Growth of Ga-face and N-face GaN films using ZnO Substrates

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Abstract

We have used plasma molecular beam epitaxy on (0 0 0 1) and (0 0 0 $\bar{1}$) ZnO substrates to induce epitaxial growth of GaN of a known polarity. The polarity of the ZnO substrates can be easily and unambiguously determined by measuring the sign of the piezoelectric coefficient. If we assume that N-face GaN grows on O face ZnO and that Ga-face GaN grows on Zn face ZnO, then we can study the growth of both Ga and N faces. The most striking difference is the doping behavior of the two faces. Growth on the Ga-face is characterized by a higher carrier concentration and a lower threshold for Ga droplet formation.

1. Introduction

Surprisingly little is known about the polarity of GaN epitaxial films. GaN has the wurtzite structure, and typically grows with its hexagonal basal plane parallel to the substrate. The orientation normal to the substrate is either $\langle 0 \ 0 \ 0 \ 1 \rangle$ or $\langle 0 \ 0 \ 0 \ \bar{1} \rangle$. The two orientations are not equivalent; the Ga-N bonds along the hexagonal axis are all oriented in one direction, resulting in faces that are either nitrogen terminated or gallium terminated. The two faces, along with the terminology conventions used in this article, are illustrated in Figure 1. The surface chemistry, epitaxial growth, doping, and defect structure on the two faces should be quite distinct. The GaN research community has by and large neglected the distinction between these two orientations, both because it is hard to measure, and because most growth technechniques should select one or the other orientation. One exception is the work of Sasaki and Matsuoka, [1] who studied the growth of GaN on the carbon and silicon terminated faces of SiC. Using x-ray photoemision spectroscopy to measure the oxidation of Ga atoms on the surface, they determined that Ga-face GaN was grown on C-face SiC, and that N-face GaN was grown on Si-face SiC. It is almost a surprise, given the differences between the two surfaces, that GaN of reasonable quality could even be grown with both polarities. Recently, the polarity identification problem has attracted the attention of electron microscopists [2] [3] [4], but there have been conflicting results.

ZnO has the same crystal structure as GaN, and a reasonably close lattice match. It is therefore expected that a GaN film grown epitaxially on a ZnO substrate should have the same polarity. Because both materials are reasonably polar, electrostatic considerations indicate that N-face GaN should grow on O-face ZnO and Ga-face GaN should grow on Zn-face ZnO. The polarity of a substrate can be measured quite easily and unambiguously by measuring the sign of the piezoelectric coefficient, or by measuring etch rates in HCl or H_2NO_3. [5]

Although ZnO has been touted as a promising substrate for GaN and InGaN growth, [5] it has had a history of disappointing results. [6] Because ZnO is attacked at high temperatures in reducing atmospheres, growth by MOVPE and similar techniques must be done under sub-optimum conditions. The results of growth by MBE [7] have been more promising, but due to the difficulty of chemically preparing both Zn-face and O-face surfaces, previous studies of growth on ZnO have only considered a single type of substrate. Studies of growth on ZnO have further been limited by the difficulty of growing substrate-quality single crystals.

In this paper, we will discuss the simultaneous MBE growth of GaN on both O-face and Zn-face (0 0 0 1) ZnO sustrates, and the differing properties of the films grown on them. The most striking differences are that the films grown on the Zn-face ZnO are much more conductive and have a lower threshold for Ga droplet formation. We use these observations to draw some general conclusions about the orientations of GaN growth.

2. Experimental Details and Growth

2.1. Substrate Preparation

The ZnO samples used for this study were Li doped samples grown at Bell Laboratories by E. D. Kolb by the hydrothermal technique. [8] [9] A 5mm thick, triangular crystal with 1.7cm sides was sawed along the (0 0 0 1) planes and mechanically polished by Keon Optics, Inc. [a] . The resulting surface finish was mostly smooth on both faces, however, some deep scratches from the initial stages of the polish could not be removed. The substrates were then rinsed in acetone and methanol. To obtain the two different faces, a substrate was cleaved, and one of the resulting pieces was flipped over. The two pieces were then soldered, side-by-side, onto the molybdenum heater block with indium.

