Research on N-face GaN for solar cells based on MOCVD method

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Abstract—*The N face GaN epilayer was prepared on the C face SiC substrate by MOCVD system, and the basic character of the N face GaN was investegated. A large number of Ga vacancies was formed by a hot phosphoric acid solution etching, which brought a yellow luminescence in the room temperature photoluminescence spectra..*

Keywords-Solar Cell; MOCVD; N-face; GaN; PL

I. INTRODUCTION

How to limit the global temperature increasing is the biggest challenge of the 21st century, one effective solution is to reduce greenhouse gas emission. To achieve this goal alternative energy sources such as power from wind and water, or solar energy should be provided. Among these, only the sun provides 10 000 times more energy than our daily consumption. And the most direct way is converting sunlight into electricity by the solar cells.

The III-nitride materials GaN is the potential material to realize high-efficiency solar cells for the bandgap of its alloy covers form the infrared to the ultraviolet. But owing to inversion asymmetry and nonvanishing piezoelectric tensors in conventional c-directions, the III-nitride materials in their wurtzite structure possess large spontaneous and piezoelectric polarization. The polarization cause a Quantum confinement stark effect (QCSE) commonly existed in the light-emitting diodes (LEDs) and laser diodes (LDs), which effect exerts a substantial influence on the carrier transport and distribution, and degrades the device performance [1]. As for photovoltaic devices, it has also been demonstrated that the internal polarization causes detrimental impact on the collection of photogenerated carriers when the devices were grown on the conventional Ga-face templates along the (0001) orientation [2]. For devices with N-face, could effectively solve the problem by a polarization inversion.

Earlier, N-face GaN was obtained generally by nitriding Al_2O_3 substrate or heavy doping Mg. Sun et al. obtain a N-face GaN by nitriding Al_2O_3 substrate at high temperature [3], while Vennegues et al. found that during the GaN epitaxial growth, heavy Mg doping can promote Mg adsorption atoms to combine with N atoms, destroyed the original stacking sequence, then formed the inversion region in GaN epilayer, thus obtained a N-face GaN [4]. In addition, N-face GaN can also be obtained on the C face SiC. However, the study is rare, only a handful of institutions to do the research. Guan et al. of Southwest Missouri State University carried out the research on N-face GaN on C face SiC substrate, and prepared the GaN/AlGaN/GaN HEMT devices [5]. The rest of the basic research is done by the Santa Barbara, University of California [6]. They use MBE to obtain a better quality of N-face GaN, and succeeded in the preparation of HEMT devices, recently, they put emphasis to the MOCVD technology, and obtained some good results by the SiC substrate with inclination angle.

Of course, there are still some technical difficulties in N-face GaN epitaxial growth, such as the surface is still relatively rough, the crystal quality is still difficult to compare with Ga-face GaN, and the research of grown N-face GaN on C face SiC substrate by MOCVD is very rare. In this paper, we preliminarily study the N-face GaN epitaxial growth.

II. METHOD

The GaN epitaxial layers were grown by low-pressure metal organic chemical vapour deposition (LP-MOCVD) on Si-terminate ($0001/\bar{1}$) n-type 6H-SiC. Trimethyl-gallium (TMGa) and trimethyl-aluminum (TMAl) were used as precursors of Ga and Al, ammonia (NH_3) was used as the nitride source, the n-type dopant was silane (SiH_4).

Three samples of GaN epilayers with were grown on Si-terminal ($0001/\bar{1}$) 6H-SiC substrates (n-type) using

MOCVD in a Thomas Swan 3×2 close-coupled showerhead reactor. The substrates used here were commercial wafers with on-axis direction. Reflectivity data and the wafer temperature were recorded in situ using a LayTec EpiTT monitor with a 633 nm laser. The samples were first ramped to 1100 ℃ for hydrogen (H_2) baking, to remove the surface damage induced by mechanical polish. Then an AlGaN buffer layer was deposited at 1040 ℃: TMGa and TMAl flow kept on 21.99 μmol/min and 4.68 μmol/min, respectively, while NH_3 flow was 3 slm. The whole process was doped with SiH_4 flow of 1.41 nmol/min. Then a 4 μm GaN template was prepared at the same temperature and the ratio of Ⅴ/Ⅲ was 1269. All samples are n-doped with a concentration of 3×10^{18} cm^{-3}.

