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# Properties of GaN on different polarity buffer layers by hydride vapour phase epitaxy*

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This paper reports on N-, mixed-, and Ga-polarity buffer layers are grown by molecular beam epitaxy (MBE) on sapphire (0001) substrates, with the GaN thicker films grown on the buffer layer with different polarity by hydride vapour epitaxy technique (HVPE). The surface morphology, structural and optical properties of these HVPE-GaN epilayers are characterized by wet chemical etching, scanning electron microscope, x-ray diffraction, and photoluminescence spectrum respectively. It finds that the N-polarity film is unstable against the higher growth temperature and wet chemical etching, while that of GaN polarity one is stable. The results indicate that the crystalline quality of HVPE-GaN epilayers depends on the polarity of buffer layers.

**Keywords:** GaN, HVPE, MBE, polarity
**PACC:** 7280E, 6855

## 1. Introduction

Gallium nitride (GaN) and related materials have recently attracted a lot of interest for applications in high power electronics which are capable of operation at high temperatures and high frequencies, due to superior material properties such as wide bandgaps, high electron mobility, high breakdown field, and availability of heterostructures. However, the development of GaN-based electronic and optoelectronic devices is limited due to the lack of high quality lattice-matched substrates. The epilayers of GaN are commonly grown on lattice and thermal expansion coefficient mismatch substrates, such as Si, sapphires, GaAs, SiC or $\mathrm{LiAlO}_2^{[1]}$ numerous threading dislocations are formed between epilayers and substrates and the quality of GaN epilayers is detrimental by using heterogeneous substrates. Therefore, lattice and thermal match substrates are very important to the growth of GaN epilayer. Fortunately, thick GaN layers grown by hydride vapour phase epitaxy (HVPE) on a heterogeneous substrate,[2] which can be used as a quasi-substrate of GaN growth by removing the heterogeneous substrate by laser lifting off,[3] are good options to overcome this problem.

The growth parameters of HVPE, such as reactor design, carrier gases, growth temperature, nitridation time, and so on, are very important for obtaining good quality epilayers. Recently, the polarity of III-nitride films grown on mismatched substrates has become a key factor due to its great influence on the qualities of the GaN epilayers. GaN films with Ga- and N-polarity demonstrate significantly different growth, morphology, optical and electrical properties, and device performances.[4−6] Therefore, the determination of the polarity is very important.

Up to now, we have known that the lattice polarity of GaN epilayers grown on sapphire substrates by metal organic vapour phase epitaxy, either GaN or AlN low temperature buffer layers lead to Ga-polar films, while, the lattice polarity of conventional molecular beam epitaxy (MBE) grown films shows mainly N-polarity.[7] At the same time, several groups have reported that GaN epilayers with different polarity have been achieved on sapphire substrates by MBE technique.[8,9] How to control its polarity perfectly is a topic to study.

In this paper, the properties of thick HVPE-GaN epilayers grown on Ga-, N-, and mixed-polarity GaN buffer layers have been studied by x-ray diffraction

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(XRD), photoluminescence (PL), atomic force microscope (AFM), scanning electron microscope (SEM), and wet chemical etching techniques.

## 2. Experimental details

GaN buffer layers with different polarity are grown on (0001) sapphire substrates in a Varian Gen II MBE system equipped with a SVT nitrogen plasma-assisted source (model 4.53). Ga and Al are provided by standard effusion cells. In situation control of the growing surface is achieved via reflection of high-energy electron diffraction (RHEED). The sapphire substrates are cleaned by standard degreasing procedures and degassed under ultra-high vacuum at 850°C for 2 hours before introduction into growth chamber. After thermally cleaned, sapphire substrates are nitrated at 200 °C for 30 min, the radio frequency (RF) power is fixed at 400 W. During the growth of Al buffer layers, the RF power is 150 W and the Al flux is varied from $1.33\times10^{-5}$ to $3.20\times10^{-5}$ Pa. The following GaN layers are grown at 720 °C for several hours with the Ga flux at $1.20\times10^{-4}$ Pa. The GaN growth rate is about 0.6 $\mu$m/h. The details of MBE growth process and the polarity selection will be published.[10]

Since the chemical etching behaviour of Ga-polar layer is different from N-polar in alkaline solution, our GaN epilayers are put into NaOH solution to determine its polarity. First, GaN epilayers are dipped into 45% NaOH solution at 100 °C for 10 min. Then, they are rinsed in deionized water. After that, the treated samples are characterized by AFM to confirm their polarities.

