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Structural properties of MOVPE GaN layers grown by a new multi-buffer aproach

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GaN undoped layers of good morphology, good crystallinity and electrical properties were grown on c-plane sapphire substrates by the atmospheric pressure MOVPE technique using a new multi-buffer growth approach. A suitable buffer layer growth technique was worked out which enabled growth of GaN layers with properties superior to those grown in a conventional process scheme. Additional buffer layers, deposited with increasing temperature and increasing V/III molar ratio, were inserted between the low temperature buffer layer and the high temperature GaN layer grown on it. The c and a lattice constants of the high temperature GaN overgrown layer were evaluated from X-ray data. The layer mosaicity and c-lattice parameter variation were determined. The relationship between c and a lattice parameters and the second buffer layer growth scheme has been studied. The effect of second buffer layer growth conditions, buffer layer annealing time as well as the influence of V/III molar ratio during the high temperature GaN deposition on the crystalline and electrical properties of overgrown GaN epitaxial layers are presented. Characterization includes surface morphology examination by SEM and Nomarski optical microscope, X-ray diffraction and C-V measurements.

1 Introduction

Wurtzite GaN is an attractive material for realization of high temperature electronic, optoelectronic devices and cold cathodes due to its direct band gap of 3.4 eV at room temperature, high thermal conductivity, high thermal stability and excellent physical properties. But its epitaxial growth presents several serious problems caused mainly by the lack of commercially available, large size, lattice matched substrates. Despite the fact that device quality GaN has been achieved, many fundamental aspects of the growth are still unclear and need further investigation. The most common substrate utilized for GaN deposition is sapphire because of its low cost and availability while MOVPE seems to be the most successful and the most promising epitaxial technique, especially for large scale production.

Typically GaN crystals nucleate and grow on sapphire by island formation. Iinitial sapphire substrate nitridation [1] and low temperature (450-600°C) AlN [2], GaN [3] or even double GaN/AlN [4] nucleation layers have been tried to promote oriented lateral growth. Although the exact role of the low temperature buffer layer is not fully understood yet, it is believed that it provides a large number of nucleation sites and is responsible for converting the growth mechanism from three dimensional to pseudo-two dimensional. After low temperature buffer layer deposition, annealing is performed before the high temperature GaN growth to cause the recrystallization of the buffer layer. Most of the recrystallization process occurs during the temperature ramp from the temperature of the buffer layer deposition to the high temperature layer growth. Wickenden [5] showed that annealing time greater than 20 min caused degradation of the morphology and buffer layer quality. Kobayashi [6] examined a multi-buffer layer growth approach in which the second buffer layer, grown at intermediate temperature (800 °C), was inserted between the low temperature buffer layer and the first high temperature GaN layer. This was found to be an effective method for avoiding the thermal desorption and mass transport of the low temperature buffer layer during the temperature ramp. He concluded also that the growth conditions and margin for formation of three dimensional islands differ from the optimal condition for their complete coalescence, needed for starting two dimensional growth mode. Furthermore it was found that insertion of a second buffer layer between the low temperature buffer layer and the high temperature overgrown layer might stop threading of screw dislocations [7]. This result confirmed our previous observation [8] and showed that addition of a second buffer epitaxial layer grown in a definite condition is an effective way to improve the quality of high temperature GaN layers.

In this article we present our newly developed multistep buffer layer growth strategy and discuss the influence of the second buffer layer deposition parameters on the crystalline quality and the electrical properties of the overgrown GaN layers.

