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Boron Nitride (BN) shows similarities to carbon, with a hexagonal (graphite-like) structure (hBN) and a cubic diamond type (cBN). Under ambient temperature conditions, hBN transforms irreversibly into wurtzitic BN (wBN) at pressures above 10.8 GPa [1]. We investigated the influences of ion irradiation on this displacive phase transition using synchrotron X-ray diffractometry (XRD) at the ID27 high pressure beamline of the ESRF, Grenoble, France. Powder samples of hBN were irradiated with swift heavy ions prior as well as during pressurization. In order to test the phase transation to wBN, and to record data of the equation of state, we pursued measurements from ambient pressure up to more than 1 Mbar. We could clearly show an irradiation dependent behaviour of the hBN $\rightarrow$ wBN phase transition.

Experimental

We investigated two species of powder samples (Sigma Aldrich): Specimens, which were irradiated under vacuum and ambient temperature conditions, and specimens, which were irradiated in a pressurized state. The former were irradiated at the linear accelerator UNILAC, and the latter were exposed to ion irradiation at the heavy ion synchrotron SIS-18. Both accelerators are constituents of the GSI Helmholtz Centre for Heavy Ion Research.

Concerning the strongly non-linear energy loss behaviour of energetic charged particles in matter, we set the initial ion energies in such a manner, that the energy loss maximum was within the sample. Therefore, ions with energies of 11.1 MeV/u were applied for vacuum conditions, whereas those ions, which were applied for samples under high pressure, possessed energies of up to 250 MeV/u in order to interpenetrate the first diamond of the DAC. Furthermore, the samples were exposed to ion fluences ranging from 0 up to 1×10^{12} ions/cm^2 (Table 1).

Pressure / GPa	Fluence / (10^{11} ions·cm^{-2})
10^{-8}	0
10^{-8}	5
10^{-8}	10
9.7	5
13.5	5
22.0	5
28.4	5
28.6	10
29.4	1

Table 1: Investigated samples, their initial pressure, and the irradiation quantity. Both were applied simultaneously.

For the pressure measurements we used ruby crystals to be read out via fluorescence spectroscopy. Rhenium as well as stainless steel served as gasket material. Pressure transmitting medium was a mixture of methanol and ethanol (4:1) for the samples with pressure up to 13.5 Gpa. The specimens with the four highest pressures were not embedded in pressure transmitting medium. After each step of pressure increase, the sample was allowed to relax for 1 hour before recording XRD data.

The XRD data collection on beamline ID27 was carried out by a MAR345 IP detector. The wavelength of the X-ray beam (focussed on 6×15 m) of λ = 0.37 Å was kept constant.

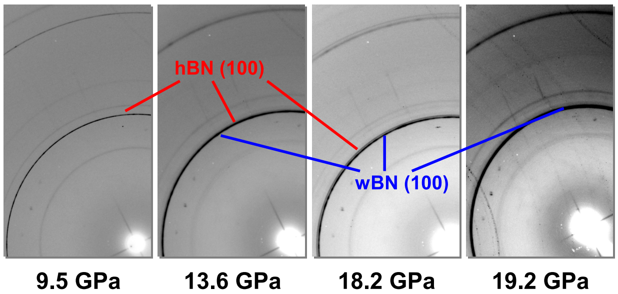

Figure 1: Recorded XRD patterns of irradiated BN powder samples, documenting the phase transition from hBN to wBN.

Results and Discussion

We integrated our recorded diffraction data (Figure 1) using the Fit2D application, and investigated the intensities as well as the positions of the reflexions. Though a significant alteration in the equation of state between pristine and irradiated samples could not be resolved, we measured obvious changes in the transformation behaviour from hBN to wBN. Figure 2 exemplarily depicts the characteristics of the (100) reflection over the determining pressure range. The intesity of the hBN reflection is normalised on the sum of both hBN and wBN. No traces of the wurtzitic phase were detected up to a pressure of 10.8 GPa, indicated by a constant value of "1" for all specimens. At the critical transformation pressure, all samples showed sharp decrease of the hBN reflections and simultaneous rising of the wBN intensities. However, the difference between highly irradiated, less irradiated, and non-irradiated samples emerges in the region of saturation beyond 13 GPa. The virgin sample as well as that exposed to 5×10^{11} Au ions per cm^2 show fractions of hBN up to 20 GPa. Only the sample, which was irradiated with 1×10^{12} Au ions per

cm^2 showed the completion of the transition to wBN at a pressure of 18 GPa.
Hence, these findings were reproduced using Raman spectroscopy on hBN single crystals. Our data clearly demonstrate that the irradiation of hBN with swift heavy ions prior to pressurization enhances the hBN to wBN phase transition. The transformation is more or less complete depending on the applied fluence. The effect is ascribed to damage creation inducing a buckling of the basal planes in hBN [3].
Acknowledgment. Provision of BN single crystals by T. Taniguchi is gratefully acknowledged.

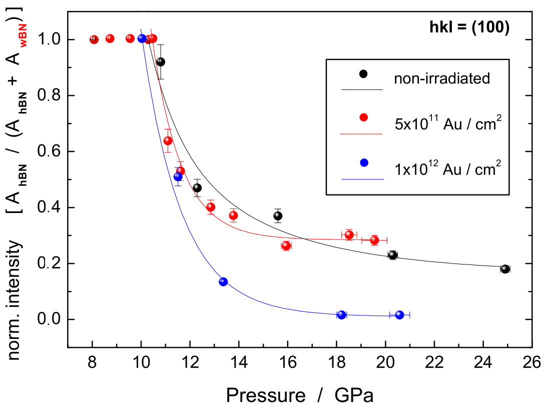

Figure 2: Normalized XRD intensities of (100) reflection of hBN compared to wBN as a function of pressure. Unity corresponds to pure hBN, zero indicates pure wBN.

References

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