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Preparation of Sapphire for High Quality III-Nitride Growth

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We developed a unique preparation technique to eliminate surface damage on the c-plane of sapphire and render it atomically flat. AFM images of c-plane sapphire annealed at 1380 °C for 1hour show terrace-like features with about 0.2 µm long terraces. The GaN layers grown by MBE on annealed sapphire have [0 0 2] symmetric and [1 0 4] asymmetric full width at half maximum (FWHM) of about 60 and 132 arcsec, respectively. This compares with 408 and 600 arcsec, respectively, for GaN grown on sapphire having gone through conventional chemical cleaning.

1 Introduction

In recent years the III-V nitrides have attracted much attention [1] because of the potential to produce high-temperature and high-power electronic devices [2], as well as bright blue light-emitting diodes (LEDs) [3], lasers [4] and solar blind UV photovoltaic detectors [5]. [a] Motivations for GaN based high-temperature, high-power electronics are due to GaN's high electron-saturation velocity, wide bandgap, high thermal conductivity and the availability of heterojunctions. Essential in exploiting all these applications is high-quality III-V nitrides.

One of the bottlenecks that have hindered the development of GaN is the lack of a suitable substrate material that is lattice matched to and thermally compatible with GaN. Due to the lack of an ideal substrate, nearly all III-V nitride materials are grown on sapphire despite its poor structural and thermal match to III-Nitrides. The predilection towards sapphire substrates is due to its availability, low cost, and its ease of handling and improving quality. Sapphire is also stable at high temperatures (about 1000 °C), a property that is required for epitaxial growth using the various deposition techniques commonly employed for GaN [7], [8]. In addition, its transparence to visible light makes it ideal for some detector application. The most commonly used orientation of sapphire for GaN, AlN and InN growth is the (0001) orientated basal plane, but the (21(-3)1), $(110\bar{1})$, $(11\bar{2}0)$ planes have also been explored. A mechanical–chemical-polish involving many process steps is employed by sapphire manufacturers which produces a reasonable overall flatness of the surface, but leaves excessive damage and visible scratches caused by the grit used.

It has been established that the crystal structure of epitaxial GaN is strongly influenced by not only the substrate material and its orientation, but to a great extent the surface preparation of the substrate. An ideal c-plane sapphire surface for epitaxy would have bi-layer steps leading to the realm where all the terrace surfaces have the same surface polarity so that stacking mismatch boundaries as well as other defects in the ensuing nitride deposition can be avoided. Therefore, in addition to a clean and damage-free surface, an atomically flat surface is imperative for 2D growth. As alluded to earlier, the surface of as-received sapphire is not acceptable for high quality epitaxial growth due, in part, to damage during polishing as a result of its hardness. While chemical etching and/or plasma etching can remove some of the damage, the resultant surface morphology is not ideal, as these etches attack the damaged regions faster [1].

A substrate surface can be likened to the foundation of a building; as such, substrate preparation [9] deserves the most attention. In this article, we report on a unique preparation technique to remedy the aforementioned shortcomings associated with the c-plane sapphire surface and render it atomically smooth. A comparison between the GaN layers grown by MBE on sapphire having undergone conventional preparation and the preparation method under discussion is also given.

2 Experimental details

The details of the procedure employed are as follows: Sapphire substrates first undergo a chemical (solvent)

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cleaning procedure [10], in which the substrate is dipped in a solution of TriChloroEthylene (TCE) for 5 minutes. The substrate is then rinsed for 3 minutes each in acetone and methanol. This procedure is followed by a 3-minute rinse in deionized (DI) water. The above steps are repeated three times to complete the degreasing process.

Following the degreasing procedure, the surface damage is removed by chemical etching. A 3:1 solution of hot H_2SO_4: H_3PO_4 (300 °C) is then used for 20 minutes to remove some of the surface material. This is followed by a rinse in DI water for 5 minutes. As will be discussed, this procedure serves to remove the surface damage but does not lead to smooth surfaces. Following this procedure, sapphire substrates (2-inch whole wafers) were subjected to a high temperature heat-treatment (in a resistively heated furnace) in air, which will be discussed in detail in the next section. Before put the sapphire into the chamber for epitaxy, it is rinsed for 3 minutes each in acetone and methanol. Followed by a 3-minute rinse in deionized (DI) water.

