Heteroepitaxial Growth of GaN on ZnO by MOVPE

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In order to establish the growth of GaN on ZnO, we studied different procedures to overcome the detrimental influence of normal GaN growth conditions on the naked ZnO surface. With a two-layer process, only poor GaN quality could be obtained. This could be remarkably improved by optimizing the growth procedure and implementing additional annealing steps. However, the finally obtained material quality is still limited due to the maximum applicable growth temperature about 150°C below the best conditions for GaN on other substrates.

1. Introduction

In recent years, the growth of GaN–ZnO heterostructures has attracted much attention due to the similar material properties of GaN (III–V type) and ZnO (II–VI type), especially a very small lattice mismatch of approximately 1.9 % of the a lattice constant and almost similar thermal expansion coefficients. This may be in particular helpful to realize a pn-junction in planar or coaxial form [1] for nano-photonics and nano-electronics applications because of the much better p-doping properties of GaN as compared to ZnO. The heterostructure of GaN on ZnO could be also used as a template for the Hydride Vapor Phase Epitaxy (HVPE) growth of a free standing GaN bulk layer by utilizing the ZnO layer as a separation layer [2]. There are several reports on heteroepitaxial growth of ZnO on GaN [3], but few are found for GaN on ZnO growth. Although some groups have successfully grown GaN on ZnO by molecular beam epitaxy (MBE) [4] or pulsed laser deposition (PLD) [5, 6] techniques, only a few groups have reported the growth of GaN on ZnO by metalorganic vapour phase epitaxy (MOVPE), and the material quality is still not on par with the device level [7, 8]. There are, basically, two major problems in the MOVPE growth of GaN on ZnO, namely, the instability of ZnO itself at high temperatures and the decomposition of ZnO after exposure to NH_3 and H_2 at temperatures in excess of 650°C. In this study, we present some approaches to cope with the above mentioned problems for growing GaN epitaxial layers on ZnO in a low pressure (LP) MOVPE system. We report here the physical and optical properties of the GaN layers grown under different growth conditions. Finally, we have determined a quite effective growth process to deal with the inherent detrimental properties of ZnO when subjected to a MOVPE system.

2. Experimental

Undoped layers of GaN were grown on c-plane ZnO layers in an AIXTRON AIX 200 RF LP-MOVPE system by using trimethylgallium (TMGa) and NH_3 as precursors. Both,

H_2 and N_2 gases were used as carrier gas and the ambient gas was H_2+N_2 and N_2, respectively. All growth temperatures indicated in this report are thermocouple read-outs in the susceptor main body. The ZnO layers used in this study were grown by pulsed laser deposition (PLD), and chemical vapor deposition (CVD) techniques. In PLD technique, undoped ZnO thin films were grown on 2-inch diameter a-plane sapphire substrates using a KrF excimer laser with 248 nm wavelength. The source target was pressed and sintered at 1150°C from commercial 5N5 ZnO powder (Alfa Aesar). A laterally homogeneous film thickness of about 600 nm on the 2-inch substrate was achieved by an offset distance between substrate center and direction of plasma plume propagation, as demonstrated in [9]. The growth temperature was about 650°C and the oxygen partial pressure during growth was 0.01 mbar. In CVD technique, a buffer layer of Zn about 150 nm thick, using zinc acetate (Zn[Ac]2) as a source, was grown on a MOVPE grown GaN template at a temperature between 300°C and 400°C followed by annealing for 1 hour at 800°C to 900°C. Then a 1 to 3 μm thick bulk ZnO layer was grown, using zinc powder (Alpha Aesar, 5N5) as a source, in an O/Ar gas atmosphere at a temperature between 700°C and 820°C. Scanning electron microscopy (SEM), and high resolution x-ray diffraction (HRXRD) measurements (with 0.6/0.2 mm slits) were carried out to observe the physical properties of GaN and ZnO layers. The optical properties were investigated by low temperature (20 K) photoluminescence (PL) measurements.

3. Results and Discussions

In preliminary studies, we observed the malignant effect of H_2 and NH_3 with a rise in temperature on the ZnO layer. We carried out several experiments of the growth of a single layer of GaN of about 500 nm thickness on a ZnO layer at different temperatures by using H_2 as a carrier gas. The detrimental effect of H_2 and NH_3 was observed at the growth temperature of 675°C and above. In optical microscopy, a number of cracks and many bubble like structures were distinctly visible. The SEM analysis showed a very random 3D growth of GaN. On the cross sectional view, a void between the GaN and ZnO layers was clearly visible at many parts of the sample. At a temperature above 600°C, the dissociation of NH_3 takes place rapidly and contributes more H_2. The etching of ZnO by these H_2 molecules at the onset of the growth process becomes very aggressive at temperatures above 675°C. However, the cross sectional observation of SEM shows that the interfaces between the GaN and ZnO layers were quite smooth in the samples grown at 600°C and below. Unfortunately, there were no indications of GaN related peaks in HRXRD and low temperature PL measurements in all samples grown below 700°C.