The HVPE growth process is carried out in a home-made vertical hot wall quartz reactor. The reactor is divided into two temperature zones, the source zone and the growth zone. The substrates with different polarity GaN buffer grown by MBE are introduced to HVPE system. HCl stream is passed through the Ga boat and reacted with melted Ga to form GaCl. Then the reactant GaCl is transported to growth zone and reacted with $NH_3$ to form GaN. After a thermal cleaning process, the 5sccm HCl is used to perform chemical cleaning for about 10 min. Then the substrate is heated to growth temperature under $NH_3$ ambience. The whole growth process is carried out at 1 atm, the source zone temperature is kept at 850 °C and the growth zone temperature is 1050 °C. All these samples are grown at the same growth conditions.

PL experiments are performed at 20 K and room temperature by using a 266 nm Verdi-6/mira900/THG-266 laser system; the laser beam is focused on the sample with a power of 10 mW. XRD is carried out by a Philips X'pert diffractometer (X'pert-pro MPD) with the Cu K$\alpha_1$ radiation. The surface morphology is characterized by a Veeco AutoProbe CP AFM and observed by a Sirion 200 SEM.

## 3. Results and discussion

The polarity of GaN epilayers grown by MBE can be clarified by RHEED. All samples show streaky (1 × 1) pattern during MBE growth, which indicates the flat surface under two-dimensional growth mode.[11] During the cooling process, for Ga-polar GaN, (2 × 2) RHEED patterns with bright 1/2-order are observed when the substrate temperature drops to 600 °C; for N-polar GaN, (3 × 3) reconstruction is observed at 500 °C, which is the typical reconstruction of N-polarity GaN film; for mixed-polar GaN, (2 × 2) pattern with dim 1/2-order streaks can be seen when the substrate temperature drops to 650 °C, and (6 × 6) patterns appear at 200 °C. At the growth temperature, when the shutters of N and Ga are closed, the RHEED pattern of N-polarity GaN changes from a streak pattern to a spotty pattern, but the RHEED pattern of Ga-polarity GaN remains streak. These phenomena provide a method to clarify the polarity of GaN epilayers by RHEED observations.[11]

Different polarities can also be identified by wet chemical etching and surface examination by AFM. The N-polarity surfaces are changed evidently, and the morphology of mixed-polarity GaN epilayer after etching shows a porous structure. The most likely reason for such a porous structure is that N-polarity surfaces are easily etched in NaOH solutions, while the Ga-polarity surface is etching-resistant. The different etching speeds result in this porous structure. And Ga-polarity surface has no obvious change in the surface morphology before and after etching. Therefore, the surface morphologies of different polarity GaN before and after wet chemical etching are in agreement with the analysis of RHEED.

20 $\mu$m GaN epilayers are grown on MBE-GaN buffer with different polarities by HVPE system. Although all these as-grown samples have smooth surfaces observed by SEM images in Fig.1, the etching characteristic of GaN grown on N-polarity buffer is

different from that of GaN grown on mixed- or Ga-polarity buffer. Figures 1(a), 1(c) and 1(e) show the SEM pictures of as-grown HVPE-GaN samples grown on Ga-, mixed- and N-polar buffers respectively. And Figs.1(b), 1(d) and 1(f) show the pictures of samples grown on Ga-, mixed- and N-polar buffers after etching respectively. First of all, from the SEM pictures of HVPE-GaN samples grown on Ga- and mixed-polarity buffers (as shown in Figs.1(a)–1(d)), we see that their surfaces have almost the same morphologies before and after etching. While, for the samples grown on N-polarity buffer, the surface morphology are changed evidently, as shown from Figs.1(e) and 1(f). At the same time, the HVPE-GaN grown on N-polar buffer has more rough surface than the samples grown on Ga- and mixed-polar buffers.