Sapphire substrates as well as the GaN layers grown on them were characterized by AFM (Digital Nanoscan III), and X-ray diffraction (Philips MRD with 10 are second resolution). The MBE growth on the sapphires was performed in an SVT system using radio frequency (RF) plasma as well as in a Riber system using NH_3.

3 Results

Shown in Figure 1 are AFM images of two c-plane sapphire surfaces, (a) before and (b) after the chemical etching. It is very clear that the etching did not remove the scratches from the surface that was introduced during the polishing process. Obviously, smoothness at the atomic level is not seen even though the root-mean-square (RMS) roughness was reduced from 0.32 nm in image (a) to 0.21 nm in image (b).

Figure 2 shows AFM images after annealing of sapphire for 30 minutes at (a) 1100°C; (b) 1200 °C; (c) 1300 °C; and (d) 1380 °C. Damage lines were reduced greatly although the atomically smooth surface did not emerge. In fact the RMS of the images increased from 0.22 nm for image (a) up to 0.49 nm for image (d). On occasion large dots appeared on the surface, as shown in (b) or many tiny dots as shown in (c).

In our quest to obtain atomically smooth surfaces, anneal time was increased to 1 hour or longer. Figure 3 (a) represents the surface annealed at 1000 °C for 1 hour while that in (b) represents the one annealed at 1300 °C for 1 hour. As one can see, the surface changed into a smooth one and the terrace structure began to appear albeit randomly. The RMS reduced from 0.29 for image (a) to 0.14 for image (b). As shown in Fig. (c), when the substrate was annealed at 1380 °C for 1 hour, however, an atomically flat surface became clearly visible as judged by the straight and uniform terrace structure. The RMS roughness value for this image is only 0.07nm. The diagonal lines from left to right are the artifacts of AFM. When the anneal time was extended to 3 hours at 1380 °C, as shown in (d), the surface roughened somewhat as the RMS roughness value increased to 0.14. The steps and the terraces assumed a zigzagged and random distribution.

Sapphire substrates subjected to this proper high temperature heat treatment exhibits very smooth morphology. Shown in Figure 4 is an AFM image showing terrace-like features with about 0.2 µm long terraces. The terrace structure could facilitate smooth 2D growth and reduce column formation during the growth of GaN epilayers other than those caused by the lattice mismatch. To ascertain the effect of the process under discussion on epitaxial GaN, MBE of GaN on the annealed and unannealed sapphire has been performed. The details and the specifics of the layered structures used in the MBE will be reported at a later date [11]. Table 1 lists the X-ray rocking curve results, which clearly indicate that the crystal properties have been improved substantially on annealed sapphire. The sample SVT 319 is a GaN layer grown by RF MBE on unannealed sapphire (the sapphire surface morphology is shown in Figure 1 (b)), while SVT 389 is a GaN layer grown on sapphire that was annealed at 1380 °C for 1 hour (the morphology is shown in Figure 4). The sample R6385 is a GaN layer grown by NH_3 MBE on the same annealed sapphire. The GaN layers grown by MBE on annealed sapphire have [0 0 2] symmetric and [1 0 4] asymmetric full width at half maximum (FWHM) of as low as 60 and 132 arcsec (sample R6385), respectively. These figures compare with 408 and 600 arcsec (sample SVT 319), respectively, for GaN grown on sapphire which did not undergo the high temperature annealing process. It should be emphasized that the X-ray results for the growth on sapphires annealed at other temperatures or for other anneal times were not as good as those on that were annealed at 1380 °C for 1 hour. The average X-ray data over some 20 GaN samples are about 180 for [0 0 2] and 300 arcsec for [1 0 4], respectively. In other words, the 1380 °C for 1-hour annealing procedure appears to represent the best heat-treatment conditions of sapphire for GaN epitaxy.

4 Conclusions

Atomically flat c-plane sapphire surfaces have been obtained through an annealing process in air at 1380 °C for 1 hour. AFM images show terrace-like features with about 0.2 µm long terraces with bi-layer steps. The GaN layers grown by MBE on annealed sapphire exhibited

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[0 0 2] symmetric and [1 0 4] asymmetric full width at half maximum (FWHM) as low as 60 and 132 arcsec, respectively. This compares with 408 and 600 arcsec for the [0 0 2] symmetric and [1 0 4] asymmetric peaks, respectively, for GaN grown on standard sapphire.

