



# Ion beam modification of the structure and properties of hexagonal boron nitride: An infrared and X-ray diffraction study



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## ABSTRACT

The vibrational mode for the cubic symmetry of boron nitride (BN) has been produced by boron ion implantation of hexagonal boron nitride (*h*-BN). The optimum fluence at 150 keV was found to be  $5 \times 10^{14}$  ions/cm<sup>2</sup>. The presence of the *c*-BN phase was inferred using glancing incidence XRD (GIXRD) and Fourier Transform Infrared Spectroscopy (FTIR). After implantation, Fourier Transform Infrared Spectroscopy indicated a peak at 1092 cm<sup>-1</sup> which corresponds to the vibrational mode for nanocrystalline BN (*nc*-BN). The glancing angle XRD pattern after implantation exhibited *c*-BN diffraction peaks relative to the implantation depth of 0.4 μm.

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## 1. Introduction

The unique characteristics exhibited by cubic boron nitride [1–5] have led to a great deal of research with an aim of synthesizing it under less extreme conditions of pressure and temperature. Previous work has shown evidence that the cubic phase could be induced from the hexagonal BN (*h*-BN) phase by the ion implantation process and was identified primarily by Raman Spectroscopy [6,7]. The Raman spectroscopy after implantation showed additional phonon peaks at wavenumbers between 1295 cm<sup>-1</sup> and 1303 cm<sup>-1</sup> which were assigned to the *sp*<sup>3</sup> phonon mode for *c*-BN phase together with the *h*-BN principal peaks at 1366 cm<sup>-1</sup>. The ion implantation process also offers the advantage of creating thin hardened layers under the surface of a previously shaped component. In this additional techniques were used to analyze the implanted *h*-BN to further corroborate the results from [7,8].

Fourier Transform Infrared Spectroscopy and Glancing incidence X-ray diffraction were used here to analyze the *h*-BN samples before and after implantation to establish the presence of *nc*-BN. FTIR was applied in order to identify the local structural order, functional groups and composition of the sample before and after implantation as it is sensitive to the local hybridization of the *sp*<sup>2</sup> and *sp*<sup>3</sup> phases of BN [9]. GIXRD is used to understand the morphology of the crystal structure. We use glancing angle in contrast to the conventional XRD because of its depth profiling

capabilities since the implanted layer extends from the surface to a few hundred nanometres below the sample surface [10].

## 2. Experimental

### 2.1. Sample and sample preparations

The *h*-BN samples which were used throughout this experiment were hot pressed polycrystalline sheets supplied by the Goodfellow Cambridge Company, England, with dimensions of  $5 \times 5 \times 0.2$  mm<sup>3</sup> and 99.9% purity. The samples were prepared by reaction of boric acid with urea followed by sintering using boron oxide and subsequent machining. The samples were cut using our Model 3032 Diamond Saw to a thickness of 0.1 mm and mechanically polished down to 0.05 mm on the side that was cut by the diamond wire saw. The implantation was performed on the original hot pressed surface of the sample.

### 2.2. Ion implantation

A Varian 200-20A2F ion implanter located at iThemba LABS (Gauteng), in Johannesburg, was used for the implantation experiments. All implants were done at room temperature using B<sup>+</sup> at energy of 150 keV at a dose rate of  $\approx 10^{13}$  ions/s. The B<sup>+</sup> ions were obtained from boron trifluoride gas ionized in the ion source chamber of the ion implanter and selected by the implanter's mass analyzer magnet. Analyses of the samples were carried out before and after implantation using the Bruker TENSOR 27 Fourier Transform

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Infra-red spectrometer and the D8 ADVANCED Bruker X-ray Diffractometer at the University of the Witwatersrand. The X-ray diffractometer was set to operate at a voltage of 40 kV and 40 mA current. Measurements were carried out in the  $2\theta$  mode at glancing incident angles ranging from  $0.01^\circ$  to  $0.5^\circ$  from  $2\theta = 20^\circ$  to  $90^\circ$  in steps of  $0.05^\circ$  per second. The  $\text{CuK}\alpha$  anticathode with wavelength of  $1.5406 \text{ \AA}$  was used to perform all the XRD measurements.

### 3. Results and discussions

#### 3.1. Fourier Transform Infrared Spectroscopy (FTIR)

Fig. 1(a) represents the FTIR transmission spectrum for the sample before implantation. The spectrum shows two distinct modes at  $778 \text{ cm}^{-1}$  and  $1374 \text{ cm}^{-1}$ . These vibrational modes have been attributed to the  $sp^2$  bonded  $h$ -BN. The mode at  $778 \text{ cm}^{-1}$  represents the  $A_{1u}$  out-of-plane bending vibration while the mode at  $1374 \text{ cm}^{-1}$  is the  $E_{1u}$  in-plane stretching vibration for  $h$ -BN also observed by [11]. There were no other modes visible in the unimplanted spectra.

After implantation, the  $A_{1u}$  and  $E_{1u}$  mode were still visible but they show a frequency shift to higher wavenumber of  $784 \text{ cm}^{-1}$  and  $1382 \text{ cm}^{-1}$ , respectively after implantation. The peak shift to higher wavenumbers implies that there is compressive stress accumulation in the material as a result of radiation damage caused by the implantation [12].