The substrate polarity was measured after film growth, to avoid sample mix-up. The sign of the piezoelectric coefficient was measured by tapping an oscilloscope probe on the substrate surface, and watching for the direction of the voltage deflection on an oscilloscope. The etch rate of the back side in HCl was observed to double-check the assignment. [5]

The substrate was outgassed at 700°C in vacuum before growth. Even at 600°C, Zn coming off the substrate was observable on the quadrupole mass spectrometer in the vacuum system. The surface thus prepared was smooth, with relatively streaky reflection high-energy electron diffraction (RHEED) patterns, shown in figure 2. The RHEED pattern from the O-face substrate was quite streaky, while the pattern from the Zn face substrate was rather fuzzy.

2.2. MBE Growth

GaN was grown using Ga rich conditions similar to those we have previously reported. [10] An RF-coupled nitrogen plasma was used to obtain active nitrogen for MBE growth. The Ga flux was set to obtain a growth rate of 0.2μm/hr on sapphire substrates. No nitridation period was used before starting GaN growth. Some cross-contamination of our Ga and Mg effusion cells resulted in moderately high Mg doping levels in some of the growths. The substrate temperature was 600°C for all of the growths reported here.

At the start of growth, the RHEED streaks became diminished in intensity, but did not disappear, indicating that the growth was initially coherent. The pattern for the Zn-face substrate, which had been fuzzy, then became much sharper and more streaky. The pattern for the O-face substrate, which had been sharp, became spotty, indicating some facetting and 3-dimensional island growth. The RHEED patterns for the two substrate at the end of a 3-hr growth are shown in figure 3.

The first striking difference between growth on the two faces was visible immediately upon observing the films in the growth chamber. The Zn-face substrate appeared black to the naked eye. Upon microscopic examination of this sample after removal from the MBE system, it was clear that gallium droplets, a few microns in diameter had formed on the Zn-face substrate, while no droplets at all were observed on the O-face substrate. There was also considerable inhomogeneity in all the films on ZnO, with areas that looked reacted or precipitated. The conductivity of the films were measured with an ohmmeter. The two-point resistivity ranged between 500Ω and 1kΩ for the films on Zn-face ZnO, and between 3kΩ and 15kΩ for the films on O-face ZnO.

2.3. Characterization

The crystalline structure of the films was characterized by x-ray diffraction using a 4-circle diffractometer with monochromatized Cu Kα radiation. In addition to the expected wurtzite peaks in the θ-2θ scans, a number of impurity peaks were observed. One set of these diffraction peaks, shown in figure 4, can be identified as Ga_2ZnO_4, an oxide with the spinel structure. Evidently, ZnO undergoes a significant reaction with Ga at the growth temperatures used. Other peaks with comparable intensities are unidentified. There are no significant differences in the impurity peaks between Zn-face and O-face samples. Our diffractometer did not resolve the 0.18° splitting between the (0 0 2) wurtzite peaks of GaN and ZnO.

The optical properties of the films on ZnO were measured using photoluminescence (PL). A He-Cd laser was used as an excitation source; the emitted light was dispersed by a 0.5 m monochromator and detected by a CCD camera. As seen in figure 5, films from one run showed a striking difference between growth on the Zn and O-faces of ZnO. The 5K luminescence from the GaN grown on the Zn-face exhibited a broad peak centered at 380 nm, while the sample grown on the O-face substrate had a broad luminescence peak centered at 425 nm. Samples from a

second growth run had weaker luminescence overall, and comparisons between the two growth faces were difficult to make. In many spots on the samples, a sharp peak at 370nm was observed and assigned to bandgap recombination in the ZnO substrate.

Samples grown on Zn and O-face substrates from one growth run were analyzed for Mg, Zn and O using secondary ion mass spectroscopy (SIMS) by C. Evans &Assoc. [b] . The films were swabbed with methanol to remove Ga droplets prior to analysis. The Mg doping was quantitated at approximately 4×10^{19} cm^{-3} for both samples. O was present at a level of 3×10^{19} cm^{-3} in the film grown on the oxygen face ZnO, and at 2×10^{18} cm^{-3} on the Zn-face substrate. Zn was near the detection limit in GaN, below 10^{18} cm^{-3}. Pinholes and cracks in the GaN film could account for the observed concentrations of Zn.

To check whether the presence of Ga droplets on one type of sample was associated with GaN growth rate differences, we measured the thickness of films from one run using Rutherford backscattering spectroscopy (RBS) with 2.8 MeV He ions. Ga droplets were removed before the measurement. The GaN thicknesses were identical on the two ZnO faces to within 2%. There was also evidence of interface reaction.

