Microscopy of nitride layers grown on diamond

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Abstract. GaN films were grown on three different orientation diamond substrates: (001), (110) and (111). In all three cases the hexagonal GaN is grown with (0001) direction parallel to the surface normal, but otherwise matching to diamond in a different way. The appropriate orientational relationships are determined by selected area electron diffraction. Besides threading dislocations a high number of inversion domains (ID) were formed in some GaN films. The preparation of the diamond surface and the growth conditions proved to affect significantly the formation of crystal defects such as threading dislocations and IDs. Single polarity GaN films with a low density of dislocations were achieved for the optimized growth conditions. The highest quality GaN layers were grown on AlN buffer in which two crystalline variants were nucleated, but one of them was overgrown already in the thickness of the buffer layer.

1. Introduction
The application area of GaN and related materials is very wide covering the optoelectronic devices, sensors and transistors as well. By now the high temperature stable high power devices reached power values above 10 W/mm. In the operation of them the most difficult technical problem is the heat dissipation during their operation. For that purpose substrates with excellent heat conductivity are needed. One of the best candidates is diamond despite the limited availability and also the limited knowledge on the growth of GaN on diamond.

Very few nitride growth experiments are known on diamond. Probably the first MOCVD (Metal Organic Chemical Vapour Deposition) growth experiment of Hageman et al. [1] was carried out on single crystalline diamond and resulted in poor quality GaN. However, overgrowing the GaN by HVPE (Hydride Vapour Phase Epitaxy) the quality improved substantially. Dreumel et al. grew also polycrystalline GaN on nanocrystalline diamond/Si template [2]. Recently the same group could grow oriented GaN crystals on polycrystalline diamond substrates [3].

This paper describes the microstructure of GaN grown on diamond single crystals by molecular beam epitaxy (MBE) with nitrogen RF plasma source [4]. The nitridation of diamond influenced the quality of the grown layers and that is discussed as well.
2. Experimental

GaN layers with the thickness about 1 µm were grown on diamond single crystals by molecular beam epitaxy with nitrogen RF-plasma source. A thin AlN layer was initially grown as the nucleation layer on diamond. In some of the growth experiments the diamond surface was nitrided before initiating the III-nitrides growth. The temperature of nitridation was varied from 125°C to 750°C, while the duration time was varied from 1 minute to 60 minutes. The single crystalline diamond substrates were 5x5 mm² large and prepared by Element6 (www.e6.com) in three different orientations (100), (110) and (111).

The grown structures have been characterized by transmission electron microscopy (TEM) on cross sectional specimens prepared by Ar ion milling. The sample preparation process itself was long because of the cutting by a special saw in which a rotating Mo disc was fed with diamond paste from a small container placed below the disc. Bright field, dark field images and selected area diffraction patterns were taken in a Philips CM 20 microscope working at 200 keV, while high resolution images were taken in a JEOL 3010 electron microscope at 300 keV. Some of the high resolution work was done on an FEI Titan microscope on which also EDS (Energy Dispersive X-ray Spectroscopy) spectra were taken on line scans.

3. Results

The GaN film grown on (100) diamond is shown in Fig. 1. (Here we have to note, that the surface of the grown GaN layer was chemically etched to determine its polarity.) The cross section shows a few dislocations and a lot of inversion domains (ID). Fig. 2 shows the appropriate selected area diffraction pattern.

For (100) diamond the grown GaN is composed of two different domains having a common 0002 direction and matching like either (1120)GaN//(022)diamond, or (1010)GaN//(022)diamond. In the case of (110) and (111) oriented diamond substrates single crystalline GaN was grown successfully. In all three cases the hexagonal GaN was grown with its (0001) direction parallel to the surface normal, but otherwise matching to diamond in a different way.

Further investigation of samples by high resolution microscopy revealed that the inversion domains were formed at the AlN/diamond interface (Fig.3). Otherwise the AlN buffer was homogeneous in thickness.
The image shows, that there are already IDs in the buffer layer as well. Consequently those were formed already on the surface of (001) diamond.

In the next set of experiments the surface preparation of diamond was modified and also thicker AlN buffer layers were grown. The next image (Fig. 4) shows the top region of a nitride structure, which was grown on (100) diamond nitrided prior to the AlN growth at 750°C for 30 minutes.

The preparation of the diamond surface and the growth initiation conditions proved to affect significantly the formation of crystal defects such as threading dislocations and IDBs. Single polarity GaN films were achieved at the optimized growth conditions.
It is well visible in Fig. 5 that the growth of AlN starts with two variants both epitaxially oriented to the (100) face of the substrate. One of the variants is locally overgrown by the other one in the first 12-15 nm of the nucleation layer. This was observed for the other investigated diamond substrate orientations as well. However, in this particular case of (100) diamond, the thick GaN was still composed of two variants rotated by 30 degree around their (0002) axis (like the case shown in Fig. 2). The interface looks atomically smooth and sharp, no intermediate layers could be observed. This observation together with the EDS line scans exclude the formation of C$_3$N$_4$ phase, which was observed by Kusunoki et al. [5], in their nitrogen implantation experiments. That may be attributed to the absence of energetic nitrogen ions in the nitrogen beam impinging the diamond surface.

4. Conclusions

In conclusion, it was shown that hexagonal GaN was grown successfully onto single crystalline diamond of all three orientations. The high density of inversion domains (and threading dislocations) was successfully reduced by the optimization of the growth conditions.

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