Free-standing 2-inch bulk GaN crystal fabrication by HVPE using a carbon buffer layer

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Abstract. A free-standing bulk gallium nitride layer with a thickness of 365 µm and a diameter of 50 mm was obtained by hydride vapor phase epitaxy on a sapphire substrate with a carbon buffer layer. The carbon buffer layer was deposited by thermal decomposition of methane \textit{in situ} in the same process with the growth of a bulk GaN layer. The bulk GaN layer grown on the carbon buffer layer self-separated from the sapphire substrate during the cooling after the growth. The dislocation density was $8 \cdot 10^6$ cm$^{-2}$. The (0002) X-Ray rocking curve full width at half maximum was 164 arcsec.

1. Introduction

Today, HVPE heteroepitaxial growth of GaN on foreign substrates is the main method for commercial production of GaN substrates. An important step in this technology is the separation of the bulk GaN layer from the substrate after the growth process. Thick GaN layers with thicknesses of several hundred microns typically separate from sapphire substrates during the cooling after the growth, but this self-separation process is accompanied by cracking of the GaN layer \cite{1-3}. The cracking of a GaN layer can be suppressed by growing a bulk GaN layer with a thickness of several millimeters, or by reducing the bonding energy between a substrate and a GaN layer. Different methods were proposed to reduce the bonding energy between a substrate and a GaN layer, including porous layers created by dry etching \cite{4}, wet etching \cite{5}, electrochemical etching \cite{6} or GaN decomposition induced by a TiN mask \cite{7}; epitaxial lateral overgrowth over dielectric masks \cite{8-11}, employing substrates with a cleavage plane parallel to the c-axis of GaN \cite{12-13}, and weakly bonded buffer layers \cite{14-15}. All these methods either require using non-standard substrates \cite{12-13} or special \textit{ex situ} pre-growth processing of the substrate like etching, buffer layer deposition, dielectric or metal mask fabrication, or GaN template structure growth.

Carbon in the form of graphite is a promising material for creating buffer layers that facilitate self-separation due to the hexagonal symmetry of the crystal lattice and a low interlayer binding energy \cite{16}. Earlier, a nanocrystalline graphite carbon buffer layer deposited by PECVD on a
sapphire substrate was used for GaN growth and self-separation. A 200-µm thick GaN layer was grown and free-standing GaN pieces were obtained \cite{17}. In this work, a bulk GaN layer with a thickness of 365 µm was grown on a sapphire substrate with a carbon buffer layer deposited \textit{in situ}, and a wafer-scale self-separation has been demonstrated (figure 1).

2. Experimental details

The experiment used a standard epi-polished 2-inch sapphire substrate with a thickness of 430 µm and a crystallographic orientation of (0001) with a miscut of 0.5° towards the m-plane.

A carbon buffer layer and a GaN film with a thickness of 20 µm were grown in a multi-wafer HVPE reactor with an installed methane supply line. The design of the reactor limited the maximal GaN layer thickness to 200 µm; therefore, to grow the bulk layer, the structure was transferred to the vertical HVPE reactor optimized for the bulk layer deposition.

A carbon layer was deposited using the methane thermal decomposition process from a CH\textsubscript{4}/H\textsubscript{2} mixture \cite{18} at a deposition temperature of 1020 °C, a total process pressure of 105 kPa and a methane partial pressure of 1.3 kPa. The deposition rate was 10 nm/min. After that, a 20-µm thick GaN layer was deposited at a temperature of 960 °C. Then, the structure was cooled down and transferred to a vertical HVPE reactor where a 345-µm thick GaN layer was grown at a growth rate of 100 µm/h, a V/III ratio of 35, a total reactor pressure of 15 kPa, and a substrate temperature ramping from 880 °C at the beginning of the growth process to 920 °C at the end of the growth process. Self-separation induced by thermal stress occurred during the cooling down after the growth process, and a single piece GaN layer with a thickness of 365 µm and a diameter of 50 mm was obtained.

3. Results and discussion

A photograph of a free-standing GaN layer is shown in figure 2(a). The surface of the layer is smooth, the V-shaped pit density is 40 cm\textsuperscript{-2}, and the opening angle of V-shaped pits is in the range of 80°-100° that is typical for GaN layers grown in the low-temperature mode \cite{19}.

The (0002) XRD rocking curve of the Ga face of the free-standing GaN is shown in figure 2(c). The FWHM value is 164 arcsec. The lattice curvature radius of free-standing GaN measured by XRD is 3.1 m. The residual bow is typical for free-standing GaN layers obtained by heteroepitaxy and is a result of a built-in strain caused by defect density gradients along the c-axis of a GaN layer \cite{20,21} and by the inclination of threading dislocations \cite{22}.

The threading dislocation density on the Ga-face surface of the free-standing GaN layer was estimated to be 8 · 10\textsuperscript{6} cm\textsuperscript{-2} (figure 2(b)), which is typical for GaN layers with thicknesses of 350-400 µm, grown on a sapphire substrate \cite{23}. The estimation was made by measuring the dark spot density using the cathodoluminescent microscopy \cite{24}.
**Figure 2.** (a) A photograph of free-standing GaN layer with a thickness of 365 µm and a diameter of 50 mm. The surface is optically smooth and the V-shaped pit density is below $40 \text{ cm}^{-2}$. (b) A cathodoluminescence micrograph of the Ga-face surface. The dark spot density is $8 \cdot 10^6 \text{ cm}^{-2}$. (c) A (0002) XRD rocking curve of the Ga face of free-standing GaN.

**Figure 3.** (a) Schematic representation of a bulk GaN layer and a growth substrate after self-separation. (b) A SEM micrograph of the N-face of a GaN layer. The inset shows the EDX spectrum of the surface, measured at point A and demonstrating remnants of the carbon buffer layer. (c) A SEM micrograph of the sapphire substrate surface shows submicron-sized irregularities formed during the process of free-standing GaN fabrication.

The surfaces of the N-face of the GaN layer and the sapphire substrate were smooth and mirror-like. Both these surfaces were examined by scanning electron microscopy combined with energy-dispersive X-ray spectroscopy. The carbon buffer layer remnants were found on the N-face of free-standing GaN layer (figure 3(b)) and the sapphire substrate surfaces (not shown). This confirms that the self-separation occurred strictly along the carbon buffer layer. The sapphire substrate surface was covered by submicron-sized irregularities (figure 3(c)), while no irregularities of the same scale were observed on the GaN surface. A possible origin of such irregularities could be the reduction of sapphire by carbon [25]. Sapphire etching and the resulting cavity formation may also lower the bonding energy between a GaN layer and a substrate and facilitate the self-separation process.
4. Conclusion
A bulk GaN layer was epitaxially grown on a sapphire substrate with a carbon buffer layer. The layer spontaneously separated from the substrate along the carbon buffer layer during the cooling down process, and a free-standing GaN layer with a diameter of 50 mm and a thickness of 365 µm was obtained. The surface morphology and crystalline structure of the free-standing GaN layer did not degrade compared to a GaN layer grown on a bare sapphire substrate in similar conditions.

5. Acknowledgments
The authors gratefully thank O. Mededev and O. Vyvenko from St. Petersburg State University for help with microscopic investigations.

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