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The direct influence of polarity on structural and electro-optical properties of heteroepitaxial GaN

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Abstract

Different polarities of heteroepitaxial GaN layers are believed to stem from different growth conditions. It follows then that the difference in structural and electro-optical properties between Ga- or N-polar samples can be assumed to have the same cause. An unintentionally n-type doped GaN layer has been grown exhibiting both polarities on the same, single two-inch sapphire substrate, which allows for a thorough study of the differences between those two polarities. In such a case the growth conditions are the same and thus the variation of all the properties must come from the sample's polarity or its influence on the growth process.

Transmission electron microscopy and etching techniques confirm the large variation in morphology across the surface of the sample to be the result of the polarity difference. Wet chemical etching in a mixture of phosphoric and sulfuric acids, as well as photo-electrochemical etching in aqueous KOH solution, reveal very different defect structures for the two polarities. Hall and PL measurements show a large discrepancy in electro-optical properties suggesting preferential impurity incorporation in the N-polar GaN, which is also confirmed by results of SIMS measurements.

1. Introduction

The application of GaN in blue-light-emitting devices has driven and still drives the research into both material properties and growth methods. The most common of the growth methods to date is metal–organic chemical vapour deposition (MOCVD), most frequently used for heteroepitaxial growth on sapphire substrates. GaN layers of both Ga and N polarity ((0001)

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and $(000\bar{1})$, respectively) can be grown by this method. One of the most obvious features of the two polarities of GaN is the dissimilar morphologies of the Ga- and N-polar samples, accompanied by remarkable differences between their resistances to chemical etching [1, 2]. The origin of this phenomenon can be traced back to the surface reconstructions of the material during growth, which are completely different for the two polarities, as shown by Smith *et al* [3–5]. The distinction between the two different polarities can be established by convergent beam electron diffraction (CBED) [2, 6], ion channelling [7], and coaxial impact collision ion scattering spectroscopy (CAICISS) [8].

The initial nitridation of the sapphire substrate and buffer layer growth have been identified as the sources of differences in polarity of the GaN films [9–11]. Variations in optical properties and impurity incorporation also originate from the difference in polarity of GaN layers [12, 13].

However, all of these reports describe two or more samples that were grown by different processes with unequal growth parameters, after which the relevant sample properties were measured. The variations in the growth processes give rise to uncertainty about attributing differences of sample properties to polarity or merely to changes of growth conditions. In this paper a heteroepitaxial GaN layer is presented which exhibits both polarities. The sample consists of MOCVD grown GaN on a sapphire substrate with a very thin buffer layer. Such a structure allowed for the creation of both polarities in one process, which ensured the identicality of all growth parameters. Therefore, all the differences in optical or structural properties must be the result of the polarities and not of dissimilar growth conditions.

2. Experiment

The GaN epilayer was grown by MOCVD using a horizontal reactor. Trimethylgallium (TMG) and ammonia (NH_3) were used as precursors with H_2 as the carrier gas. A two-inch polished (0001) sapphire wafer with a misorientation within $\pm 0.01^\circ$ was used as a substrate. The substrate was first cleaned in organic solvents, etched in aqua regia, rinsed with deionized water, and blown dry with filtered N_2 gas. It was then placed on a SiC-coated susceptor that was RF heated and which contains a rotating disc to ensure optimum uniformity during the growth process. The rotation of the susceptor disc is driven by a flow of hydrogen gas. The discharge of this flow causes a small temperature decrease on the growing surface from the centre to its periphery. The first growth step consisted of nitridation of the substrate surface, carried out in a NH_3/N_2 gas stream at gradually changing temperature between 1100 and 950 °C. Then the temperature was lowered to 525 °C and a $\sim$5 nm GaN buffer was deposited. This thickness of the nucleation layer was found to provide the boundary between Ga- and N-polar growth environments. Finally, the main 2.75 μm GaN layer was grown at 1170 °C. Differential initial optical contrast (DIC) microscopy confirmed the existence of areas with two distinct types of surface morphology. Hall measurements were performed at room temperature on pieces of both polarities in the van der Pauw configuration. Photoluminescence (PL) spectra were measured for both polarities at 4 K using a 100 cm long SPEX 1704 monochromator and ISA CCD camera for detection and HeCd laser for excitation.

