

# GaN MOCVD on Si via Single Crystal Rare-Earth Oxide Buffer Layer

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## Abstract

**GaN layers were grown on Si (111) by MOCVD using epitaxial single crystal rare-earth oxide buffer which helps to solve mechanical strain related problems arising from lattice and thermal expansion mismatch between the III-N layer and the substrate. Chemical stability of the rare-earth oxide in contact with silicon as well with GaN is analyzed. Transformation of rare-earth oxide to rare earth nitride during GaN MOCVD process is studied. It is demonstrated that the oxide layer serves as Si diffusion barrier to GaN thus preventing back-etching effect.**

## INTRODUCTION

Efforts to grow GaN on large diameter Si wafers are driven by lower substrate price compared to native GaN or other foreign substrates like sapphire, SiC, as well as the possibility to use depreciated Si fabs and thus reducing the cost of GaN wafer. The technology is already adopted by some major companies for fabrication of GaN power devices based on high electron mobility transistors (HEMTs) and, to a lesser extent, for light emitting diodes (LED) on 150 mm Si wafers and recently on 200mm wafers, as for example it was advertised by IMEC [1]. Generally, the GaN-on-Si epitaxy requires an AlN buffer layer which serves for strain management and prevention of Si diffusion into GaN. Still, AlN is not an ideal material for either of the tasks. For example, Si diffusion which results in back etching of GaN layer still remains an issue because of Si solubility in AlN at the eutectic point of 577°C. Application of other types of the buffer layers are considered [2] [3]. However, these are early stage developments that are not implemented into the technology.

We introduce new material engineering solutions for the GaN-on-Si process by utilization of an epitaxially grown single crystal rare-earth oxide (REO) buffer on Si, which is ready for production stage. As it will be demonstrated in this work, it offers flexibility to the epitaxy process by opening up a possibility to use approaches typical for GaN epitaxy either on sapphire or Si: GaN or AlN first, respectively. Here, we study advantages of the oxide buffer, its chemical and structural properties that influence process at the oxide/silicon and oxide/III-N interfaces during III-N MOCVD process. We explore possibilities to implement the developed technology keeping in mind to make minimal changes to the existing III-N processes used for fabrication

of GaN on foreign substrates, so that it could be used by industry taking minimal efforts to transition to this new process.

## EXPERIMENT

The erbium oxide was grown in a custom-made MBE system capable of handling up to 200 mm diameter wafers. HF dipped 100 mm Si(111) wafers were loaded into the reactor and heated for 20 min at 750 °C in a low silicon flux in order to remove residual silicon dioxide from the surface and to obtain a flat 7x7 reconstructed silicon surface. The erbium oxide layers were grown at a growth rate of 0.25 Å/s by the evaporation of the metal from an effusion cell, and molecular oxygen was delivered from a gas manifold. Oxygen partial pressure in the chamber was approximately  $5.2 \times 10^{-6}$  mbar during oxide growth. The substrate temperature was 720 °C during growth of the oxides. More details about the oxide growth on Si can be found elsewhere [4] [5].

Thomas - Swan close shower head reactor capable of processing up to 200 mm wafers was used for GaN metal organic chemical vapour deposition (MOCVD). Trimethylgallium (TMG) and NH<sub>3</sub> were used as gallium and nitrogen sources, respectively. Layer growth was in-situ monitored by spectrometric reflectometry.

X-ray diffraction (XRD), transmission electron microscopy with energy-dispersive X-ray spectroscopy (EDX) was used for analysis of crystal structure and composition of the oxide and nitride layers.

For analysis of electrical properties and possible implementation of the layers for HEMT, 26 nm Al<sub>0.25</sub>Ga<sub>0.75</sub>N was grown on top of the GaN layer. Capacitance-voltage (C-V) measurements were performed using the mercury-probe method.

## RESULTS AND DISCUSSION

The interface between the rare-earth oxide layer and silicon substrate is critical for strain management in the heterostructure. Single crystal erbium oxide with abrupt interface without any SiO<sub>2</sub> – like interlayer is formed as shown in Figure 1a. In this case, very strong crystallographic coupling between the layer and the substrate is built due to ionic Si-O-Er bonds [6]. This ensures that a compressive strain is induced in the oxide-silicon system resulting in the convex shape of the wafers (Fig. 2). The mechanism of

building compressive stress during REO epitaxy is based on the oxide's cubic-bixbyite structure with mobile oxygen vacancies that arrange themselves depending on the stress in the layer at typical epitaxial process temperatures. However, additional analysis is required for complete understanding of the phenomenon. The building of a compressive strain is one of the advantages of the rare-earth oxide buffer because a compressively pre-strained substrate should help to decrease the final tensile strain in the wafer after GaN is grown.

