Microstructural study of MBE-grown ZnO film on GaN/sapphire (0001) substrate

Hua Li¹²*, Jianping Sang², Chang Liu², Hongbing Lu², Juncheng Cao¹

¹ State Key Laboratory of Functional Materials for Informatics, Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences, 865 Changning Road, Shanghai 200050, China
² Key Laboratory of Acoustic and Photonic Materials and Devices of Ministry of Education, Wuhan University, Wuhan 430072, China

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Abstract: Single crystalline ZnO film is grown on GaN/sapphire (0001) substrate by molecular beam epitaxy. Ga₂O₃ is introduced into the ZnO/GaN heterostructure intentionally by oxygen-plasma pre-exposure on the GaN surface prior to ZnO growth. The crystalline orientation and interfacial microstructure are characterized by X-ray diffraction and transmission electron microscopy. X-ray diffraction analysis shows strong c-axis preferred orientation of the ZnO film. Cross-sectional transmission electron microscope images reveal that an additional phase is formed at the interface of ZnO/GaN. Through a comparison of diffraction patterns, we confirm that the interface layer is monoclinic Ga₂O₃ and the main epitaxial relationship should be (0001)_{ZnO}/(001)_{Ga₂O₃}//(0001)_{GaN} and [2-1-10]_{ZnO}//(010)_{Ga₂O₃}‖[2-1-10]_{GaN}.

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1. Introduction

ZnO has attracted great interest for its excellent optical, electrical, catalytic, and gas sensing properties, and for potential applications in various fields [1–6]. The most attractive properties of ZnO are its wide band gap of 3.3 eV at room temperature and high exciton binding energy (60 meV) compared to those of ZnS (20 meV) and GaN (25 meV) [7, 8]. Due to its wide band gap, ZnO can be used for short wavelength light emitting devices such as light emitting diodes (LED) and laser diodes (LD), surface acoustic wave (SAW) bandpass filters, optical waveguides, and laser deflectors. Furthermore, experiments have approved that ZnO is one of the most pronounced candidates for diluted magnetic semiconductors (DMS) [9]. In a word, ZnO is a useful material for optoelectronics and other applications.

Recently, significant progress in ZnO crystal quality has been made. High-quality ZnO films have been grown with molecular beam epitaxy [10, 11], metal–organic chemical vapor deposition [12–14], pulsed-laser deposition [15, 16], and sputtering [17, 18]. By reason of the high electron concentration in as-grown ZnO films, the fabrication of p-type ZnO, which represents the bottleneck of fabricating...
ZnO-based light-emitting devices, is still unstable due to the self-compensation effect. However, n-type ZnO and p-type GaN can be easily realized. Because the lattice mismatch between ZnO and GaN (1.8% mismatch) is much smaller than that between ZnO and sapphire (18% mismatch) [19, 20], it is easy to realize the hybrid growth of ZnO and GaN. Furthermore, the growth and process techniques of GaN are quite mature. Therefore, the hybrid growth of n-ZnO and p-GaN for optoelectronic devices has been an idea receiving a great attention [21, 22]. To grow high crystalline quality ZnO/GaN films for optoelectronic devices, the microstructural study on ZnO/GaN interface is an interesting and significant work.

In this article, we present the detailed hybrid growth of ZnO and GaN on sapphire (0001) substrate by molecular beam epitaxy. Ga$_2$O$_3$ is intentionally introduced into the ZnO/GaN heterostructure by oxygen-plasma pre-exposure on GaN surface prior to ZnO growth. Studies on the crystalline quality and microstructure of ZnO/GaN hetero-interface are performed.

