Transmission electron microscopy study of semi-polar gallium nitride layer grown by hydride-chloride vapour-phase epitaxy on SiC/(001)Si heterostructure

L M Sorokin[1], A E Kalmykov[1], A V Myasoedov[1], V N Bessolov[1], A V Osipov[2] and S A Kukushkin[2]

[1]Ioffe Physical-Technical Institute, Russian Academy of Sciences, St. Petersburg, 194021 Russia

[2]Institute for Problems of Mechanical Engineering, Russian Academy of Sciences, St. Petersburg, 199178 Russia

aekalm@mail.ioffe.ru

Abstract. The structure of 10-µm-thick GaN layer grown by chloride vapour-phase epitaxy on 1.5-inch SiC/(001)Si templates has been investigated by transmission electron microscopy (TEM). The silicon carbide buffer layer has been fabricated by a new method of solid-phase synthesis. It was found that the GaN layer consists of oriented grains with size of tenths of a micron. The grains have wurtzite structure, and the {0001} GaN planes are oriented parallel to {111} Si, that is, the deviation of the axis c of GaN crystallite from the normal to the substrate is about 52°. The revealed epitaxial relationship between substrate and most grains is $(02\bar{2}3)$GaN||(001)3C-Si||(001)Si and $[2\bar{1}\bar{1}0]$GaN||[110]3C-SiC||[110]Si. Some inclusions of sphalerite gallium nitride were also found in the epilayer.

1. Introduction

GaN is a suitable material for high-performance green and ultraviolet light-emitting devices. But the luminous efficiency of the devices is low, because of the presence of electrostatic fields within the active layers which are generated by the spontaneous and piezoelectric polarization along the [0001] axis (c-axis) in wurtzite GaN grown along this c-axis [1]. This crystallographic orientation corresponds to the natural growth direction of GaN layer deposited on currently available substrates (silicon carbide, sapphire). One way of the field reduction is to grow GaN layers on semi-polar planes. Nonpolar and semi-polar GaN films are most frequently grown by methods of metalorganic chemical vapour deposition and molecular beam epitaxy on m-Al_2O_3 [2], $(11\bar{2}0)$4H-SiC [3] and (113)Si [4] substrates. Silicon is a promising material for GaN growth: there are the prospects for integration of the gallium-nitride and silicon electronics technologies and the possibility of using inexpensive single crystal silicon substrates, available in large diameters (> 200 mm). Furthermore, Si substrates have reasonable thermal and electrical conductivity. (001)Si substrate orientation is preferred as it is the one used in the silicon industry. Thus, for example, the growth process of semi-polar $(10\bar{1}2)$GaN on (001)Si offcut substrates with 3C-SiC buffer layers was realized by metal-organic vapour-phase epitaxy (MOVPE) [5]. Recently, the growth of semi-polar $(1\bar{1}01)$GaN has been attempted on a patterned (001) silicon substrate adopting selective area MOVPE [6]. The growth was initiated on

(111) facets of the Si, which had been prepared by anisotropic etching.

The aim of this study is to investigate orientation and structural quality of GaN layer grown on SiC/(001) Si template by the method of hydride-chloride vapour-phase epitaxy (HVPE).

2. Experimental details

A new method was used for synthesis of SiC buffer layer wherein the Si substrate itself is involved into the chemical reaction and the reaction product grows into the interior of substrate layer [7,8]. This method ensures the relaxation of arising elastic stresses during the growth.

To evaluate the layer microstructure TEM investigation was performed with a PHILIPS EM420 microscope operated at 100 kV. (011)Si oriented cross-sections were prepared by cutting and mechanical polishing followed by Ar^+ ion milling.