In the following experiments we implemented a two-layer growth process by using either H_2 or N_2 as a carrier gas. An initial buffer layer of GaN with varying thickness was deposited at 550°C. The buffer layer should be thick enough to closely cover the ZnO layer to protect it from etching by H_2 during the high temperature of the final layer growth. The thickness also depends upon the surface quality of the ZnO layer. Then the buffer layer was annealed in NH_3 or N_2 ambient up to the maximum corresponding temperature of 950°C or 1050°C. Since the edges of the samples are normally not fully covered by the buffer layer, NH_3 etches the ZnO very rapidly through these edges at higher annealing temperature. A final GaN layer of about 1µm thickness was grown at 1000°C and 950°C in case of N_2 and H_2 as a carrier gas, respectively. The precursor flow rates of both layers were kept constant. In SEM analysis, we observed a GaN surface containing densely arranged hexagonal crystallites with different sizes oriented in random directions (Fig. 1).

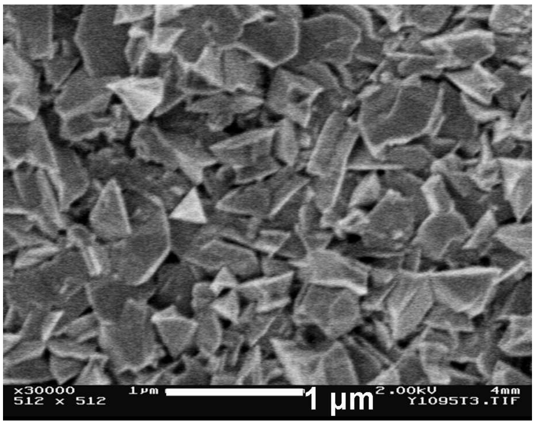

Fig. 1: SEM image illustrating a large number of crystallites of GaN having random size grown by using a two layer growth process.

This was even more pronounced in case of N_2 as carrier gas. The comparatively larger size of the crystallites in the samples grown with H_2 as a carrier gas indicates the stronger occurrences of coalescence of small 3D islands during the final layer growth of GaN. It shows that H_2 helps to enhance the lateral growth of GaN. Low temperature PL measurements show a broad GaN peak having very low intensity. There is always a high probability of etching ZnO at any instance either from the edges of the sample or down through the trenches of 3D islands of GaN by diffusion during the growth or annealing period in NH_3 ambient. This may cause the incorporation of Zn or O elements into GaN during the growth process. The resulting very high defect density along with the observed structural defects which certainly act as non-radiative centers and the possibility of further absorption in the ZnO layer explain the observed weak and broad GaN PL spectra [7]. We could not detect a distinct GaN peak in HRXRD measurement in this growth process. From these observations, it is clear that a perfect coverage of the ZnO layer by a low temperature GaN buffer layer is the most important issue. However, we also observed that a very thick buffer layer consequently deteriorates both the surface and the crystal quality. Hence, we implemented a multilayer growth process to overcome the limitations of the buffer layer thickness. In this process, we deposited a GaN buffer layer of about 150 nm thickness at 550°C. Since the quality of the subsequently grown layers was not much dependent on the usage of N_2 or H_2 as a carrier gas in the underlying first buffer layer growth, we used N_2 as a carrier gas here to minimize the risk of etching ZnO at the onset of the growth process. For the growth of the subsequent layers, we used H_2 as a carrier gas. The buffer layer was heated under NH_3 up to 700°C and then annealed in N_2 ambient up to 1050°C to re-crystallize it. An intermediate GaN layer of about 50 to 100 nm was grown at 800°C with the same precursor flows as used for the first buffer layer. The insertion of such an intermediate layer could also minimize the further diffusion of Zn and O elements into the subsequently grown layers. Moreover, this layer produced a substantial change on the surface quality of the final GaN layer. The intermediate

