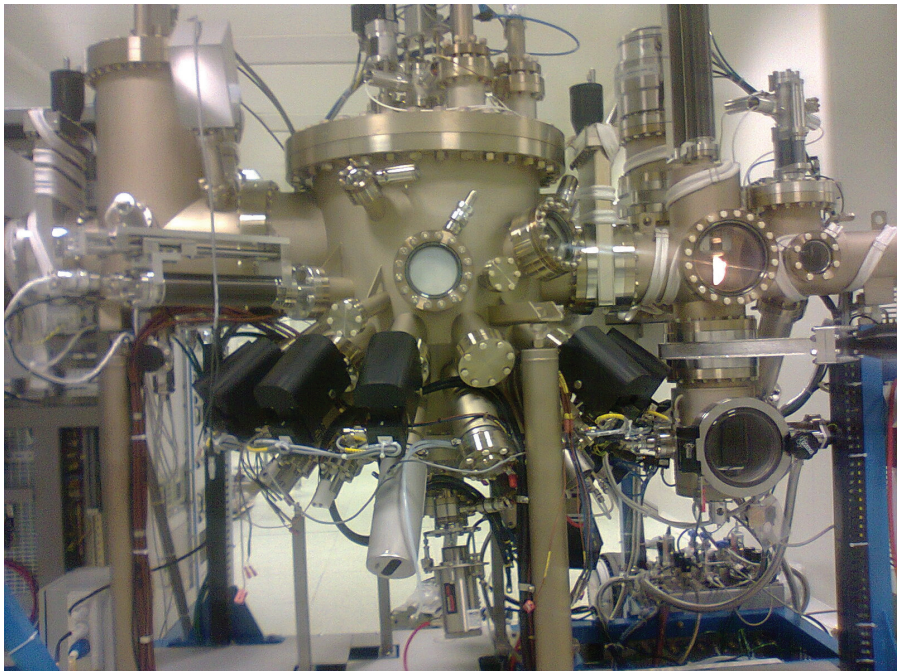


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N-IBCELL



## RECORD (7.7%) OF B INCORPORATION INTO GAN BY MOLECULAR BEAM EPITAXY

RO14-0010, 2014-2017

The first step in attending the objective 3: "The growth and characterization of device-quality  $B_{1-x}Ga_{1-x-z}N/GaN$  alloys with diluted boron and low indium contents ( $z \leq 5\%$ ,  $x < 20\%$ ) and strained engineered  $In(Ga)N/BInGaN/InGaN$  QDs array for IBSCs applications." is presented in this material and published first under the same title by E.-M. Pavelescu<sup>1)</sup>, O. Ligor<sup>1)</sup>, M. Danila<sup>1)</sup>, F. Comanescu<sup>1)</sup>, R. Gavrilă<sup>1)</sup>, M. Dinescu<sup>1)</sup>, M. Carp<sup>1)</sup>, S. Zolud<sup>2)</sup>, R. Kudrawiec<sup>2)</sup> at 19<sup>th</sup> International Conference on Molecular Beam Epitaxy, 4<sup>th</sup>–9<sup>th</sup> September 2016, Le Corum, Montpellier, FRANCE.

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## INTRODUCTION

The full potential of III-nitride materials is hampered by the lack of suitable substrates. The lattice constant and thermal expansion coefficient mismatch usually lead to a high dislocation density, mosaic crystal structure, biaxial stress, and wafer bonding. Introduction of boron might be one of the possible solutions to mitigate the problems. Characteristics of BGaN alloys are expected to be similar to those of InGaN and AlGaN materials with the additional advantage of a better lattice-matching to AlN and SiC substrates. Moreover, the lattice constant of BGaN with boron content in the range of up to 12% is expected to match the lattice constant of AlGaN in the entire range from GaN to AlN.

Boron-containing GaN alloys have mainly been grown so far by MOCVD [1,2] but, unfortunately, the amount of the incorporated B by this technique appears to be limited  $< 6\%$ . This limitation appears to be related to a miscibility gap of B incorporation into GaN material which cannot be easily circumvented by this growth technique, as it promotes growth close to thermodynamical equilibrium.

# RECORD (7.7%) OF B INCORPORATION INTO GaN BY MOLECULAR BEAM EPITAXY

The project, N-IBCell, aims to fabricate high efficiency intermediate band solar cells (IBSCs). These are solar cells design to absorb also below bandgap energy photons by means of an electronic energy band that is located within the host semiconductor bandgap, producing thus enhanced photocurrent while ideally maintaining the photovoltage given by the host photovoltaic material bandgap.

Hence, another growth technique may be used with better results. It is well known that lowering growth temperature is a useful way to alleviate the theoretical (based on thermodynamics) miscibility gap of a constitutive element of an alloy. This suggests that MBE could be a better alternative [3,4] compared to MOCVD for growing BGaN alloys with higher B contents. Indeed, using MBE and an e-beam evaporator as boron source up to 3.5% of boron was recently incorporated into GaN, hinting towards an alternative source for boron.