SIMS analysis has been applied to verify the amounts of foreign atoms in pieces of both polarities. In particular, the concentrations of O, C, and Si has been assessed.

Two etching methods have been used for defect visualization and analysis: photo-enhanced chemical (PEC) etching in a weak KOH solution and wet chemical etching in a mixture of concentrated H_2SO_4 and H_3PO_4, referred to further as HH solution.

The main characteristic of PEC etching is the fact that only defect-free material is etched away while all structural flaws that induce carrier recombination are left untouched. The carriers generated by the UV source are separated due to band bending at the interface of

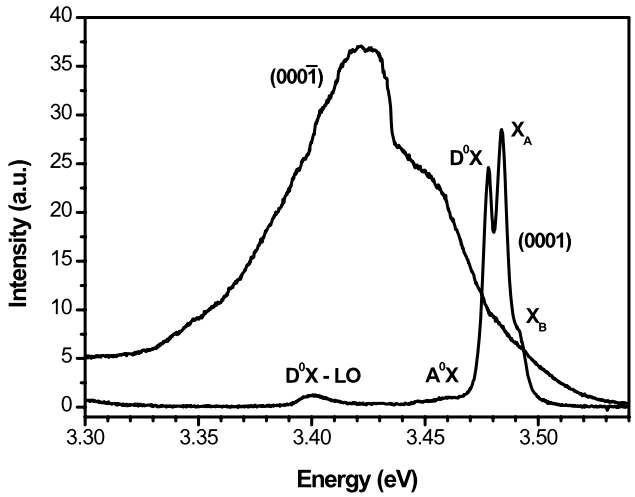

Figure 1. PL spectra for both (0001) and (000$\bar{1}$) growth directions.

the GaN and KOH solution; electrons are carried away while holes take part in a dissolution process described by Nowak *et al* [14].

Thus, any defects such as dislocations, stacking faults, and inversion domain (ID) boundaries [15], which are sites of recombination, will not be etched due to lack of holes. The exact nature and details of the PEC method can be found elsewhere [16]. Samples of both polarities have been subjected to 20 min etching in 0.004 M KOH solution in H_2O illuminated by a xenon lamp with a power density of 250 mW cm^{-2}. Etching in HH solution, which is a classical type of wet chemical etching, is designed to utilize the internal energy of structural defects and thus open them up for etching. The combination of these two methods gives very detailed information about the defect composition in any given sample.

3. Results and discussion

The as-grown sample clearly displayed two different kinds of surface morphology. DIC microscopy revealed that hexagonal pyramids populate the N-polar part, taking up roughly 60% of the surface, and concentrate in the centre of sample. The diameter of the pyramids in this section varied from 10 to 30 μm in diameter. Near the edges the surface remained flat with RMS roughness of $\sim$0.4 nm on a 1 μm square, as confirmed by AFM measurements. The rough and smooth areas were separated by a $\sim$2 mm transition region where the pyramids were gradually spaced further apart until they were completely replaced by a smooth surface.

Hall measurements showed an average resistivity of 246 mΩ cm for the Ga-polar area and 3 mΩ cm for the N-polar area. The free carrier concentration was 5.2×10^{17} and 1.1×10^{20} cm^{-3} for Ga-polar and N-polar pieces, respectively. The mobilities of the carriers were of comparable magnitudes for the two polarities, being 48.6 and 20.4 cm^2 V^{-1} s^{-1} respectively. The actual results for N-polar piece have to be taken as approximate values due to thickness variations. Hall samples are prepared in the Van der Pauw configuration with a distance between contacts of 5 mm and a middle area of around 1 mm^2 in size, which is large compared to the size of the pyramids.