Typical root mean square (RMS) roughness of the oxide surface measured by AFM over  $5 \mu\text{m} \times 5 \mu\text{m}$  area is 0.43 nm, and maximal roughness R-max (valley-to-peak value) 4.51 nm.

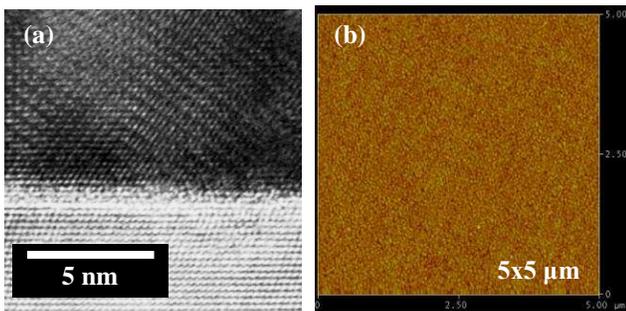


Figure 1. High resolution TEM image of  $\text{Er}_2\text{O}_3$  layer on Si(111) before GaN MOCVD (a), and AFM image of the oxide surface (b).

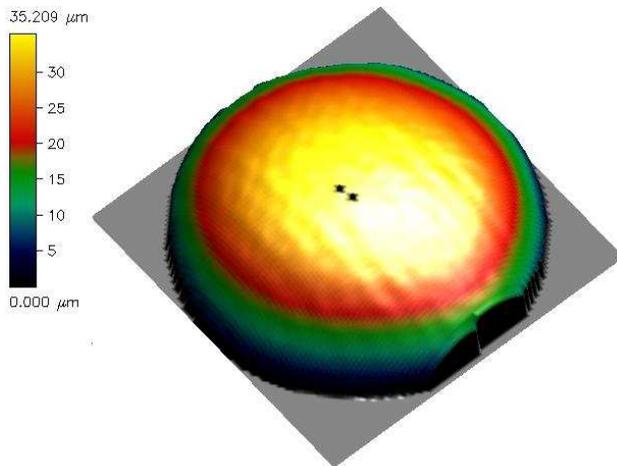


Figure 2. Bow of a wafer with 300 nm thick erbium oxide grown on Si(111).

Two approaches were used for MOCVD growth of GaN on the  $\text{Er}_2\text{O}_3$ : with an AlN buffer layer (similar to a process generally used for GaN growth on Si), and with a low-temperature (LT) GaN buffer (similar to a GaN-on-sapphire process).

In the first case, 50 nm AlN buffer layer was grown at  $950^\circ\text{C}$  followed by  $1.5 \mu\text{m}$  GaN grown at  $1080^\circ\text{C}$ . Although the compressively pre-strained substrate helps to manage tensile strain during the GaN MOCVD process (particularly during

the cooling-down phase), additional stress engineering was implemented by formation of three 50 nm thick LT-AlN interlayers inserted into the GaN layer.

In the second approach, the growth was started with 100 nm LT-GaN layer. As it was discussed by Niermann et al. [7], there are several possible configurations of chemical bonding between GaN and the oxide: -Ga-O-RE-, -Ga-N-O-RE-, and -Ga-N-RE- with the first one the most energetically favorable, which defines N-polarity of the GaN layer. On the other hand, the second and third bonding configurations result in metal-polar GaN which would be of advantage for 2DEG. A possible way for stabilization of the Ga-N-RE- bonding configuration is nitridation of the oxide surface as it was used for GaN MBE on a rare-earth oxide layer [5]. In the MOCVD, we expose the oxide surface to  $\text{NH}_3$  just before growth of the LT-GaN buffer. Subsequently,  $1.5 \mu\text{m}$  GaN layer, with the AlN interlayers as in case of the Al-first process, was grown.