2 GaN growth and measurement methods

The GaN epitaxial layers were grown on c-plane sapphire (α-Al_2O_3 (0001)) in an atmospheric pressure, single wafer, vertical flow MOVPE system redesigned for nitride deposition [8]. Trimethylgallium (TMGa) and ammonia (NH_3) were used with H_2 carrier gas. Before the growth process, the substrate was degreased in organic solvents and etched in a hot solution of H_2SO_4:H_2PO_4 (3:1). After annealing the substrate in the growth chamber for 20 min at 1040 °C under H_2 flow, a nitridation was performed at 1040 °C for 27 min in an NH_3/H_2 ambient. The temperature was lowered to 480°C to grow the first GaN thin (about 20 nm) layer. The low temperature buffer layer deposition condition was optimized [9] and was as follows: 480°C, 5 min, 9300 V/III molar ratio. Then the temperature was linearly raised to 1040 °C for 10 min. During the temperature ramp a second buffer layer was grown with different linearly changed TMGa flow. After a series of experiments, three TMGa flow patterns, named A, B, C, (see table 1) were chosen to examine the second buffer layer growth condition influence on the structural properties of the overgrown high temperature GaN layers. (A - TMGa flow changing linearly from 13.4 µmol/min to 0, B - TMGa flow changing linearly from 9.6 µmol/min to 0, C - TMGa flow changing linearly from 9.6 µmol/min to 3.3 µmol/min) Prior to high temperature GaN layer growth the buffer layers were annealed in an NH_3/H_2 ambient for10 min at 1040 °C. Then, a thick high temperature GaN layer was grown. The GaN layer deposition sequence and the gas flow rates are presented in Table 1.

The surface morphology of GaN layers was observed with SEM and with a Nomarski optical microscope. X-ray diffraction measurement were performed using a 4-crystal Philips Materials High Resolution Diffractometer. Reciprocal lattice space maps of the (00·2) GaN peak were measured. Both triple axis ω and $2\theta/\omega$ scans were made to separate two components of X-ray peak broadening: one related to variations in the lattice parameter (measured in the $2\theta/\omega$ scan direction) and the other due to mosaic structure caused by slight misorientations (measured in the ω scan direction). We observed the influence of the second buffer layer growth conditions on the overgrown GaN layers lattice parameters, the c lattice parameter variation, and the mosaicity. GaN lattice parameters were calculated on the basis of the (00·2) and (01·5) peak positions on the 2θ axis.

Electrical properties of the GaN layers were determined by C-V measurements performed at 100 kHz and 1 MHz using a mercury probe. Because no "pinning”effect is observed in GaN [10] in contradiction to other $A^{III}B^{V}$ semiconductors the GaN-mercury Schottky contact exhibits non repeatable breakdown voltage and a high value of leakage current, causing errors in the capacitance measurements. The capacitance should therfore be measured in a range of frequencies and the results have to be fitted to the model. The distributed element equivalent circuit regarding the series resistance and the junction conductance was used. It allowed proper evaluation of the junction capacitance-versus-voltage dependence and eliminated the junction capacitance frequency dispersion problem. As a result, the value of the electron concentration in the GaN overgrown layers was obtained.

3 Result and discussion

Since it is known [11] [12] [13] that the GaN lattice parameters, mosaicity and strain changes with layer thickness, 1 µm thick samples were measured for comparison.. Figure 1a and Figure 1b show the influence of the second buffer layer growth scheme on the properties of the GaN high temperature overgrown layers. It should be mentioned that the TMGa flow rate change during the second buffer layer growth affected the GaN lattice parameters, mosaicity and c-lattice parameter variation. High TMGa flow, at the beginning of this step (scheme A, 6600 V/III molar ratio) results in increasing c-lattice parameter of GaN overgrown layers compared to those grown on a second buffer layer deposited according to scheme B and C. A notable increase of the GaN a-lattice parameter was observed for layers grown on second buffer layer deposited with V/III molar ratio changing from 9300 at the beginning to 27400 at the end of this step (scheme C). High TMGa flow increases the second buffer layer growth rate [14]. This prevents formation and coalescence of 3D islands during the temperature ramp. Lower TMGa flow (scheme C) lowers the second buffer layer growth rate and causes the buffer material to be more mobile and fully reorganized before the high temperature GaN deposition. If the change in TMGa flow was too fast (scheme B) we observed a slight increase of layer mosaicity that was always accompanied by a noticeable c-lattice parameter variation reduction. Explanation of this behavior needs further study.

Generally the smallest value of ω was obtained if the GaN high temperature layer was deposited on the second buffer layer grown under scheme C (see table 1), while layer mosaicity was smallest for layers grown on a second buffer layer deposited under scheme B. The buffer layer annealing time was 10 min, V/III molar ratio of high temperature layers was 6600.