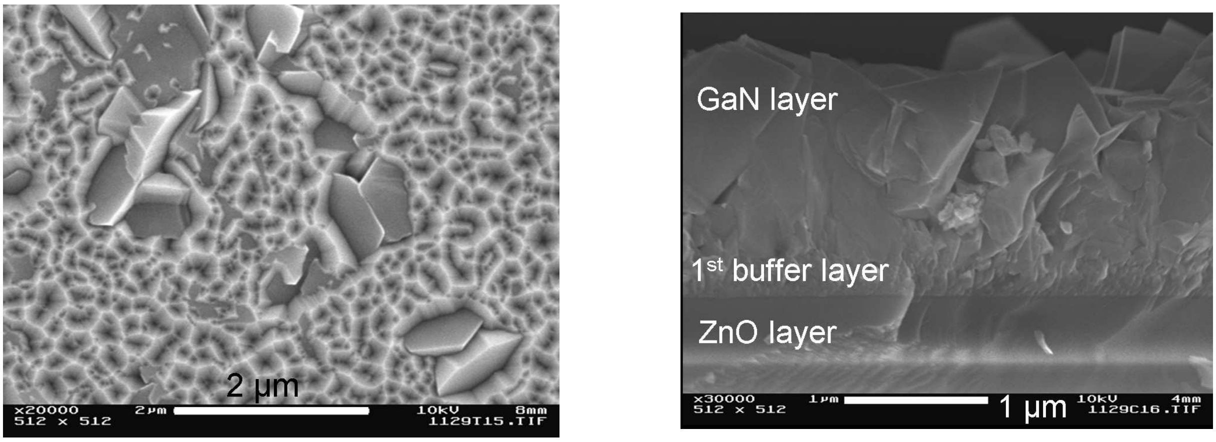

Fig. 2: SEM images of GaN grown by using a multi layer growth process. Top view (left) showing a reduced number of crystallites. A large number of hexagonal pits are visible in between the large crystallites. Cross sectional view (right) illustrating GaN and ZnO layers.

layer was heated in NH_3 ambient up to 950°C and then annealed in N_2 ambient up to 1050°C. Then, a final layer of GaN at a temperature of 950°C was grown with a reduced flow of NH_3 because of the higher cracking efficiency of NH_3 at high temperature. After about 150 nm, we stopped the growth and annealed up to 1000°C in NH_3 ambient for a short period of 30 seconds and again started growing at 950°C. Such an annealing step enhances the coalescence of the GaN islands and we observed significant improvement of the surface flatness (Fig. 2).

Although the growth mode was not 2D, we observed a well ordered crystalline structure in many areas of the sample. Thus, the decrease in the density of crystallites and emergence of fairly flat areas demonstrate the effectiveness of our growth process. Figure 3 shows the ω-2θ scan of the (002) reflection of HRXRD measurement.

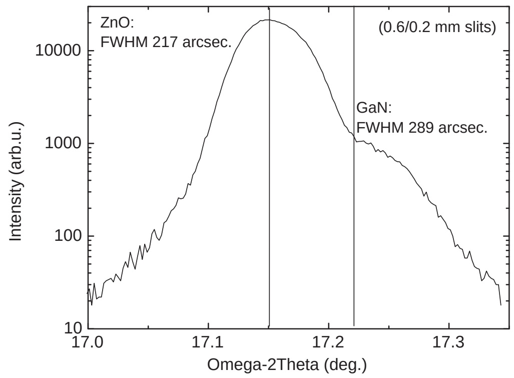

Fig. 3: ω-2θ scan for (002) reflection of HRXRD measurement. A separation of ≈ 0.07° between the peaks of ZnO and GaN fits the lattice mismatch.

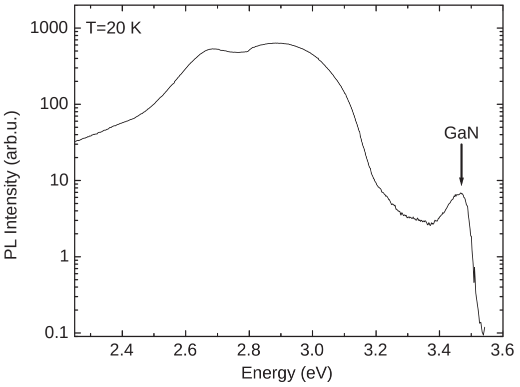

Fig. 4: Low temperature PL spectra illustrating the GaN related peak .

The reflection from the GaN layer is distinctively visible at the right shoulder of the

ZnO peak. Due to the broadening of the ZnO peak, we do not see two separate peaks of ZnO and GaN. However, the FWHM of GaN is estimated to be about 290 arcsec. The separation between the two peaks of GaN and ZnO is approximately 0.07° which fits with the approximate lattice mismatch. In PL measurements (Fig. 4), we observe a clear signal from GaN, although with low intensity and fairly broad linewidth. The broad luminescence at the lower energy region peaking at about 2.9 eV is attributed to an excessive incorporation of impurities in the GaN layer due to the diffusion of Zn and O. Moreover, we also grew the final GaN layer at 1000°C by using N_2 as a carrier gas and annealed up to 1050°C in N_2 ambient. Although the low temperature PL spectra were similar to Fig. 4, the surface quality in SEM observation and the HRXRD spectra were relatively inferior.

4. Conclusion

The major issue of successful MOVPE growth of GaN on ZnO is how to protect the underlying ZnO layer from the etching effect of H_2. The presence of H_2 during the growth period is an unavoidable fact in MOVPE technology. However, by implementing our multilayer growth process, we are successfull to some extent to address this issue. We demonstrated the successful growth of GaN by using H_2 as a carrier gas at 950°C. In our MOVPE system, a high quality GaN layer is normally grown at a temperature above 1100°C. At such high temperatures, even a pinhole in the covering layer could be sufficient to dissociate the underlying ZnO due to the strong reactivity of H_2 with ZnO. Thus, a complete covering of ZnO is an indispensable requirement before growing the GaN at such a high temperature. Hence, it is still a great challenge to successfully grow device level quality of GaN on ZnO in MOVPE.

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