3. Discussion

3.1. Droplets

Ga droplet formation during GaN growth is widely observed, and is hardly surprising, given the thermodynamics of the Ga-N system. MBE growth is typically done under temperature and nitrogen pressures where GaN is not thermodynamically stable against decomposition to nitrogen molecules and gallium metal. However, due to very slow decomposition rates, it is possible to use active nitrogen so that the formation rate of GaN exceeds the decomposition rate. [11] A droplet, once formed, will grow at a rate that depends on adatom flux and surface mobility. Since Ga adatom mobility on a Ga terminated surface should be much higher than on a N-terminated or faceted surface, Ga droplets should grow much more rapidly on the Ga-face of GaN. This is consistent with our observations, assuming that Ga-face GaN grows on Zn-face ZnO.

It is interesting that the growth rate is independent of the substrate polarity. It suggests that under the conditions used for these growths, both Ga- and N- face surfaces are saturated with Ga and thus the growth rate is limited by the active nitrogen arrival rate. But what happens to the excess Ga if it doesn't go into droplets? Other mechanisms for the removal of Ga atoms include re-evaporation, sputtering or scrubbing by background hydrogen.

3.2. Impurities and Defects

It is very likely that impurity incorporation and defect formation can be strongly affected by the polarity of the growth surface. The defects most commonly cited as likely causes for the n-type native carriers in GaN are the nitrogen vacancy and the oxygen donor. In the absence of data, one would expect that oxygen would most easily be incorporated during growth of a Ga-face, and that nitrogen vacancies might most easily occur during growth of a N-face. With regard to oxygen incorporation, our data indicates the opposite. Oxygen, in the form of H_2O and CO, is present in even the cleanest vacuum system, and if the sticking coefficients are near unity, their incorporation will occur at high levels. In our case, it appears that high incorporation of O in N-face GaN films results in compensation of the Mg dopant and higher resistivity. This interpretation is consistent with the shift of the luminescence peak observed in the PL data. It is interesting to note that the 425 nm peak we observe for N-face GaN was observed for Ga-face GaN by Sasaki and Matsuoka, [1] who studied undoped films. The details of the photoluminescence spectra may have more to do with impurities and their incorporation than on the growth face directly.

4. Conclusions

Despite its good lattice match and ideal structure, ZnO is not a promising substrate for commercial applications of epitaxial GaN. It is hard to obtain, it reacts with Ga, and is not sufficiently stable at high temperatures. However, careful studies of growth on ZnO substrates can yield scientifically interesting information. Now that we have characterized growth on the two faces, we can identify the two faces and thereby learn to control and exploit them. Our preliminary results in this direction suggest that the establishment of polar growth by AlN buffer layers is a crucial step in the growth of high quality films.

Acknowledgments

Footnotes

[a] Keon Optics, 30 J. F. Kennedy Drive, Stony Point NY 10980.

[b] S. Mitha, C. Huang, Charles Evans & Associates, 301 Chesapeake Drive, Redwood City CA 94063