PL results, as seen in figure 1, clearly show different optical properties for the two polarities. Ga-polar GaN exhibits a well-defined spectrum showing a donor bound exciton

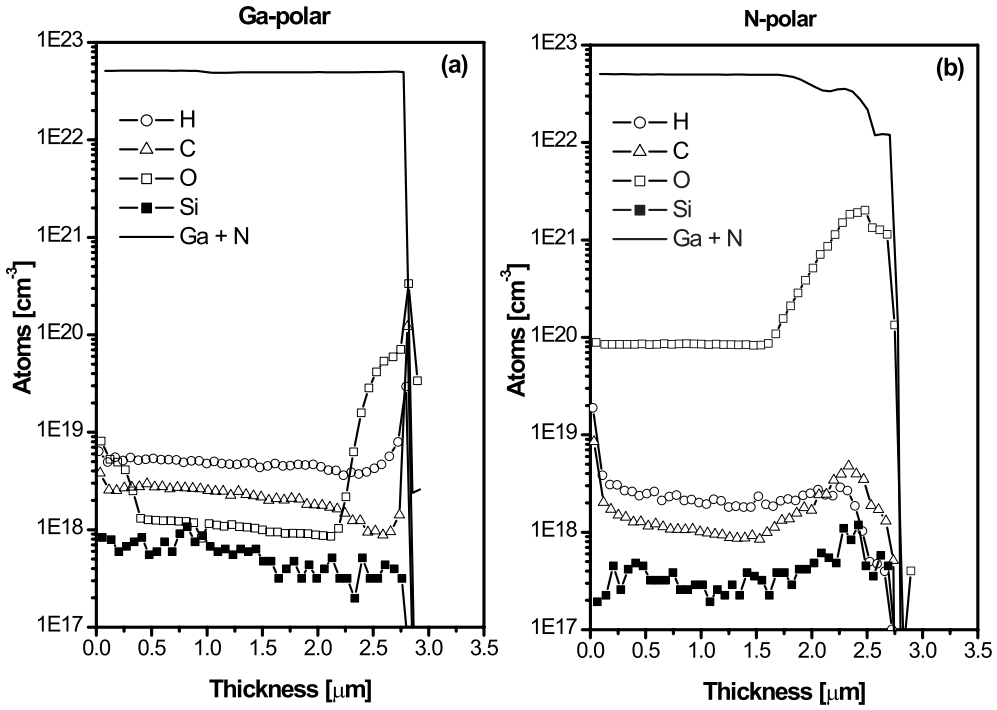

Figure 2. SIMS results for both Ga-polar (a) and N-polar (b) areas.

(D^0X) peak at 3.478 eV with FWHM of 4.3 meV, which indicates a good, but not outstanding optical quality. The free exciton A (X_A) at 3.484 eV and the free exciton B (X_B) at 3.492 eV are also clearly visible, supporting the view of the quality of the material. The less prominent peak at 3.455 eV is attributed to recombination of the neutral acceptor and bound exciton (A^0X). On the other hand, a PL spectrum from the N-polar GaN is completely featureless, showing an extremely broad peak centred on 3.42 eV with high overall intensity. The PL luminescence is very inhomogeneous for the N-polar area, mainly due to fact that the surface can modulate the emitted radiation by interference. The variation in the PL spectrum for the Ga-polar piece across the surface is only as regards the intensity ratio between D^0X and X_A peaks and their respective FWHMs.

SIMS analysis performed on both kinds of polarity with respect to O, C, Si, and H is shown in figures 2(a) and (b). The difference between the Ga and N profiles near the interface at the depth of about 3 μm stems from the fact that the surface is not smooth. The ion beam does not strike the interface at a single moment but uncovers it in a more gradual manner. The SIMS profile of the N-polar part exhibits much higher concentration of O atoms than the Ga-polar part, while the C- and H-atom concentrations are slightly lower.

Figure 3 shows a SEM image of a Ga-polar piece after PEC etching. The 'whisker' structure is very regular and predictable for that kind of sample. Every whisker represents a dislocation and is terminated at the surface of the sample. Some whiskers join together and may annihilate before reaching the surface. Figure 4 shows an SEM image of N-polar, PEC-etched (a) and HH-etched pieces (b). The first of these shows that the pyramids have been etched away in a peculiar fashion. All pyramids have a single ID in the centre, which has been etched away more quickly than the surrounding material. PEC etching is very sensitive