3. Results and discussion

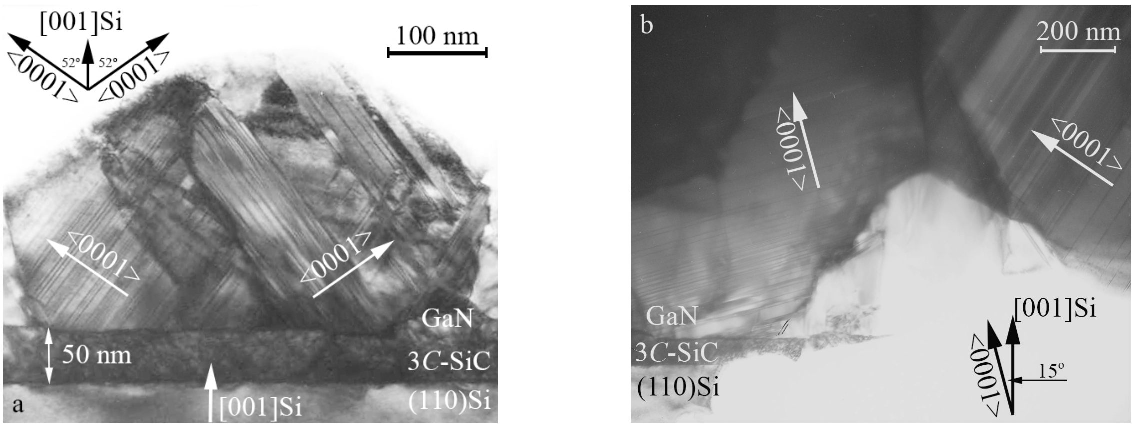

Figure 1. Cross-sectional TEM images of different areas of GaN/SiC/(001)Si heterostrucrure.

TEM study showed that the gallium nitride layer consists of individual grains of different orientations (figure 1). The sizes of grains are in the range of 0.1 - 10 μm. Grains contain basal plane stacking faults with a density varying from grain to grain within 2×10^5 - 3×10^6 cm^{-1}. Figures 2-4 show typical selected area diffraction patterns (DP) taken from the sample.

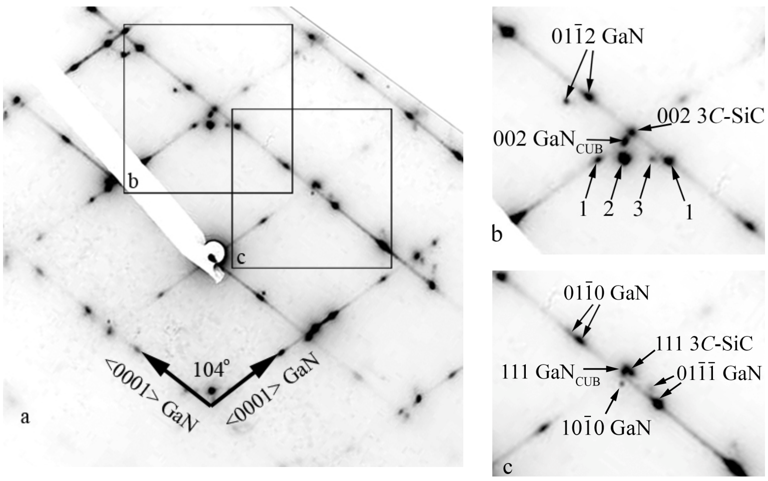

Figure 2. a: DP taken from the area shown in figure 1a; b, c: magnified photo of the DP outlined in figure 2a. In figure 2b the diffraction spots 1 and 3 correspond to wurtzite grains with common *a*-axis. *C*-axis of the grain giving the diffraction spot 1 is parallel to <111>Si. As to the grain giving diffraction spot 2, its *a*-axis does not coincide with [011]3*C*-SiC direction.

There are three groups of diffraction spots in the DPs which are the results of electron scattering by Si substrate, SiC buffer layer and GaN grains, respectively. Most GaN grains have a common zone axis, which coincides with the direction of the incident electron beam: [011]3*C*-SiC/Si is parallel to $[2\bar{1}\bar{1}0]$GaN. DP analysis has shown that the main part of GaN grains have wurtzite structure.