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FIGURES

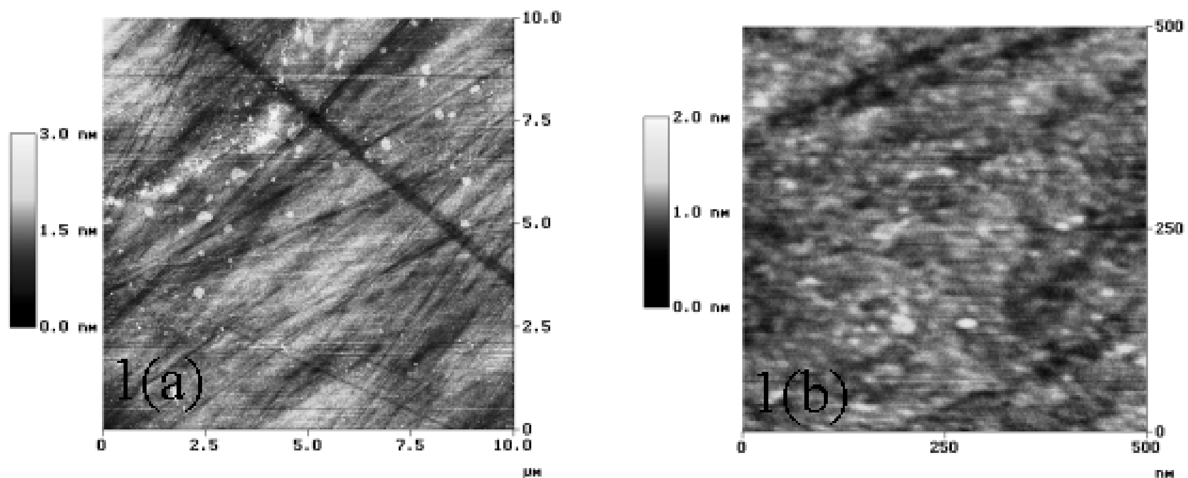

Figure 1. AFM images of sapphire surface (a) before etching, and (b) after etching in hot H_2SO_4: H_3PO_4 at 300 °C for 20 minutes.

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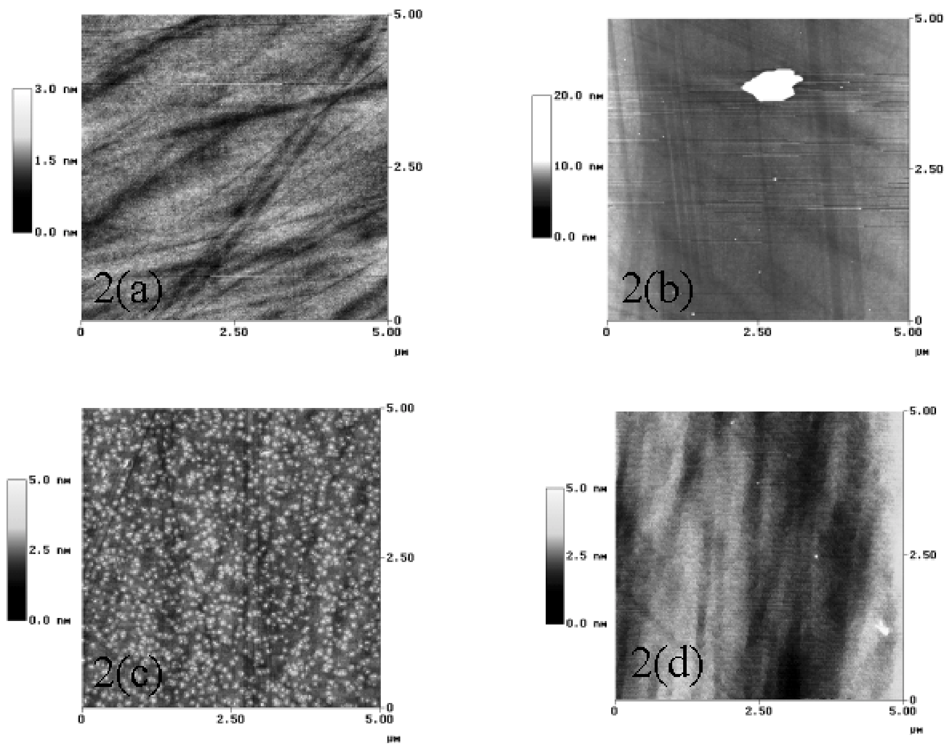

Figure 2. AFM images after annealing of sapphire for 30 minutes at (a) 1100°C; (b) 1200 °C; (c) 1300 °C; and (d) 1380 °C, respectively.

