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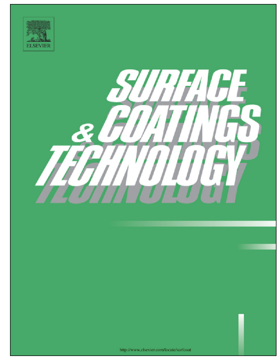

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Allotrope Conversion and Surface Hardness Increase in Ion Implanted Boron Nitride.

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Abstract.

Previously, it has been shown that the implantation of hexagonal boron nitride with light ions (e.g. He^+, Li^+, B^+) produces a surface layer containing nanoparticles of the much harder cubic form, as revealed by Raman spectroscopy, X-ray diffraction and electron microscopy. The present study shows that the irradiated layer is measurably harder when interrogated by micro-indentation which probes a layer comparable to the ion range. The hardness value increases reproducibly with the ion fluence, confirming that the latter is responsible for it. There are possible implications for the surface hardening of BN components after they have been configured in the easily machinable hexagonal form. Some aspects of the hardening mechanism are discussed.

Keywords: boron nitride, hardening, ion implantation

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1. Introduction.

Boron nitride is a useful material in both its hard cubic and soft hexagonal crystalline allotropes. With its elements bracketing carbon in the Periodic Table, it has structures analogous to diamond (cubic) and graphite (hexagonal), although c-BN is the stable form at ordinary pressures. The latter's hardness is second only to diamond and it is less reactive in machining applications with ferrous alloys.

Cubic BN is synthesized in industrial quantities under pressure, but it has been shown that the implantation of light ions into h-BN can trigger a phase change to c-BN, which forms a thin layer of nanoparticles (9nm) within the implanted region. From Raman, X-ray and infrared analyses [1-5] there is an optimum ion fluence for He^+, Li^+, B^+ and N^+ which decreases as the ion mass increases. The creation of interstitial defects is thought to tip the structure from hexagonal layers to the tetrahedral cubic form.

Apart from the inherent interest, one can envisage improving components fabricated from polycrystalline h-BN (easily machinable) by creating a hard layer of c-BN just under the surface. However, for engineering applications one wishes to answer the questions: is it harder? Can one measure this using the mechanical technique of indentation testing? Is it too shallow to be useful?

It is problematic to relate results from shallow nano-indentation testing to real engineering situations, which may disturb the surface region to depths of micrometres. However, according to SRIM simulations [6], the penetration depth of 150 keV light ions into h-BN is a few hundreds of nm (e.g. 400 nm for B^+ and 800 nm for Li^+) which puts it within the range of the more applicable micro-hardness testing; e.g. for a 100 g load, a Vickers indenter penetrates about 20 μm.

2. Experimental Methods.

2.1. Sample preparation

A hot pressed polycrystalline hexagonal boron nitride (h-BN) sample in the form of a rod (50 mm long and 15 mm in diameter) supplied by Goodfellow Cambridge Ltd. was used. It was cut into 2 mm thick slices using a well 3032 Diamond Wire Saw at the School of Physics, University of the Witwatersrand and then polished to a surface roughness of 0.5 μm.

2.2. Ion Implantation

The implantations were done using the Varian-Extrion 200-20A2F ion implanter at iThemba LABS (Gauteng), South Africa. For these measurements the same ions implanted in previous studies [1-5] were used with the addition of Ne^+ as a check on possible chemical effects. The basic implantations were carried out at room temperature and other sets were carried out with the target stage at 150ºC and 300ºC. A sliding shutter, operable from outside the vacuum chamber, was used so that all the fluences ($1x10^{14}$, $5x10^{14}$, $1x10^{15}$, $5x10^{15}$, $1x10^{16}$ and $5x10^{16}$ ions/cm^2) for each set conditions could be implanted in one run, in a set of parallel strips, for direct comparison; there was also an unimplanted area.

2.3. Raman Characterization

Raman spectroscopy was used to analyse the samples to confirm any ion induced phase change reported in [1-5]. This was done by taking Raman measurements (the 514.5nm argon laser line was used) of the h-BN samples before and after implantation. Measurements were done using the Jobin-Yvon T64000 Raman spectrometer at room temperature at the School of Physics, University of the Witwatersrand.

2.4. Micro-indentation

Hardness testing of the implanted BN samples was carried out using the FM-700 micro-hardness tester in the School of Mechanical Engineering at the University of the

Witwatersrand. Each strip had a beige colour but they differed in brightness due to the ion fluence on each strip, enabling them to be readily identified. The implanted specimen was mounted on the micro-hardness tester stage and the relevant portion aligned using the focusing lenses. The applied load was 100g. Five indentation measurements (each for 10 seconds) were done for each ion dose on each implanted sample, plus an unimplanted region. This machine automatically returns the Vickers hardness value on a screen, using a standard algorithm.

3. Results and Discussion

3.1. Stopping and Range of Ions in Matter (SRIM) Simulation.

The simulations were done at 150 keV for ions used in the actual experiment (He^+, Li^+, B^+, Ne^+) and are shown in Figure 1. As expected, the heavier ions have a shorter range but produce more damage than the lighter ions.