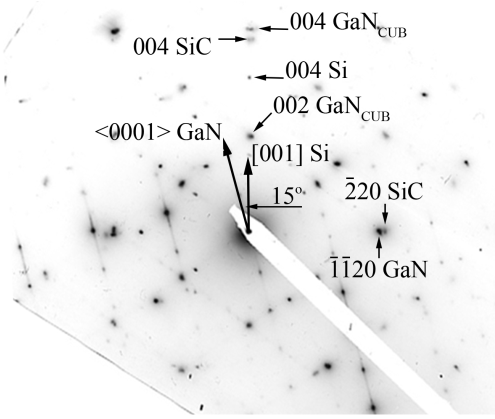

Figure 3. DP recorded from the area represented in figure 1b.

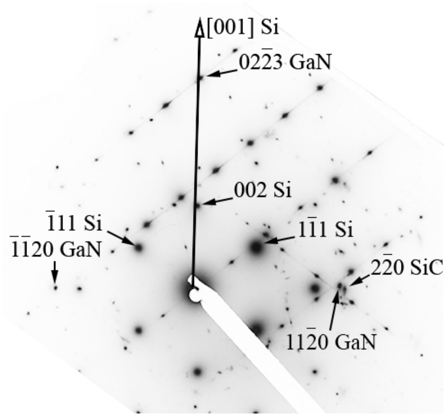

Figure 4. DP recorded from the interface area.

According to figures 2-4 the orientation of *c*-axis of most wurtzite grains coincides with <111> substrate directions and deviates from the normal to the substrate by an angle of 52°. Thus the orientation of the most grains is semi-polar and should be the same as GaN layer orientation in [6] where substrate masking and selective etching were used for (111)Si facets forming.

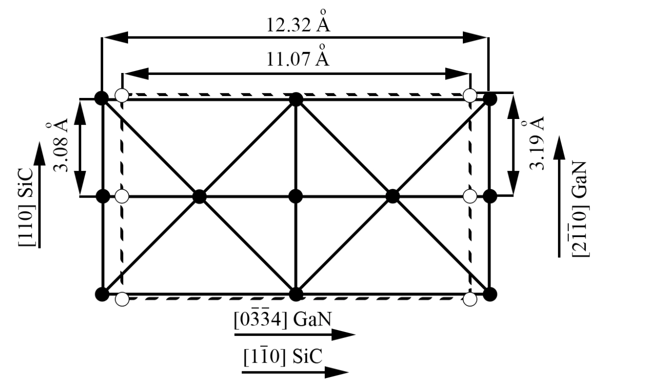

Figure 5. GaN layer and 3*C*-SiC buffer layer matching. The black circles mark SiC lattice points positions and the solid lines show the (001)SiC plane unit cell. The open circles mark GaN lattice points positions and the dashed lines show the (02$\bar{2}$3)GaN plane unit cell.

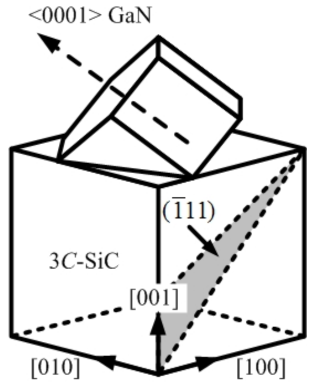

Figure 6. Schematic of grown semi-polar structure <111>SiC||<0001>GaN. The idea of the schematic belongs to [9].

Miller indices of the matching planes of the interface can also be determined by DPs. There is a 02$\bar{2}$3 diffraction spot marked in figure 4. Obviously this is the spot with the lowest index which lies on the [001] Si direction in reciprocal space. Accordingly, the matching planes are (02$\bar{2}$3)GaN and (001)SiC, and taking into account that $a = [2\bar{1}\bar{1}0]$ axis coincides with the [110] substrate the following epitaxial relationships were found for these grains: (02$\bar{2}$3)GaN || (001)3*C*-Si || (001)Si and $[2\bar{1}\bar{1}0]$GaN || [110]3*C*-SiC || [110]Si.