## EXPERIMENTAL

Growth of (B)GaN epitaxial films was performed on (0001) sapphire with  $<0.2^\circ$  miscut using a Riber Compact 21DZ MBE system equipped with an automated nitrogen RF plasma source supplied with ultra-high purity 7N nitrogen further purified by an in-line filter. The plasma discharge power was 500 W and the nitrogen flows were 1.4 and 2.2 sccm, corresponding to 20 and 60 nm/h GaN nominal growth rates during deposition of the BGaN epilayer and GaN buffer, respectively. 7N5 Gallium was evaporated from a dual filament Knudsen cell. The growth was performed on a quarter cut from a 3" wafer, degreased in solvents and backside metallized with 50 nm titanium and mounted on a 4-inch molybdenum block. High-purity 6N boron was evaporated from an e-TUBO cell from Createc heated to 1550°C. Epitaxial growth was initiated by first exposing the sapphire substrate at 370°C (Tch) to N plasma (500W/1,5 sccm) for 15 min. Then the temperature was raised at 550°C (Tch) in 10 min for growth of the GaN (465°C by pyrometer) and BGaN (500°C by pyrometer) layers. The crystal quality and boron content was examined using high resolution X-ray diffraction

(HRXRD, Rigaku SmartLab). The surface properties were studied by atomic force microscopy (AFM). Photoluminescence was recorded using a 50 mW CW 266 nm laser for excitation and an UV-enhanced PMT detector from Hamamatsu for collection. Raman spectra were collected using a Horiba LabRam HR 800 spectrometer.

## RESULTS AND DISCUSSION

The AFM image taken from the BGaN surface is presented in figure 1. The surface roughness is around 10 nm, close to that previously seen for BGaN on AlN/sapphire templates [1].

Figure 2 shows an XRD  $2\theta$ - $\omega$  scan (continuous black line) of the (0002) reflection of (B)GaN grown on sapphire. Also shown is a simulation (continuous blue line) of the BGaN/GaN/sapphire assuming 7.7% of B into BGaN as well as 21 and 28 nm for BGaN and GaN layers, respectively. The lack of reflectivity fringes in the diffraction curve is likely due to the lower temperature used for (B)GaN growth (to promote higher B uptake) and subsequent deterioration of surface/interfaces, as seen in Figure 1. Knowing that the highest ever reported boron content of 7% in BGaN [5] film was obtained using ion implantation, it appears that the reported 7.7% boron concentration is a current record for any epitaxial techniques.

Figure 3 shows room-temperature photoluminescence (PL) recorded from the investigated sample and from a commercial GaN/AlGaN-based buffer/sapphire sample from NTT-AT Japan, for comparison. Beside the shoulder at 365 nm, related to the GaN buffer beneath, one can observe two other peaks at 388 and 407 nm, which can originate from the BGaN layer, taking into account the expected bandgap shrinking of GaN with incorporation of boron.

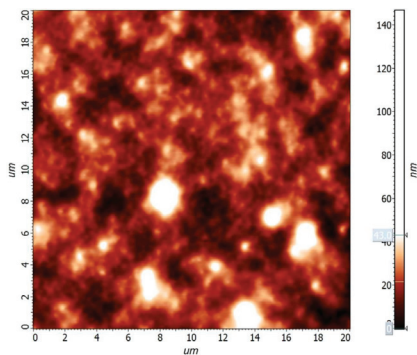


Fig. 1. AFM picture 20x20 nm<sup>2</sup> taken from the B GaN surface after growth

Raman spectra taken from different location of the samples (for example: a black spot on the Raman confocal optical microscope – red line). Besides the characteristic lines of the GaN  $E_2(H)$  and  $A_1(LO)$ , whose intensities drastically diminished in B GaN/GaN/sapphire sample (see 488 nm excitation), other unidentified peaks appeared at 292.7, 504.5, 921.7, 1369.4 and 1399.8 cm<sup>-1</sup> (633 nm excitation) and at 518.1 cm<sup>-1</sup> (488 nm excitation). The identification of these lines will be the subject of further investigations.

## SUMMARY

B GaN/GaN on sapphire substrate with record content of boron of 7.7%, as derived from X-ray diffraction measurement, was grown by molecular beam epitaxy equipped with nitrogen RF plasma source and a special Knudsen cell for solid boron evaporation. Longer wavelength emission peaks as compared to GaN bandedge emission were seen in the photoluminescence spectrum whereas several lines appeared in the Raman spectra, besides the Raman characteristic peaks of the GaN layer.

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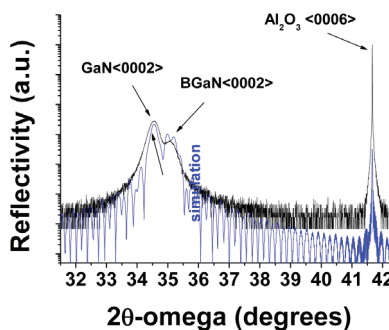


Fig. 2. X-ray diffraction curve (black line) of the B GaN/GaN/sapphire heterostructure together with a simulation of the grown structure (blue)

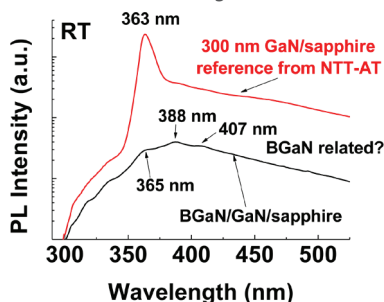


Fig. 3. RT photoluminescence of the investigated B GaN/sapphire sample and of a reference GaN/sapphire sample grown by MOCVD at NTT-AT.

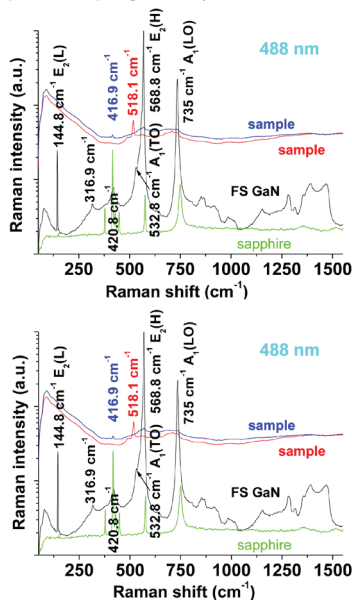


Fig. 4. Raman spectra taken at RT at two excitation lines (633 and 488 nm) from different locations on the surface of the B GaN/GaN/sapphire sample