The crystalline quality of the GaN thin film was estimated by high-resolution X-ray diffraction (XRD) rocking curves using Bede D1 XRD equipment. Photoluminescence (PL) was carried out by a HR-300 CCD spectrometer with He-Cd 325 nm laser. Olympus BX51M optical microscope was taken to examine the surface morphology.

III. RESULTS AND DISCUSSION

A. *Surface morphology*

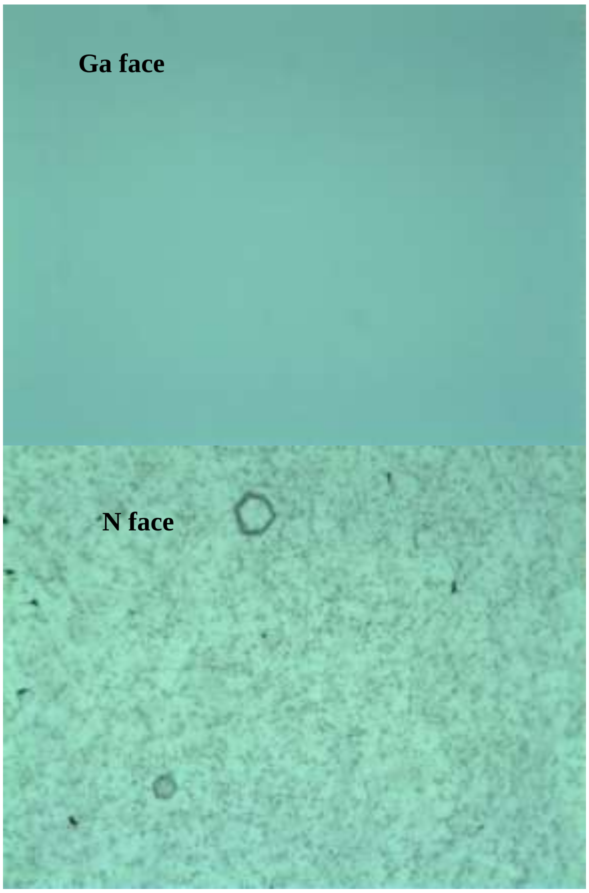

Figure 1. Optical microscopic images of GaN epilayers

Figure 1 shows the optical microscope image of the two samples. The Ga-face GaN obtains a smooth surface, while there are many black spots and hexagonal structures on the N-face GaN surface. For the VK mode is the dominate mode during the N-face GaN growth, there will exist some incomplete fusion areas, forming the black spots. The hexagonal structure is the typical defect structure of N-face GaN, the migration of Ⅲ metal atoms is very weak on the N-face GaN surface [175], which will form some Ga-face GaN inversion zone, and the gowth of Ga-face GaN is much faster than N-face GaN, thus hexagonal structure is observed in the optical microscope image.

B. *Crystal charactor*

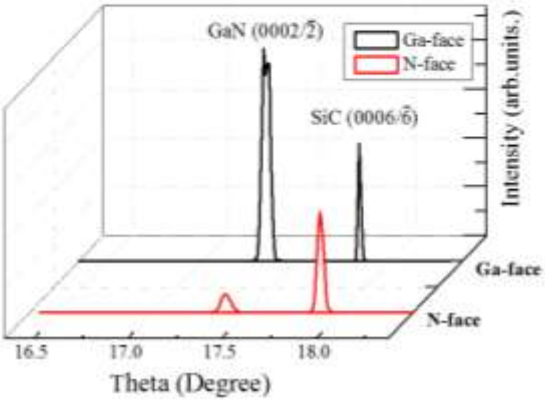

Figure 2. XRD of GaN epilayers

Figure 2 exhibits the XRD spectrum of two samples, we can observe two distinct diffraction peaks, the right diffraction peak around 17.795 ° is the SiC substrate ($0006/\bar{6}$) face, while the diffraction peak of left side around 17.28 ° is derived from GaN ($0002/\bar{2}$) face. Even if the surface is very rough, the FWHM of N-face GaN ($000\bar{2}$) is narrow as 188 arc sec, which indicating that there is less curved defects in the N face GaN epilayers, and has a c-axis preferential orientation. However, the diffraction intensity of N-face GaN is much less than Ga-face GaN, and the FWHM is larger than 150 arc sec of the Ga-face GaN, particularly, the FWHM of ($10\bar{1}\bar{2}$) is up to 1992 arc sec, far more than the 266 arc sec of Ga-face GaN. This indicating that there are a lot of twisted structure existed in N-face GaN epilayer by the VK growth mode, lots of edge and mixed dislocations produced a poor crystal quality.