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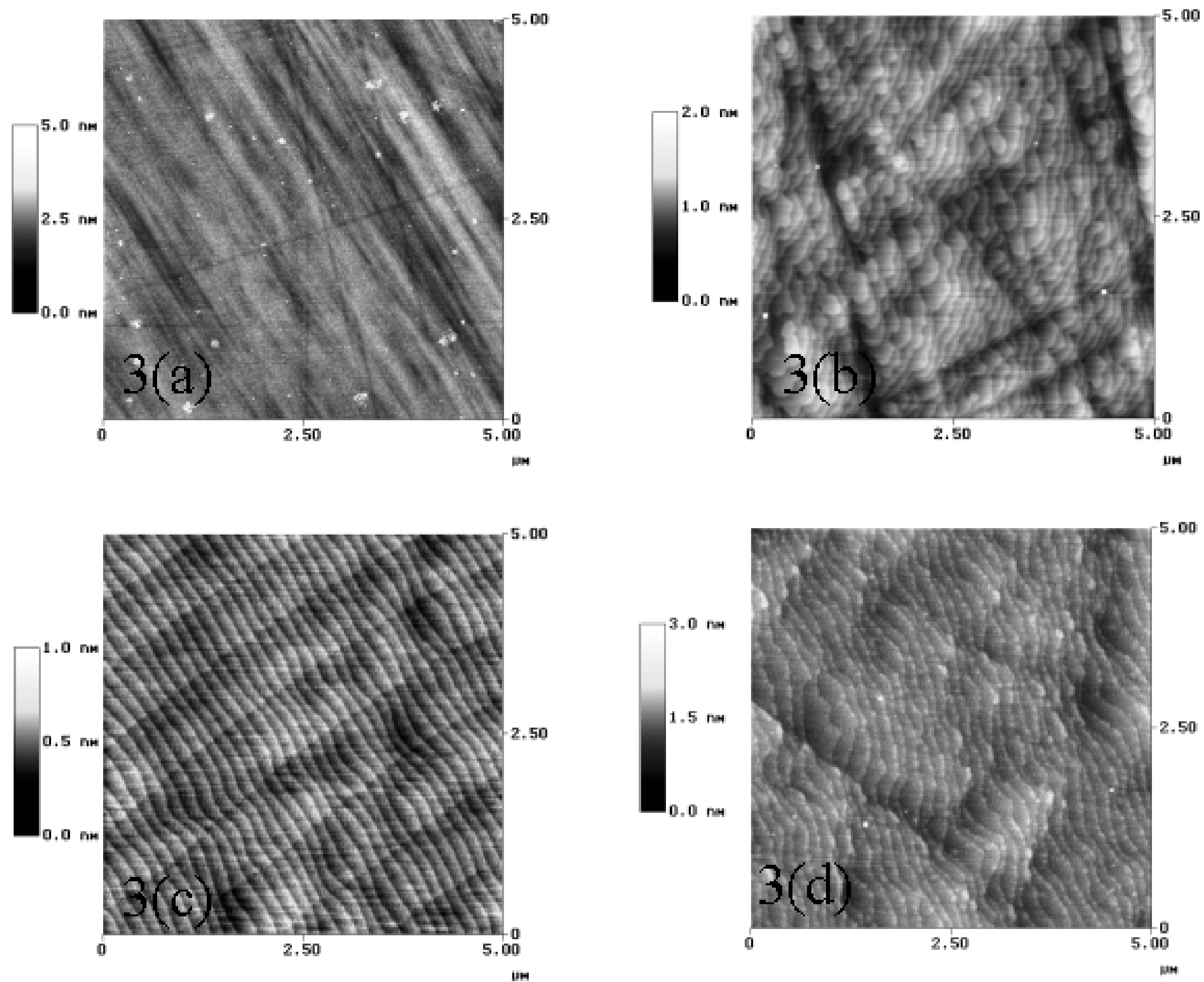

Figure 3. AFM images after annealing of sapphire for 1 hours at (a) 1000 °C; (b) 1300 °C; (c) 1380 °C; and for 3 hours at 1380 °C (d).