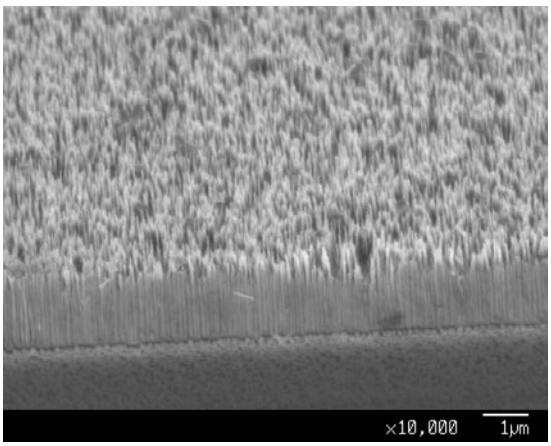

Figure 3. A SEM image of a PEC-etched Ga-polar area.

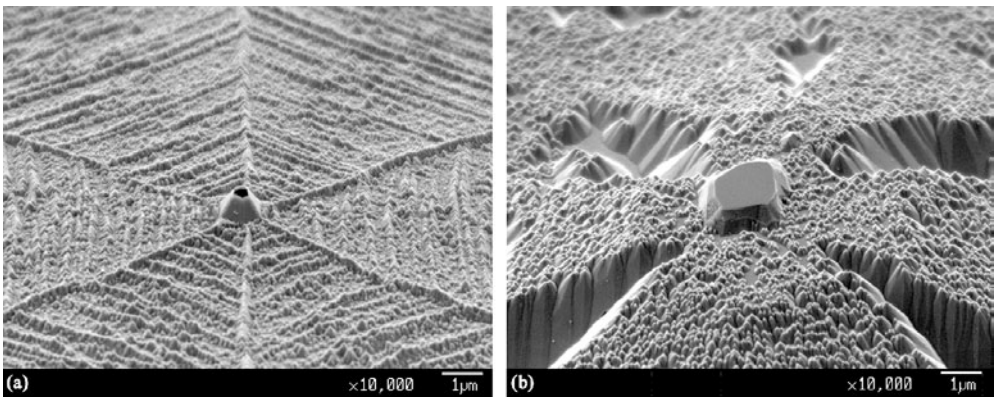

Figure 4. SEM images of an N-polar area after PEC etching (a) and HH etching (b).

to the carrier concentration; material with a higher carrier concentration etches more slowly, and at values of about 10^{20} cm^{-3} etching stops completely. Intensifying the power of the UV radiation or increasing the KOH concentration may raise this limit, but not significantly. Thus, etched IDs lead us to believe that the carrier concentration inside is much lower than outside, which agrees with the results from macroscopic Hall measurements [17, 18].

The edges of all pyramids remained less etched than the rest of surrounding material, which again suggests that they are recombinative sites. This is due to easier incorporation of impurities such as Si or O [19, 20] and also due to the existence of stacking faults. Another feature is formed by the ridges perpendicular to lines bisecting the angle between pyramid edges, which also etches less than the surrounding material. These ridges are not visible on the as-grown sample. When the Ga-polar ID grows within an N-polar matrix, all impurities that are incorporated into the surface close to it are swept away along the step flow direction. Their further advance is stopped on a macrostep where they are included in ridge-like structures and serve as recombination sites. The nature and origin of the macrosteps is as yet unknown. The second part of the same picture shows a similar pyramid etched in HH solution. The mechanism of etching is based on releasing stored energy of structural defects and releasing it in the process of etching. In this case it can be seen that edges of pyramids have etched

much more than the surrounding material while the ID in the middle remained unetched. This result is complementary to the one obtained from PEC etching. Incorporated impurities and structural defects concentrate in the pyramid edges.

4. Summary

It is certain that the buffer layer is crucial for the growth of GaN on sapphire and is the selecting factor for growth of Ga- or N-polar samples. Thus, by careful control of the buffer layer's thickness we can obtain either of the two polarities.

All experimental results show very large differences in carrier concentration, resistivity, and impurity incorporation between these two polarities. It has also been demonstrated that preferential incorporation of oxygen in the N-polar part is the reason for the peculiar effect of PEC etching on large IDs. The fact that growth of N-polar and Ga-polar material occurred in the same process guarantees that polarity is the factor responsible for those differences.

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