The changes of the GaN high temperature layer lattice parameters, mosaicity, c-lattice parameter variation and the background carrier concentration with two buffer layer annealing times are presented in Figure 2a, Figure 2b and Figure 2c, respectively. The second buffer layer was grown under scheme C, the V/III molar ratio for the high temperature GaN layers was 6600. We observed that in our case, because of the second buffer layer deposition during the temperature ramp, it is necessary to anneal buffer layers before the high temperature GaN deposition. The annealing time influences mainly the layer's mosaicity and should be chosen carefully. We also observed changes in the background carrier concentration with annealing time variation. It is in some disagreement with the observation of Wickenden [5] who saw no advantage in annealing the conventional low temperature buffer layer for prolonged periods before the epitaxial process.

The background carrier concentration, the growth rate, mosaicity, c-lattice parameter variation and lattice parameters of the GaN cell versus the V/III molar ratio (fixed by changing the NH_3 flow rate and keeping TMGa constant) during the main GaN layer growth are presented on Figure 3a, Figure 3b and Figure 3c respectively. We observed that the layers with the best background carrier concentration and the best crystalline quality were grown with V/III molar ratio of around 6600. It is in good agreement with Hwang [15]. Furthermore Briot [16] observed that increasing the V/III molar ratio reduces the incorporation of impurities by decreasing the density of native defect creation. For V/III molar ratio larger than 7000, we observed the increase of the background carrier concentration. It needs further investigation to explain the observed effect.

4 Conclusion

We proposed a new three-step growth approach, which allowed us to growth smooth, mirror like GaN MOVPE layers with good crystalline and electrical properties. This new method enabled us to control lattice parameters, mosaicity and c-lattice parameter variation of the overgrown high temperature GaN epitaxial layers. Introduction of the second buffer layer during the temperature ramp enhanced lateral growth rate and influenced the buffer layer recrystallization process. The smallest mosaicity was obtained for high temperature GaN layers grown on a second buffer layer grown according to scheme C. This three step growth approach significantly improved the control of the MOVPE process parameter's impact on the high temperature GaN structural and electrical properties.

We found that no simple correlation exists between GaN layers structural quality and their electrical properties. The background carrier concentration depends only on the growth process parameters, especially the V/III ratio during the high temperature growth and the buffer layer annealing time.

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FIGURES

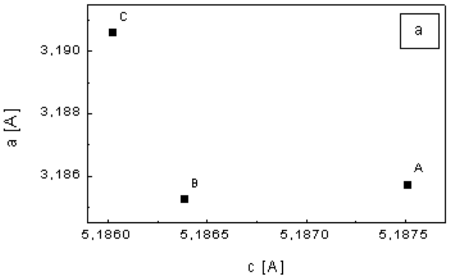

Figure 1a. The GaN high temperature layers lattice parameters. Labels A, B, C indicate the second buffer layer growth scheme.

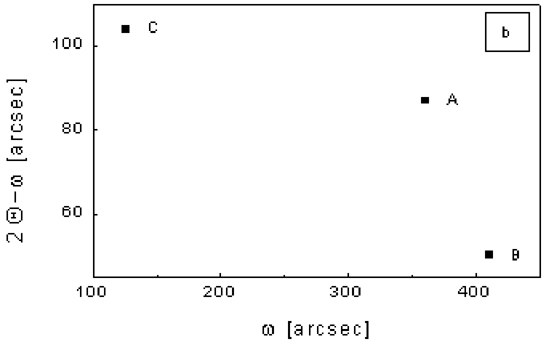

Figure 1b. The GaN high temperature layers c-lattice parameter variation and mosaicity. Labels A, B, C indicate the second buffer layer growth scheme.

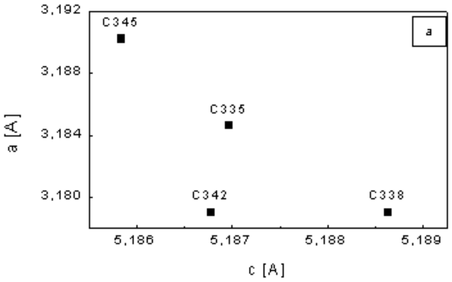

Figure 2a. The GaN high temperature layers lattice parameters. Labels indicate the second layer growth scheme (C) and sample number.