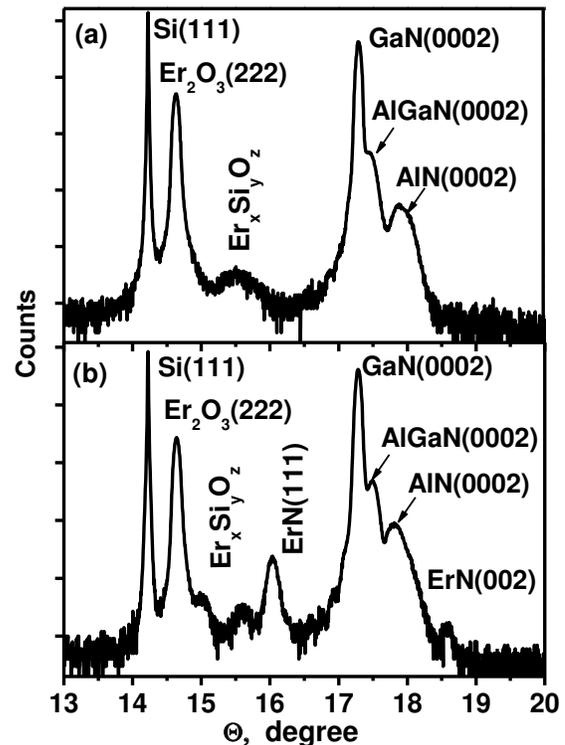


Figure 3. XRD scan of a III-N HEMT structure growth on Si(111) via rare-earth oxide buffer layer of AlN-first (a) and GaN-first (b) samples..

For both processes, a 2DEG structure was formed by the growth of 26 nm  $\text{Al}_{0.25}\text{Ga}_{0.75}\text{N}$  on top of the GaN layer in order to investigate electrical properties of the samples.

Both the AlN-first and GaN-first processes result in good crystal structure nitride layers as can be concluded from XRD measurements (Fig. 3). FWHM on GaN (0002) peak in both cases is acceptable for  $1.5 \mu\text{m}$  GaN: 563 arcsec and 788

arcsec for AlN-first and GaN-first process, respectively. In addition to the strong XRD peak of  $\text{Er}_2\text{O}_3(222)$ , there is a peak at  $15.71^\circ$  which we attribute to a thin erbium silicate interlayer formed at the interface with the substrate. Erbium oxide distinguishes itself by high thermal stability in contact with silicon at typical MBE process temperatures [5] [6]. However, during GaN MOCVD growth with temperatures above  $1050^\circ\text{C}$ , a reaction between silicon and the oxide takes place at the very interface between the layer and the substrate forming erbium silicate which is also confirmed by transmission electron microscopy (Fig. 4). According to X-ray dispersion spectroscopy (Fig. 5a) the erbium silicate thickness is about 15 nm. As it was discussed by Ono and Katsumata [8], chemical reactivity of rare-earths decreases with increase of atomic number. This is explained by their smaller atomic radius and, consequently, shorter chemical bonds between oxygen and rare-earths. It must be noted that erbium oxide is one of the most stable in contact with silicon at high temperatures.

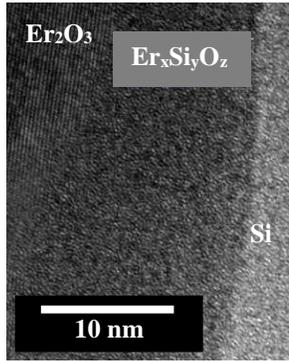
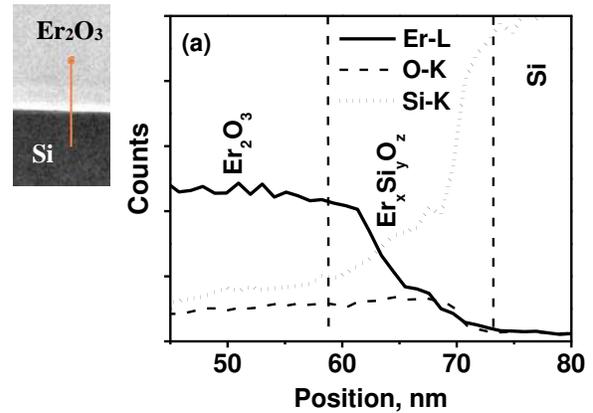


Figure 4. TEM picture of the erbium silicate interlayer of the GaN-first sample.

