconstruction was reported in the growth of the O-polar ZnO films, where LT MgO and ZnO buffers were used. We found that, with pregrowth oxygen radical treatment and LT nitridation, the O-polar ZnO films could be also obtained with a characteristic 3×3 reconstructed surface. The surface reconstructs to optimize the surface energy, and different surface stoichiometry and crystallographic orientation give rise to different stable surface structure, which can be a fingerprint of film polarity, such as the case of GaN(0001) and GaN(0001). Under this context, we speculate that the ZnO films may have a Zn polarity.

To confirm this, we carried out a TEM study of the sample prepared under the optimal conditions stated above. Figures 2(a) and 2(b) show the (0002) and (0002) dark-field images, respectively. No IDs are observed, and our sample is unipolar. The total density of threading dislocations in the sample is lower than 3×10$^5$ cm$^{-2}$. A CBED pattern was then taken slightly away from the [10$ar{1}$0] zone axis toward [11$ar{2}$0] direction [Fig. 2(c)]. Since the (0002)$_{Zn}$ face can reflect the electron beam much more strongly than the (0002)$_{O}$ face, the central fringes at (0002) and (0002) disks should appear bright and dark, respectively. From the tokens in the CBED pattern [Fig. 2(c)], the ZnO film is determined to have [0001] polarity. The formation of an Al-polar AlN layer can thus be inferred. The dark-field images and CBED clearly show that the IDs of O polarity were effectively suppressed and a single-domain Zn-polar film was formed. Therefore, the 4×4 reconstruction is a characteristic structure of the Zn-polar ZnO film, and can be used as a fingerprint to identify the Zn polarity and conveniently establish the optimal growth conditions for high-quality Zn-polar ZnO films by in situ RHEED observation.

The HRTEM image along [11$ar{2}$0]$_{sapphire}$ direction (see Fig. 3) clearly shows the interface microstructure between the nitridation layer and sapphire substrate. A continuous unrelaxed cubic AlN layer of ~2 nm thick was seen, which does not reduce the lattice mismatch between ZnO and sapphire (18.3%). It should be noted that the interface is smooth and sharp without any indication of interdiffusion or an amorphous structure. The zincblende AlN layer is confirmed to have an epitaxial relationship with α-Al$_2$O$_3$ (0001) of...
AlN polarity, has been studied systematically and will be discussed elsewhere. In our experiments, we found that nitridation temperature plays a key role in AlN polarity selection, interface microstructure, and ZnO polarity. Figure 4 shows the ZnO film polarity as a function of the nitridation temperature (400 °C–550 °C) to achieve Zn-polar films is seen.

[111] AlN//[0001]Al2O3, and [112]AlN//[11\overline{2}0]Al2O3. More details can be found in our previous work.17 The correlation between substrate pretreatment and nitridation temperature and the microstructure of the nitridation layer, as well as its polarity, has been studied systemically and will be discussed elsewhere.

In summary, the role of nitridation temperature in the polarity selection of ZnO films was systematically examined by RHEED, CBED, and TEM. A 4 X 4 surface reconstruction was observed, which we show can be used as a fingerprint for the growth of uniform Zn-polarity ZnO films on sapphire.

This work is supported by the National Science Foundation (Grant Nos. 60476044, 60376004, 60021403, 10174089) and the Ministry of Science and Technology (Grant No. 2002CB613502) of China.