2. Experimental details

The ZnO wafer used in the study had a thickness of 1 µm and was grown on a single crystalline GaN template. The GaN template was grown on a sapphire (0001) substrate. Both ZnO and GaN layers were deposited by different molecular beam epitaxy (MBE) systems. The GaN layer was grown on sapphire (0001) substrate by radio frequency (RF) plasma-assisted MBE. Elemental Ga and RF plasma-enhanced N$_2$ were used as sources. After thermally cleaning the sapphire substrate surface at 900 °C, it was nitrided under the N$_2$ flux of 1.0 SCCM at 600 °C for 1 hour. A 150 nm thick GaN buffer layer was grown at a substrate temperature of 600°C. Then, a 20 nm thick GaN layer was grown on the GaN buffer layer at 650°C followed by a thermal treatment at 750°C for 30 min. Next, the sample was transferred to another RF oxygen plasma-assisted MBE system. RF oxygen plasma and solid K-cell were used as oxygen and zinc sources, respectively. Plasma oxygen irradiation at 500°C for 10 min was performed prior to the ZnO film growth to insert Ga$_2$O$_3$ at the interface of ZnO/GaN heterostructure intentionally. Next, a 1 µm thick ZnO layer was grown at 600 °C. A typical beam equivalent pressure 2×10$^{-1}$ Pa for Zn and a flow rate 0.5 SCCM for oxygen gas were employed.

After growth, crystalline quality and orientation of the ZnO film were evaluated by D8 Advanced X-ray diffraction (XRD) which employed a high-resolution diffractometer with Cu Kα radiation, operating at a voltage of 40 kV and a current of 40 mA. Transmission electron microscope (TEM) measurements were carried out using a JEM-2010FEF with an accelerating voltage of 200 kV. Microstructural properties of the ZnO/GaN hetero-interface were characterized using cross-sectional TEM. The specimens for the cross-sectional TEM measurements were prepared by cutting, polishing with boron carbide powder to a thickness of approximately 100 µm, then dimpling one face down to 20 µm and finally Ar$^+$ ion milling down to electron transparency at a voltage of 4-6 keV with an incident angle of 6°.
3. Results and discussion

![Figure 3](image-url)  
**Figure 3.** Cross-sectional high-resolution TEM image of ZnO/GaN interface along [2-1-10] zone axis of ZnO. The rectangular region shows a different lattice structure from ZnO and GaN.

Fig. 1 shows a typical XRD diffraction pattern of the as-grown ZnO film grown on GaN/sapphire substrate measured with 2θ-θ scan. Pronounced ZnO (0002) diffraction peak located at 34.4° and ZnO (0004) diffraction peak located at around 73° are observed clearly from it. The ZnO (0002) rocking curve is shown in the inset of Fig. 1 and the corresponding full-width at half-maximum (FWHM) value is 0.22° which indicates that the ZnO film has a strong c-axis preferred orientation. The (0006) diffraction peak corresponding to the sapphire (0001) substrates is also clearly observed.

A bright-field cross-sectional TEM image of the ZnO film on GaN/sapphire is shown in Fig. 2. It is clear to see the top ZnO preferentially oriented film, GaN layer, GaN buffer layer and sapphire substrate. The inset of Fig. 2 is the corresponding selected area diffraction pattern (SADP) taken from the ZnO/GaN interface, in which 1 and 2 are GaN (01-10) and (0001) reflections, and a and b are ZnO (01-10) and (0001) reflections. The electron beam parallel to the [2-1-10] zone axis of ZnO or GaN. The ZnO thin film is a highly c-axis oriented layer from the analysis of the SADP. We can conclude the perfect main epitaxial relationship of the sample: (0001)$_{ZnO}$/[2-1-10]$_{GaN}$ and [2-1-10]$_{ZnO}$/[2-1-10]$_{GaN}$.