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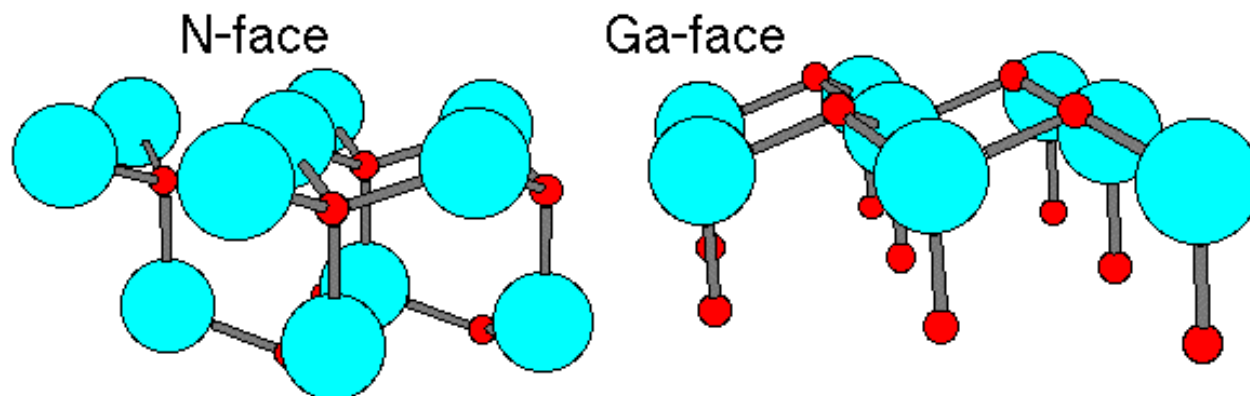[11] N. Newman, J. Ross, M. Rubin , *Appl. Phys. Lett. 62*, 1242-1244 (1993).
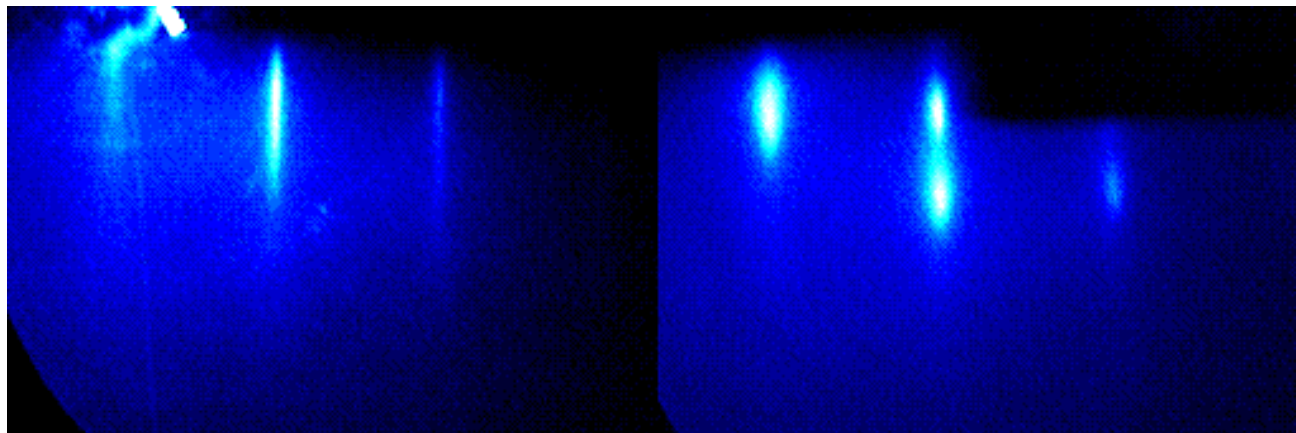
Figure 1. Ga and N (0 0 0 1) faces of GaN.

Figure 2. Reflection high energy electron diffraction (RHEED) patterns of ZnO before growth of GaN. The plane of the substrate is at top. On the left is the O face, and on the right is the Zn face.
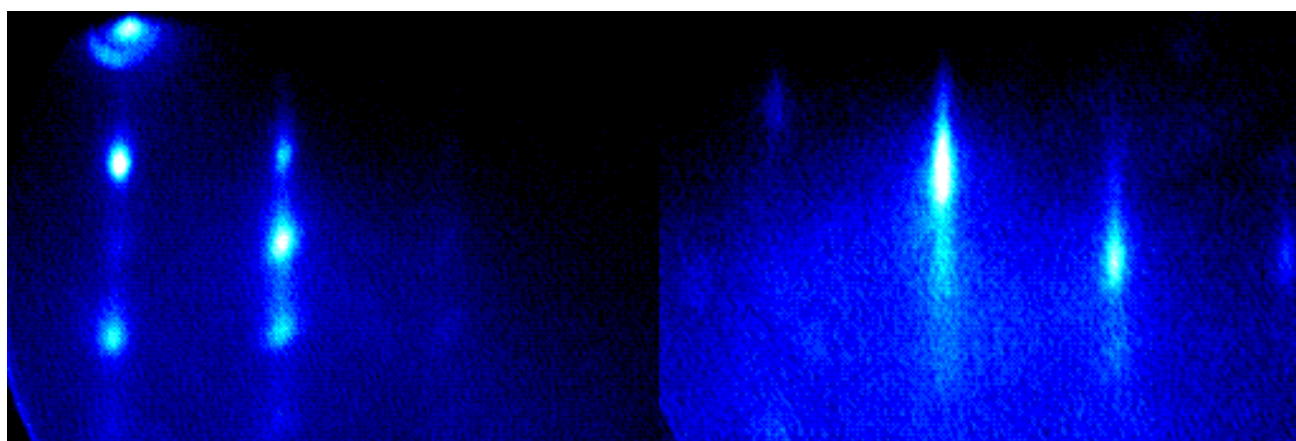