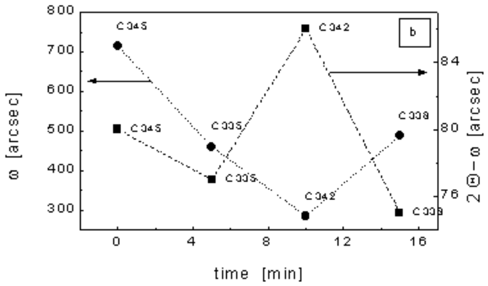

Figure 2b. Two buffer layers annealing time versus mosaicity and c-lattice parameter variation of the GaN high temperature layers. Labels indicate the second layer growth scheme (C) and sample number.

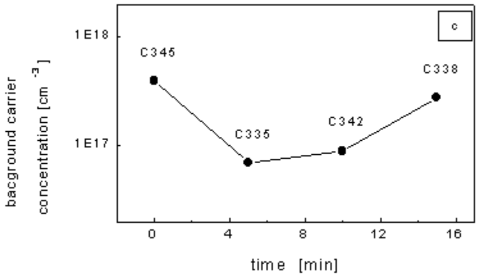

Figure 2c. Two buffer layers annealing time versus the background carrier concentration of the GaN high temperature layers. Labels indicate the second layer growth scheme (C) and sample number.

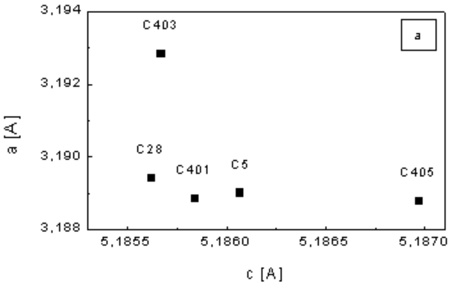

Figure 3a. The lattice parameters of the GaN high temperature layers grown with different V/III molar ratio. Labels indicate the second layer growth scheme (C) and sample number.

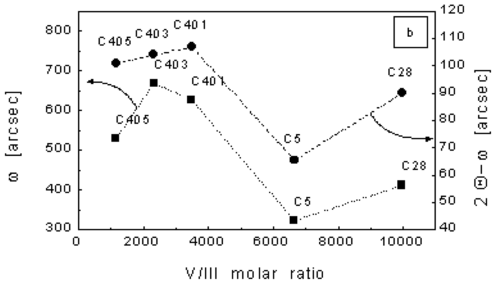

Figure 3b. The V/III molar ratio during the main GaN layer growth versus layers: mosaicity and c-lattice parameter variation. Labels indicate the second layer growth scheme (C) and sample number.

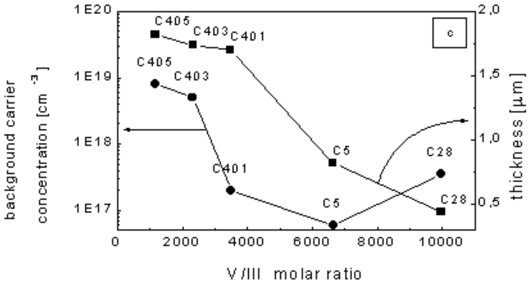

Figure 3c. The V/III molar ratio during the main GaN layer growth versus layers: background carrier concentration and thickness. Labels indicate the second layer growth scheme (C) and sample number.

TABLES

Table 1. GaN layers deposition sequence and the gas flow rates.

	Substrate annealing	**Nitridation**	**1st buffer layer growth**	**2nd buffer layer growth**	**Buffer layers annealing**	**High temp. growth**
TMGa [µmol/min]			9.6	13.4⇒0 9.6⇒0 9.6⇒3.2		13.4
NH_3 [mmol/min]		89	89	89	89	15.6-133.5
H_2 [slm]	2	2	2	2	2	2-3.5
Temperature [°C]	1040	1040	480	480⇒1040	1040	1040
Time [min]	20	27	5	10	0⇒15	60⇒