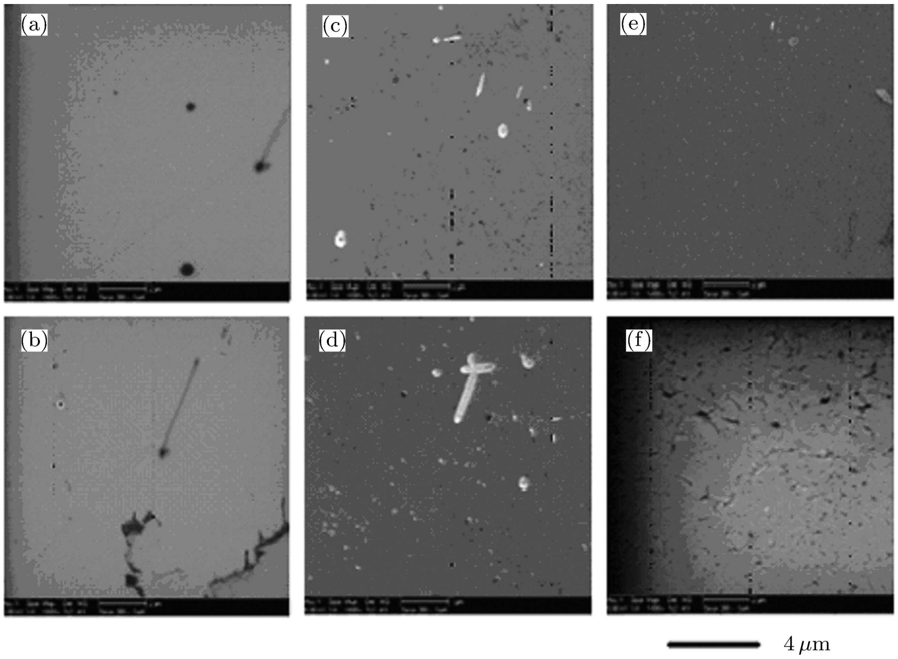

**Fig.1.** SEM images for HVPE-GaN. (a) on Ga-polarity buffer, (b) on Ga-polarity buffer after etching, (c) on mixed-polarity buffer, (d) on mixed-polarity buffer after etching, (e) on N-polarity buffer, (f) on N-polarity buffer after etching.

Another evident difference between the samples grown on N-polarity and mixed- or Ga-polarity is the growth rate of HVPE. In the same growth conditions, the rates of HVPE-GaN grown on N-, mixed-, and Ga-polarity are about 12, 55, and 60 $\mu$m/h respectively. It is inferred that the Ga- and mixed-polarity GaN samples are more stable than the N-polarity GaN, and the N-polarity GaN is easily decomposed at high growth temperature. The surface thermodynamics is proposed to explain the phenomena. It is necessary to notice that the growth is carried out under the high growth temperature. The growth rates of the HVPE-GaN epilayers are determined by the rate of GaN crystallization and re-evaporation on the growth front. In the case of Ga-polar epilayers, the Ga atoms are much stable on the surface since the Ga atoms have three Ga bonds to the N beneath them. In the case of surfaces of N-polar epilayers, the thermal decomposition of GaN may be greatly enhanced in the growth front, since only a single Ga–N bond is exposed to the high growth temperature. Therefore, Ga atoms within the N-polar epilayers are easily evaporated from the surface during growth process, leading to lower growth rate. This is also consistent with the changes of RHEED patterns during the MBE process.[11]

Based on the etching results, the HVPE samples grown on N-polarity buffer layers are easily etched by the NaOH solution to verify their N-polarity. The HVPE samples grown on Ga-polarity buffer layers illustrated uniform, smooth morphology and are resistant to the etchant, confirming their Ga-polarity. However, the samples grown on mixed-polarity buffer layers are hardly etched by etchant and show typical Ga-polarity surfaces. The fact means that the polarity of these samples grown on mixed-polarity buffer layers changes from mixed-polarity layers to Ga-polarity layers. It is well known that the Ga-polarity GaN has stable chemical and thermal properties. Therefore, the possible reason of this polarity change is that the growth rate of Ga-polarity regions is faster than that of N-polarity regions and the thermal decomposition of N-polarity GaN may be greatly enhanced at higher growth temperature, which results in that the area of Ga-polarity regions increases gradually, coalesces and finally forms continuous, flat Ga-polarity surface.