Surprisingly, there were two peaks (at  $\Theta = 15.03^\circ$  and  $\Theta = 15.62^\circ$ ) detected for the GaN-first sample. We speculate that these are different stoichiometries of erbium silicate. However, we were not able to identify the exact composition of the silicate in either case due to the absence of crystallographic data. EDX measurements reveal similar thickness of the silicate interlayer (Fig. 5b). The profile of the concentrations of elements is different in Figures 5a and 5b, indicating different relative compositions of the interlayers in the samples, which might explain the difference found in the XRD results discussed above. Formation of the silicate interlayer is a self-limiting process, therefore the silicon diffusion is stopped at the interface between the oxide and the silicon. This is why no silicon was detected in III-N layer grown on top of the oxide (Fig. 6). There is also no trace of erbium or oxygen detected in the GaN layer.

A peak at  $\Theta = 16.03^\circ$  detected in the XRD scan of the GaN-first sample (Fig. 3b) is attributed to  $\text{ErN}(111)$  with the rocksalt structure. Additional experiments with the surface nitridation step and the low-temperature buffer layer

revealed that the main contribution to formation of this layer is due to growth of the bulk GaN layer which results in substitution of oxygen in the oxide by nitrogen diffusing from the GaN layer. We speculate that the path of the diffusion of nitrogen atoms is through oxygen vacancies in bixbyite structure of erbium oxide. Intensity of the nitride XRD peak correlates with the temperature and time of the process. There is also a small  $\text{ErN}(002)$  peak detected, which indicates strong nitrogen diffusion induced disturbance of the crystal structure and formation of  $\text{ErN}$  nano-crystallites. No  $\text{ErN}$  peak was detected in the AlN-first sample because the strong Al-N bonds of AlN block diffusion of nitrogen into the oxide. The AlN layer at the very interface with the oxide exhibits lattice mismatch



induced network of defects as revealed by TEM (Fig. 7a). There is no indication of any chemical reaction between the oxide and the nitride.

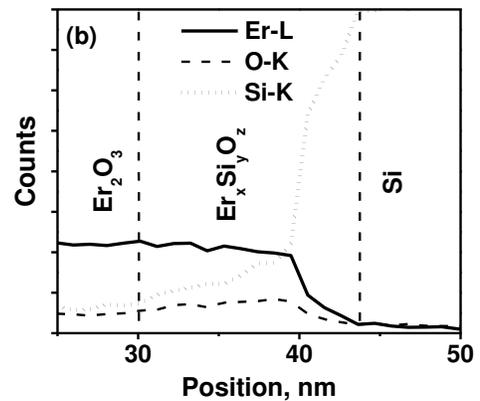


Figure 5. EDX elements concentration profile of erbium oxide and silicon interface of AlN-first (a) and GaN-first (b) samples.

In case of the GaN-first process, the interface between the rare-earth nitride and the GaN layer is also easily distinguished by different crystal structure on TEM images (Fig. 7b).

The surface morphology of the structure with the  $\text{Al}_{0.25}\text{Ga}_{0.75}\text{N}$  barrier layer on top is smooth for both samples as shown by AFM results. (Fig. 8). RMS/R-max of  $5 \mu\text{m} \times 5$

$\mu\text{m}$  area is 0.897 nm/6.672 nm and 0.352 nm/10.580 nm for AlN-first and GaN-first samples, respectively. For a 20  $\mu\text{m}$  x 20  $\mu\text{m}$  area is the RMS/R-max are 1.227 nm/9.558 nm and 1.403 nm/10.580 nm for AlN-first and GaN-first samples, respectively.

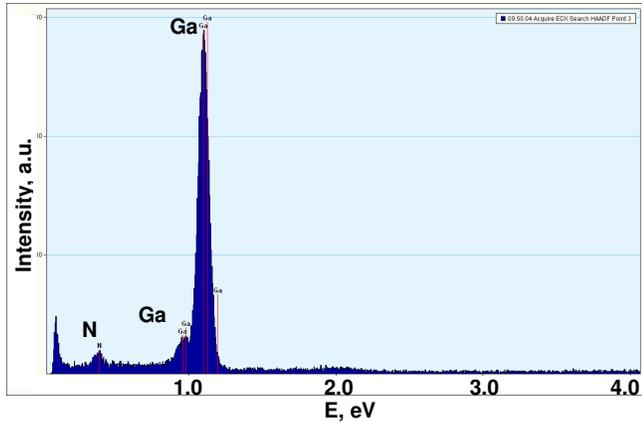


Figure 6. EDX spectra of GaN layer close to interface with  $\text{Er}_2\text{O}_3$ .