The lattice mismatch is only 3.5% in the silicon carbide [110] direction, although it is 10% in the $[1\bar{1}0]$ direction. Figures 5 and 6 show the experimental epitaxial orientation of GaN and SiC layers and a schematic of the heterostucture. [110] and $[1\bar{1}0]$ are two equivalent directions in the (001)SiC plane. Therefore there should also be GaN grains with the *c*-axis inclined from the normal of the substrate by rotating around $[1\bar{1}0]$ SiC at 52º. This is confirmed by the presence of $11\bar{2}0$ GaN diffraction spots in the DP, figure 3. Figure 6 shows only one of the four possible orientations of GaN grains relative to the substrate. All possible orientations of GaN grains in the figure can be obtained by rotating the schematic around [001]3*C*-SiC axis through 45°.

The *c*-axis of smaller part of GaN grains deviates from the normal to the substrate at an angle of 15° (figure 3). Similarly, it was found for these grains: $(01\bar{1}7)$GaN||(001)3*C*-Si||(001)Si and $[2\bar{1}\bar{1}0]$GaN||[110]3*C*-SiC || [110]Si. The lattice mismatch in the $[1\bar{1}0]$ SiC direction is 6%.

Occasionally, there are grains in the layer the *a*-axis of which is not parallel to the <011>3*C*-SiC direction. For example, the zone axis of the grain corresponding to diffraction spot 2 in figure 2 is $[\bar{4}\bar{1}53]$.

An adequate regular spot array has been found for each of the identified diffraction spots in the DP (figure 2). This enabled to identify these reflections reliably, which, in turn, allowed us to detect the presence of sphalerite gallium nitride (GaN_{cub}) by DP analysis (figure 2b,c). There are also well resolved 004 GaN_{cub} and 004 SiC diffraction spots in figure 3. Following the results of [5] it can be supposed that the thin sphalerite GaN layer, which may have been initiated by a cubic buffer layer, is initially grown with {111} facets, and then wurtzite GaN film was initiated on the {111} facets of sphalerite GaN. There is some tilt between the GaN_{cub} planes in the film and 3*C*-SiC planes (figures 2, 3). This tilt is due to small difference in lattice constants of GaN_{cub} film and 3*C*-SiC buffer layer.

4. Conclusions

For the first time, semi-polar GaN layer consisting of oriented grains has been grown by HVPE on 1.5-inch Si(001) substrate with SiC interlayer without any masking or etching. The *c*-axis of most wurtzite grains deviates from the normal to the substrate at an angle of 52°. Meanwhile, the GaN film suffers from high basal plane stacking fault density in comparison to the conventional *c*-plane GaN. This result enables us to hope that using offcut substrates will make it possible to fabricate single-crystal semi-polar GaN layers. It should be emphasized that HVPE allows us to grow thick (tens of micrometers) epilayers.

Acknowledgements

This study was supported by the Department of Physical Sciences of the Russian Academy of Sciences (programs “New Materials and Structures”), the Russian Foundation for Basic Research (project nos. 11-02-00496, 12-02-00935-a, 13-08-00074), the St. Petersburg Foundation for Support of Science and Education, the Skolkovo Innovation Centre (registration number 1110023) and in part by Ministry of Education and Science of the Russian Federation. TEM investigation was made on the equipment of the Joint Research Centre «Material science and characterization in advanced technology» (Ioffe Institute, St. Petersburg, Russia).

References

[1] Deguchi T et al. 1999 *Jpn J. Appl. Phys.* **38** L914–L916
[2] Baker T J et al. 2006 *Jpn. Appl. Phys.* 2 45 L154
[3] Wagner B P et al. 2006 *J. Crystal Growth* **290** 504
[4] T. Tanikawa et al. 2008 *Phys. Status Solidi C* **5** 2966
[5] Yoshihisa Abe et al. 2009 *Materials Science Forum* **600-603** 1281-1284
[6] Sawaki N and Honda Y 2011 *China Tech. Sci*. **54**: 38–41.
[7] Kukushkin S A, Osipov A V, Feoktistov N A Patent No 2008102398, filed on 22 January 2008
[8] Kukushkin S A and Osipov A V 2013 *J. Appl. Phys.* **113** 024909
[9] Romanov A E et al. 2006 *J. Appl. Phys.* **100** 023522