The structural epilayer quality can be indicated by measuring its full width at half maximum (FWHM) of XRD peak. Figure 2 exhibits the XRD rocking curves ($\omega$-scans) of (0002) symmetry planes of 20 $\mu$m HVPE-GaN epilayers grown on different polarity buffer layers. The FWHM of HVPE-GaN grown on N-, mixed-, and Ga-polarity are 15.36, 10.98, and 9.6 arcmin respectively. The rocking curves of symmetric planes are normally responsive to mosaic distortions but insensitive to the pure edge threading dislocations because these planes are undistorted by pure threading dislocations (TDs) and the (0002) plane rocking curves can be broadened by the screw and mixed TDs.[12] The narrow peak of (0002) diffraction suggested that some screws and mixed TDs are reduced. The XRD results suggest that the sample grown on Ga-polar buffer has much better crystalline quality than that grown on N-polar, and the sample grown on N-polar buffer has the worst quality among the three kinds of samples.

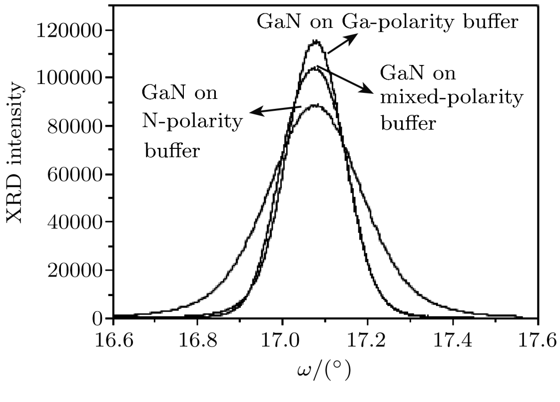

**Fig.2.** XRD patterns for HVPE-GaN epitaxial layers grown on Ga-, mixed- and N-polarity buffer.

Figure 3 shows room temperature PL spectra obtained for HVPE-GaN grown on different polarity buffer. The broad band between 2.0 and 2.4 eV in the PL spectra is known as 'yellow luminescence' (YL), and is commonly detected regardless of the growth technique. It is generally believed that this YL involves electronic states associated with intrinsic defects in the material.[13] To the HVPE-GaN grown on N-polarity buffer, the intensity ratio of the band edge peak ($I_0$) and YL ($I_{\rm Y}$) is about 2.66. For the HVPE-GaN grown on mixed-polarity buffer, $I_0/I_{\rm Y}$ is about 4.73. While, for HVPE-GaN grown on Ga-polarity buffer, any YL is not observed. From these, $I_0/I_{\rm Y}$ is found to be increased with the increase of the Ga-polarity ratio in the buffer layers. Since $I_0/I_{\rm Y}$ is strongly related to the density of screw-type dislocations, and more insensitive to the edge-type dislocations,[14−16] our PL results indicate that the Ga- and/or mixed-polarity GaN buffers are very helpful to the improvement of crystalline quality of HVPE-GaN epilayers.

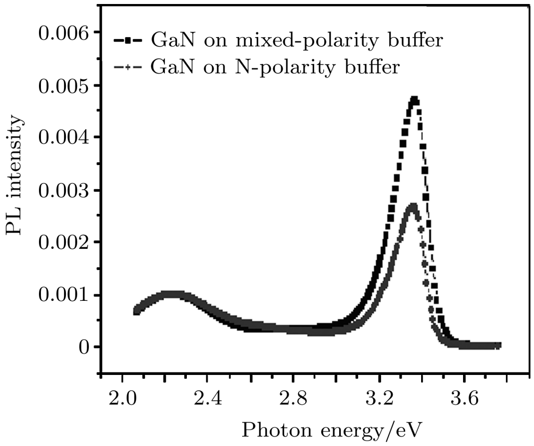

**Fig.3.** Room temperature PL spectra of HVPE-GaN grown on mixed- and N-polarity buffer.

## 4. Conclusions

The properties of GaN grown on the buffer layers with different polarities by hydride vapour phase epitaxy are investigated. The different polarity buffer layers are formed by MBE in different growth conditions. The wet chemical etching, SEM, XRD and PL measurements are carried to characterize the crystalline quality of HVPE-GaN epilayers. The results are indicated that the N-polarity film is unstable against the higher growth temperature and wet chemical etching, while that of GaN-polarity one is stable. The HVPE-GaN grown on Ga-polarity and/or mixed-polarity buffer layer has good structural and optical qualities and is expected to obtain high-quality epilayers for device applications.

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