A cross-sectional high-resolution TEM study is carried out to determine the microstructure of ZnO/GaN heterointerface. Fig. 3 shows a cross-sectional high-resolution TEM image of the heterostructure along the [2-1-10] zone axis. It is clear to see the interfaces of ZnO/GaN and GaN/GaN buffer layer, which are indicated by black arrows. Lattice mismatch between ZnO and GaN results in a high density of misfit dislocation at the interface. It is worthy to pay more attention to the interfacial area between ZnO and GaN indicated by a rectangular box in Fig. 3. Along the interface, the atoms’ positions are highly displaced, suggesting the existence of a high strain in the film. We can also see that the interfacial area shows a different lattice structure from ZnO and GaN, i.e., atoms of the first five monolayers in the interface layer rotate an angle off the [0001]-axis of GaN. In our former research [23], we conjectured that the first five monolayers may form another phase (such as monoclinic Ga$_2$O$_3$) or just be the lattice faults. To clarify this, we take a further high-resolution TEM study. Fig. 4 shows another cross-sectional high-resolution TEM image of the interface of ZnO/GaN. About 20 monolayers show a different lattice structure from ZnO and GaN, which are indicated by a rectangle in Fig. 4. Thanks to the thicker interface layer (compared to the five monolayers in Fig. 3), we can carry out a simulated experiment to confirm the phase of the interface layer as follows.

In order to confirm the phase of the interface layer, we carry out a diffraction pattern analysis. Fig. 5(a) is a digital diffraction pattern obtained by fast-Fourier-transform (FFT) of corresponding interface layer of Fig. 4. On the
other hand, we calculated the electron diffraction pattern based on monoclinic Ga$_2$O$_3$ (space group is A2/m) structure. Fig. 5(b) shows the simulated diffraction pattern of the monoclinic Ga$_2$O$_3$ with the [010]-zone axis. Arabic numerals 1, 2 and 3 in Fig. 5(a) can be proved to be (001), (201) and (200) reflections of monoclinic Ga$_2$O$_3$ by comparing the FFT image Fig. 5(a) with the calculated diffraction pattern Fig. 5(b). Thus, we conclude that the interface layer which shows a different lattice structure should be monoclinic Ga$_2$O$_3$. Integrated with our previous results, we could deduce the main epitaxial relationship of ZnO and GaN is (0001)$_{ZnO}$//(0001)$_{GaN}$ and [2-1-10]$_{ZnO}$/[2-1-10]$_{GaN}$. The formation of monoclinic Ga$_2$O$_3$ at the interface layer is attributed to the oxygen-plasma pre-exposure on GaN prior to ZnO growth and other unintentional oxidations. The insertion of Ga$_2$O$_3$ may have negative effects on the luminescence of devices and result in degradation of the crystal quality of ZnO films compared to ZnO films grown with Zn-exposure technology [24, 25]. However, monoclinic Ga$_2$O$_3$ interface layer has a center of symmetry which leads to the realization of crystal polarity control, i.e. an O-polar (anion-polar) ZnO film can be grown on Ga-polar (cation-polar) GaN by inserting a Ga$_2$O$_3$ layer at the interface [25]. Therefore, this work which demonstrates a closer look of monoclinic Ga$_2$O$_3$ is helpful for us to understand the important role of Ga$_2$O$_3$ in ZnO/GaN heterostructure.

4. Conclusions

In summary, 1 µm thick ZnO film is grown on oxygen-plasma pre-exposed GaN/sapphire (0001) substrate by MBE. X-ray diffraction results show a strong c-axis preferred orientation of the ZnO film. Interfaces of different layers could be observed clearly by bright-field cross-sectional TEM and the main epitaxial relationship of ZnO and GaN is (0001)$_{ZnO}$//(0001)$_{GaN}$ and [2-1-10]$_{ZnO}$/[2-1-10]$_{GaN}$. Cross-sectional high-resolution TEM images reveal that the interface layer of ZnO/GaN shows a different lattice structure from ZnO and GaN. By comparing the FFT image with the calculated diffraction pattern, we confirm that the interface layer is monoclinic Ga$_2$O$_3$ and the main epitaxial relationship should be (0001)$_{ZnO}$//(0001)$_{GaN}$ and [2-1-10]$_{ZnO}$/[2-1-10]$_{GaN}$.

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