Together with the  $h$ -BN vibrational modes, another phonon peak is observed at  $1092 \text{ cm}^{-1}$  (arrowed) in Fig. 1(b) after implantation. This peak has been observed to represent the TO mode for  $sp^3$   $nc$ -BN [13]. The frequency mode of the  $c$ -BN is dependent on the particle size, impurity level and the stress level in the material [14]. For  $c$ -BN with no internal stress, the peak is centred at  $1000 \text{ cm}^{-1}$  [15]. For bulk samples with residual compressive stress, the peak occurs at  $1050 \text{ cm}^{-1}$  and as the crystal size decreases to a nanoscale, the peak shifts to higher wavenumbers of between  $1090 \text{ cm}^{-1}$  and  $1120 \text{ cm}^{-1}$  [16]. From this information, it is suggested that  $nc$ -BN particles or regions are formed in the implanted layer complementing the Raman results reported in [8].

Also observed is a slight split of the  $h$ -BN  $E_{1u}$  mode after implantation forming another peak centred at  $1388 \text{ cm}^{-1}$ . We tentatively attribute this mode to the rhombohedral/ $r$ -BN vibrational mode which may have been induced due to the distortion of the  $h$ -BN lattice as a result of the radiation damage created during the implantation [17]. An additional feature is also observed at  $938 \text{ cm}^{-1}$  whose origin is unknown.

A fluence dependent analysis at  $150 \text{ keV}$  was carried out on the samples by implanting them with boron at various fluences to investigate the effect of varying the defect density in the implanted layer. We assume that little or no self annealing takes place during the implantation process and hence increasing the dose increases the damage density in the implanted region.

The fluence dependence of the TO mode for the  $nc$ -BN production is shown in Fig. 2. In the spectra the  $h$ -BN modes have been cut off so as to bring the peak associated with  $nc$ -BN to a clear view. The peaks are centred at  $1098 \text{ cm}^{-1}$ ,  $1092 \text{ cm}^{-1}$  and  $1105 \text{ cm}^{-1}$  for the respective fluences. The integrated peak intensity shows the highest intensity of the TO mode at  $5 \times 10^{14} \text{ ions/cm}^2$  and decreased when the dose was increased to  $1 \times 10^{15} \text{ ions/cm}^2$ .

Fourier Transform IR transmission intensities have been used to obtain the estimated amount of  $c$ -BN in a hexagonal-cubic mixed phase sample. This has been achieved using intensities of the peaks as indicated in the equation below [18]:

$$\%(c\text{-BN}) = \frac{I_{c\text{-BN}}}{(I_{c\text{-BN}} + I_{h\text{-BN}})} \times 100 \quad (1)$$

where  $I_{c\text{-BN}}$  is the integrated transmission intensity for  $c$ -BN for the respective wavenumbers in the mixed phase and  $I_{h\text{-BN}}$  is the integrated intensity for the  $h$ -BN principal peak before implantation at  $1374 \text{ cm}^{-1}$ .

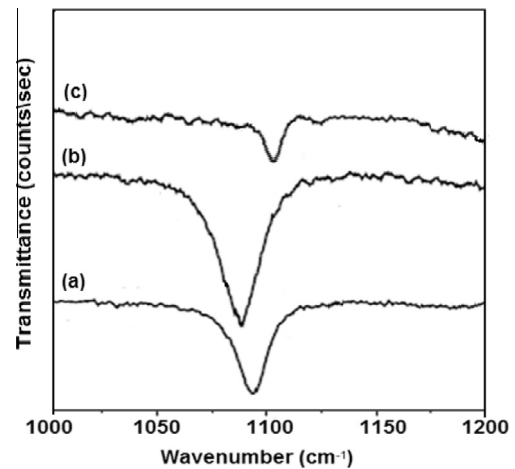


Fig. 2. FTIR spectrum for samples implanted at (a)  $1 \times 10^{14} \text{ ions/cm}^2$  (b)  $5 \times 10^{14} \text{ ions/cm}^2$  and (c)  $1 \times 10^{15} \text{ ions/cm}^2$ .

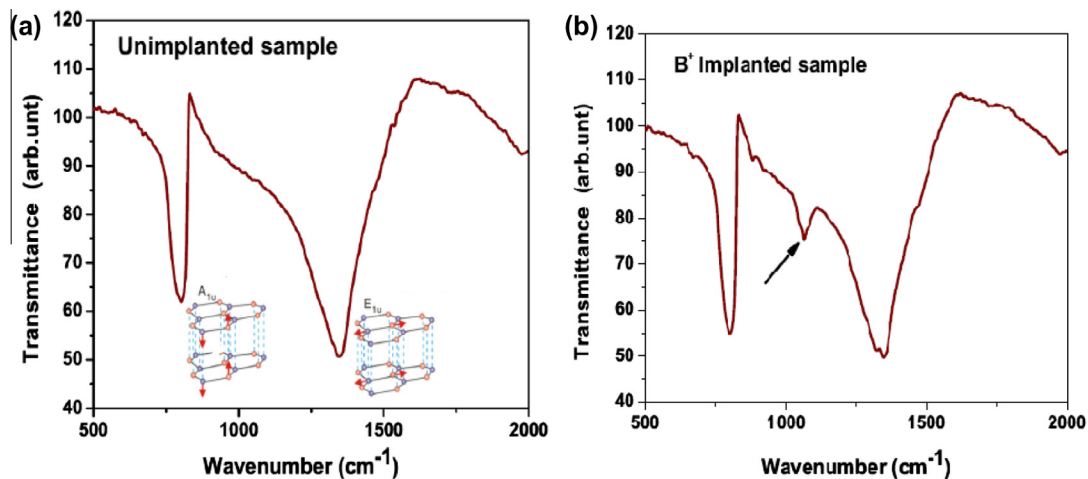


Fig. 1. Fourier Transform Infrared spectrum for (a) unimplanted  $h$ -BN and (b)  $h$ -BN implanted with boron ions at  $5 \times 10^{14} \text{ ions/cm}^2$  at  $150 \text{ keV}$ .

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