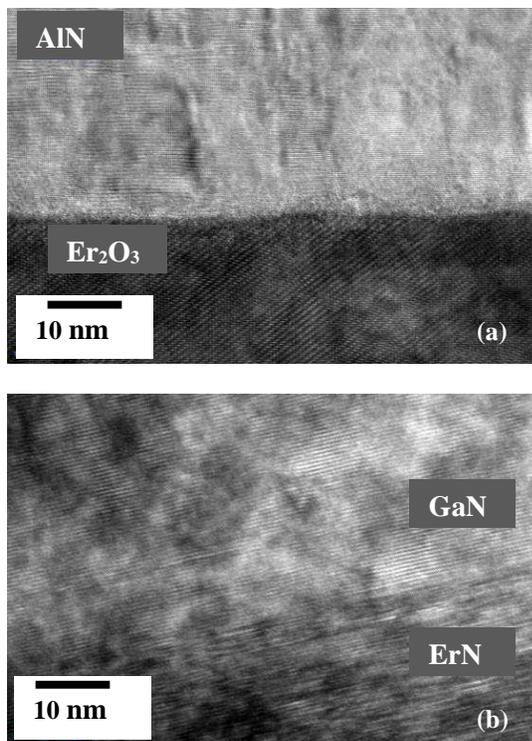


Figure 7. TEM image of AlN- $\text{Er}_2\text{O}_3$  (a) and GaN-ErN (b) interface.

The electrical measurements of the structure with 26 nm  $\text{Al}_{0.25}\text{Ga}_{0.75}\text{N}$  barrier layer on top of the GaN indicate formation of 2DEG with calculated electron density of  $5 \times 10^{12} \text{ cm}^{-2}$  (Fig. 9). Both samples demonstrate similar electrical properties.

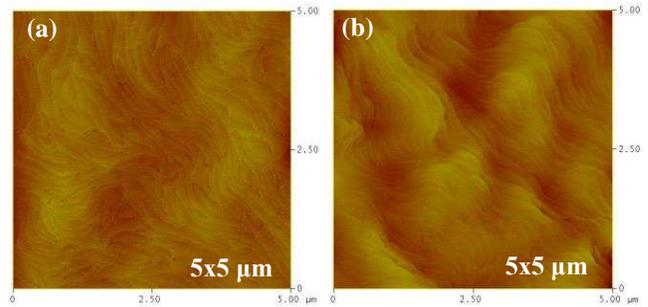


Figure 8. AFM 5 x 5  $\mu\text{m}$  scan of the surface of the AlN-first (a) and GaN-first (b) samples.

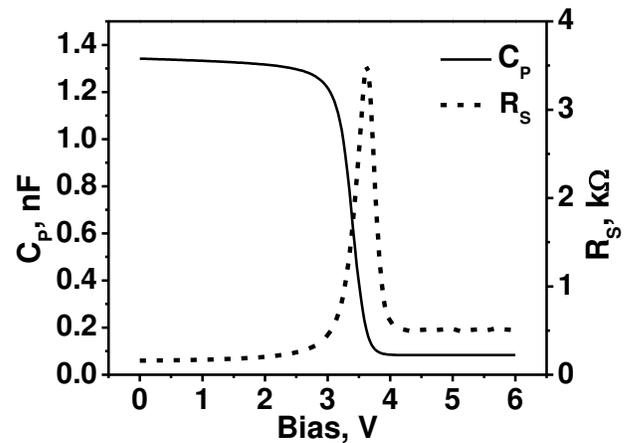


Figure 9. Electrical measurements of a sample with the AlN-first process.

## CONCLUSIONS

A novel combined MBE and MOCVD process approach is introduced for growth of 2DEG structure with GaN layer on rare-earth oxide buffer on Si(111) substrate. The REO layer serves as a barrier for Si diffusion to GaN and prevents back-etching of the later.

The proposed technological solution with application of GaN-on-Si and GaN-on-sapphire processes offers great flexibility for existing GaN technology.

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