Figure 3. RHEED patterns of a 0.5μm thick GaN film grown on ZnO substrates. On the left is the film grown on the O face, and on the right is the film grown on the Zn face.
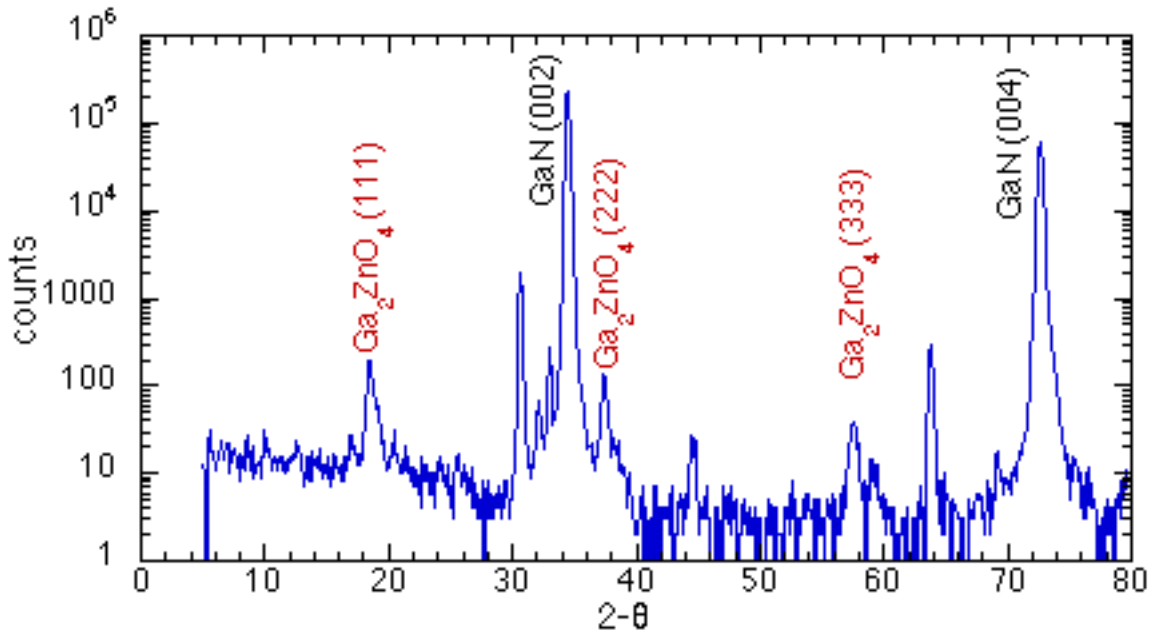
Figure 4. θ-2θ x-ray diffraction scan for a 0.5 μm thick GaN film on ZnO. This sample is grown on the O face of the ZnO; no consistent differences between the two faces were noted. The GaN and ZnO peaks are not resolved.
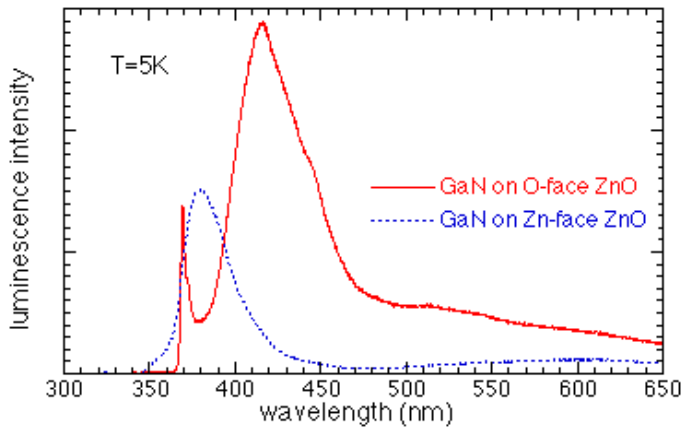

Figure 5. Comparison of the photoluminescence (PL) spectra, at 5K, of GaN films grown on Zn-face ZnO and O-face ZnO in the same growth run.

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