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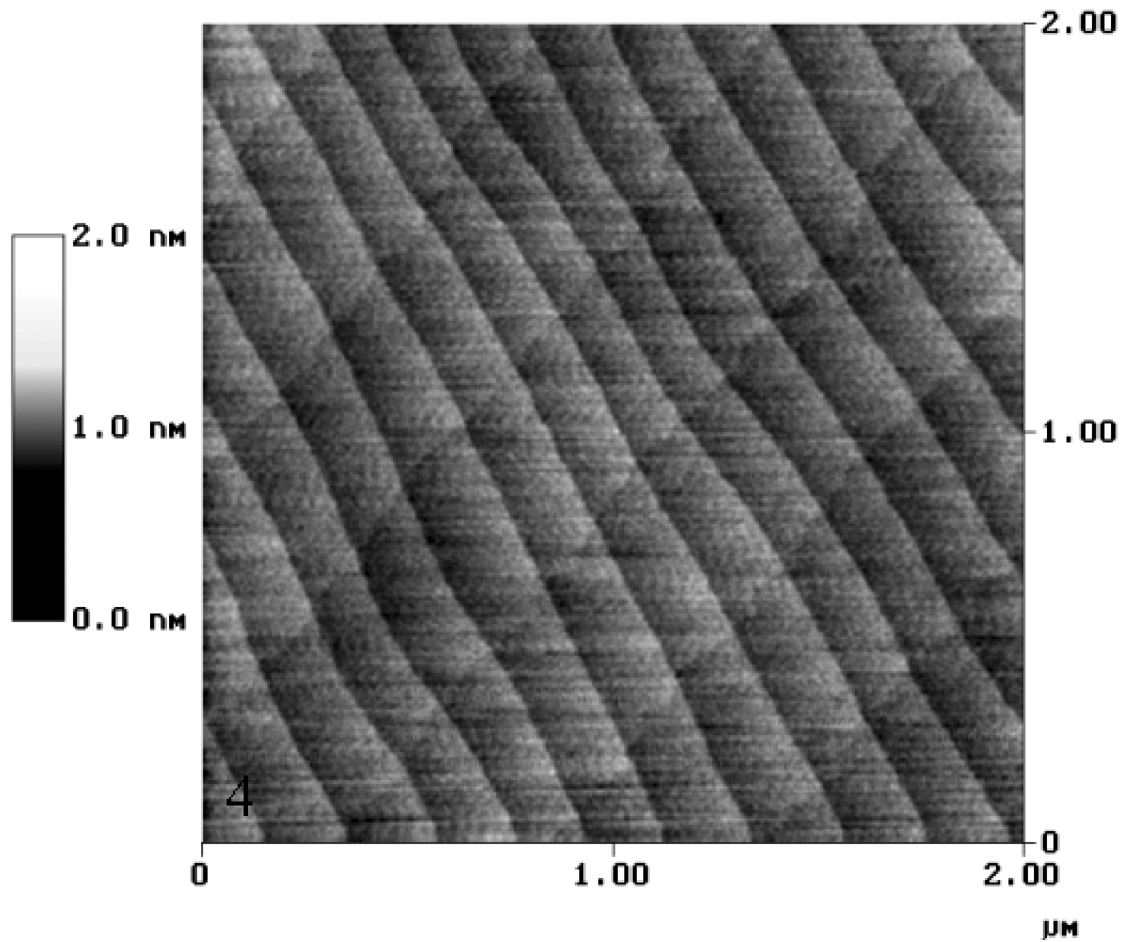

Figure 4. AFM image of sapphire annealed at 1380 °C for 1 hour showing terrace-like features with about 0.2 micrometer long terraces.

TABLES

Table 1. A list of X-ray rocking curves data in the samples.

Sample	Substrate	MBE	Thickness (µm)	X-ray[0 0 2] arc second	X-ray[1 0 4] arc second	X-ray[0 0 6] arc second
Sapphire substrate	Annealed sapphire				28	42
GaN SVT319	Un-annealed sapphire	RF	0.45	408	600	
GaN SVT389	Annealed sapphire	RF	0.98	69	252	
GaN R6385	Annealed sapphire	NH3	0.54	60	132	

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