C. *Optical charator*

Figure 3 shows the room temperature PL spectra of two samples. There is an obvious luminescence band around 2.2 eV which called luminescence band (YL) in the PL spectra of Ga-face GaN, while not observed in the N-face GaN. YL is is thought to be associated with a deep level defect of GaN, which commonly existed in bulk GaN, or in GaN epilayers grown by MOCVD, MBE, HVPE. Neugebauer et al. using first principles calculation to study the origin of YL, their results indicated YL is original from the deep acceptor level of gallium vacancies (V_{Ga}) and its related compounds for the relatively small formation energy [7]. Oila et al. have established that n-GaN usually has 10^{17} ~ 10^{18} cm^{-3} concentration of V_{Ga} by cation annihilate experiments [8]. Armitage pointed out that C related defects in GaN can cause YL [9]. In addition, the dislocation is also thought to be origin of YL [10]. In general, C impurity content of the N-face GaN is usually much higher than Ga-face one [11], C impurity is hard to be GaN the origin of YL. From the point of the results of XRD, the dislocation density of N-face GaN is far greater than the Ga-face one, thus the dislocation is not the origin of YL. So we concluded that YL is likely original from V_{Ga}.

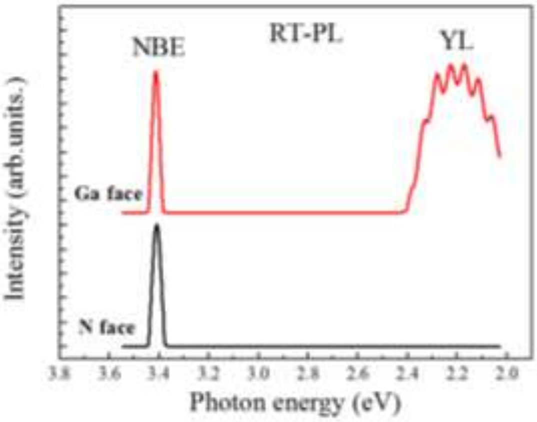

Figure 3. Room temperature PL spectra of GaN epilayers

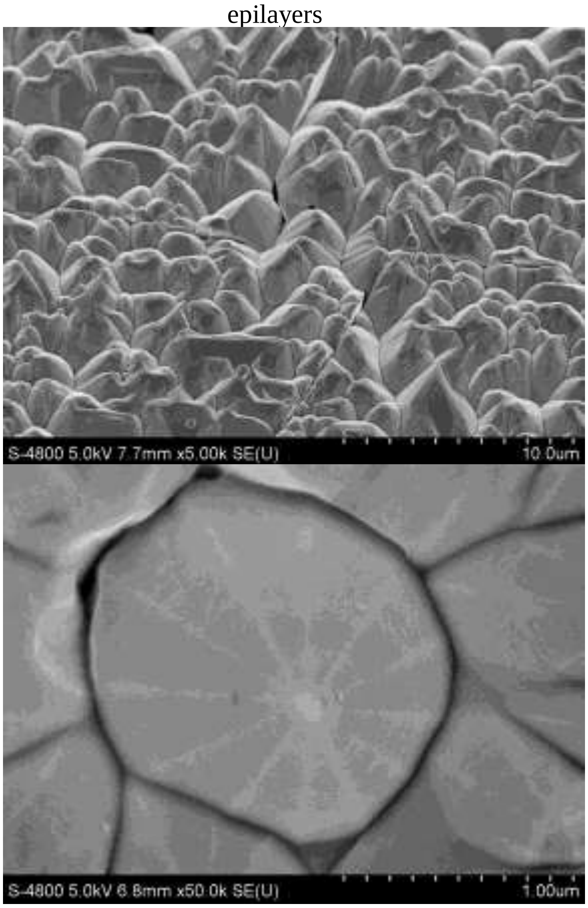

Figure 4. SEM images of surface morphology after etching 10 min

Figure 4 shows the SEM images of surface morphology of N-face GaN after H_3PO_4 etching 10 min. A large number of dodecagonal pyramidal structures are formed. In N-face GaN, there is only one dangling bond point to surface of N atoms, thus the Ga atom is easy to react with acid solution, formed Ga_2O_3, then dissolved in acid solution [12]. H_3PO_4 plays a role of catalyst and the dissolution agent of Ga_2O_3 also. In the process of corrosion, Ga is very easy to corrode, a large number of V_{Ga} will be formed on the surface, and thus, room temperature PL will exhibit YL.

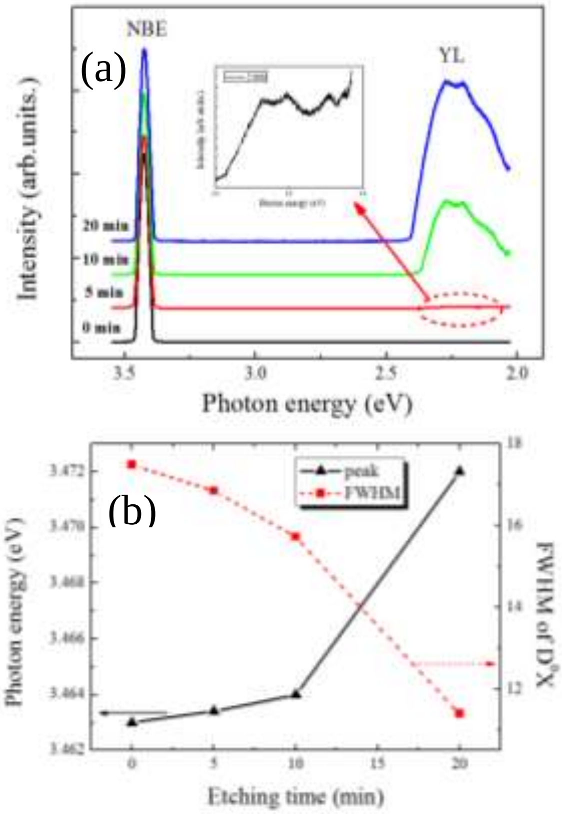

Figure 5. (a): Room temperature PL spectra of samples with different etching time;(b) Variation of D^0X peaks and FWHM of D^0X as a function of Etch time

The room temperature PL spectrum of N-face GaN after H_3PO_4 corrosion is shown in Figure 5 (a). The YL is observed after corrosion, and increasing with corrosion time. Xu et al. also found the same phenomenon; they found that after KOH etching the concentration of V_{Ga} in N-face GaN is as high as 10^{20} cm^{-3}, which can lead to a sharp increase of the YL intensity.

Figure 5(b) shows the Variation of D^0X peaks and FWHM of D^0X as a function of Etching time. As the increasing corrosion time, the peak positions had a blue shift, indicating a certain strain relaxation. According to the SEM images, some dodecagonal pyramidal structures were observed, and with the corrosion time increased, the density of dodecagonal pyramidal structures decreased, thus gave a relaxation of tensile stress in the GaN epilayer. After 20 min of corrosion, the emitting peak of D^0X moved to 3.472 eV, indicating that the strain in the epilayer get complete relaxation. Also, with the increase of corrosion time, the FWHM of D^0X decreased, indicated a better optical quality. In general, corrosion commonly occurred in the fault [13], which is the result of a dislocation selection, the samples after corrosion has less dislocation density, thus giving a narrower FWHM.

IV. CONCLUSION

This paper studied the N-face GaN epitaxial growth and properties. The surface of N-face GaN is rough and existed lots of typical hexagonal structures. The FWHM of ($000\bar{2}$) is small as 188 arc sec, but value of FWHM of ($10\bar{1}\bar{2}$) is large to 1992 arc sec, there are a large number of edge and mix dislocations in the epilayer. But despite the thin film of a large number of Si doping, room temperature PL spectra of N-face GaN was not observed YL. By thermal phosphoric acid solution to corrosion of epilayer, GaN surface produces a large amount of V_{Ga}, correspondingly YL was observed in PL spectrum, which indicated that V_{Ga} is the origin of YL. The GaN exhibited dodecagonal pyramidal after corrosion, the formation of dodecagonal pyramidal gave a relaxation of tensile stress in epilayer, and a completely relaxation was obtained after 20 min corrosion. In addition, the corrosion gave a narrower FWHM of low temperature PL spectrum.

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