3.2. Raman characterization

Sample Raman spectra are shown in Figures 2 to 4; where figure 2 is for virgin BN, which displays the intense vibrational mode at 1367 cm^{-1} due to the sp^2 hybridized BN planar bonding. This peak decreases in intensity with increasing fluence, thus it is evident that there is some radiation damage to the h-BN sample.

The Raman signal for single crystal c-BN shows two vibrational modes, the translational optical (TO) mode at 1056 cm^{-1} and longitudinal optical (LO) phonon mode at 1305 cm^{-1}. Cubic BN with nanoscale particles tends to show the LO phonon modes [4,7-8], shifted to lower energies, as we see here after implantation as broad peaks around 1300 cm^{-1}; this peak indicates a phase change to cubic-BN, as reported in detail before [1-5].

The present results mirror those of previous work, showing an optimum ion fluence followed by a decrease with accompanying radiation damage, confirming a phase change to nano-cBN in the implanted layer of a few 100 nm.

3.3. Micro indentation

All the micro-indentation hardness results are presented together in Figures 5, 6 and 7. The implants were done at room temperature, 150ºC and 300^{o}C at the same ion fluences with the same ions and energy. The maxima in the curves are more pronounced, especially when plotted logarithmically, showing that there is a clear increase in hardness value over the unimplanted sample, with an optimum fluence followed by a decrease depending on the fitted curves. There is a trend with ion mass, except for Ne^+.

From the Figures, it is noticeable that an increase in fluence increases the measurable hardness of hexagonal boron nitride, which is a possible confirmation that some of the h-BN is structurally deformed to c-BN. There is an optimum level of radiation damage for this. Slightly higher hardness levels are obtained with the heavier ions; but Ne^+ ions do not fit well with the trends.

The 150ºC implants gave comparable results but higher Vickers hardness values compared to 300ºC and room temperature implants. The room temperature sample implanted with Ne^+ ions has a higher hardness value than 150^{o}C and 300ºC Ne^+ implants. This could be that implanting at 150^{o}C and 300ºC is like annealing the sample and restoring some of the damage which would otherwise promote the h-c phase change.

A comparison of the optimum fluences determined by Raman spectroscopy and by indentation testing is important and is shown in Table I. The values are fairly similar, considering the errors inherent in ion implantation experiments. The optimum indentation values tend to be higher than the Raman values, possibly because the radiation damage itself may increase hardness.

Table I. Optimum fluences determined by Raman spectroscopy and by indentation testing (Units are 10^{15} ions/cm^2)

Ions:	**Helium (He^+)**	**Lithium (Li^+)**	**Boron (B^+)**	**Neon (Ne^+)**
Raman	3.0 ± 0.2	1.0 ± 0.2	0.5 ± 0.4	4.0 ± 0.1
Indentation	4.8 ± 0.4	3.9 ± 0.5	3.5 ± 0.5	5.5 ± 0.4

3.4. Ion Implantation: Varying temperature and ion fluence at 150 keV

It is important to take account of the heating effect of the ion beam as a function of fluence. Energy is delivered as volts x amps (or kV x mA) by the accelerator, and lost from the target mainly by radiation in vacuum, according to the fourth power of its Kelvin temperature, leading eventually to an equilibrium temperature. Some measurements were carried out and are plotted logarithmically in Figure 8; very similar trends are shown by all the ions with Ne^+ being a little higher. Fortunately, most of the fluences of interest here are low, ~10^{15} cm^{-2}, but for greater than 10^{16} cm^{-2} the slightly different realm of Figure 6 and 7 is being entered. Better target temperature control, or at least measurement, is required; but it is difficult to do this for the very surface.

4. Conclusions

The ion implanted h-BN samples showed a structural phase change from h-BN to c-BN as evidenced from the Raman measurements that showed a broad peak around 1300 cm^{-1} and a decrease in the characteristic h-BN peak intensity at 1367 cm^{-1}. The micro-indentation results confirmed that ion-implantation increases hardness until an optimum hardness is reached then the hardness decreases as the ion fluence increases. Any light ions seem to produce this effect, with neon behaving somewhat differently. The possibility exists of modifying structural materials usefully by this method.

Acknowledgements.

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Figure 1: SRIM simulation for the number of vacancies per ion and unit length (Å) versus depth for boron, lithium, helium and neon ions implanted into h-BN at 150 keV. The similarities of He^+ and Li^+ depths has been confirmed.

Figure 2: Raman spectrum of unimplanted/virgin h-BN sample.

Figure 3: Raman spectra of h-BN samples implanted with helium ions (He^+).

Figure 4: Raman spectra of h-BN samples implanted with neon ions (Ne^+).

Figure 5: Hardness as a function of logarithmic fluence for all h-BN samples implanted with He^+, Li^+, B^+ and Ne^+ ions at 150keV and room temperature.

Figure 6: Hardness value as a function of logarithmic fluence at 150keV and a measured temperature of 150ºC.

Figure 7: Hardness value as a function of logarithmic fluence at 150keV and a measured temperature of 300ºC.

Figure 8: Temperature as a function of logarithmic fluence. The reason for the slight deviation of the Ne^+ results is unkown.

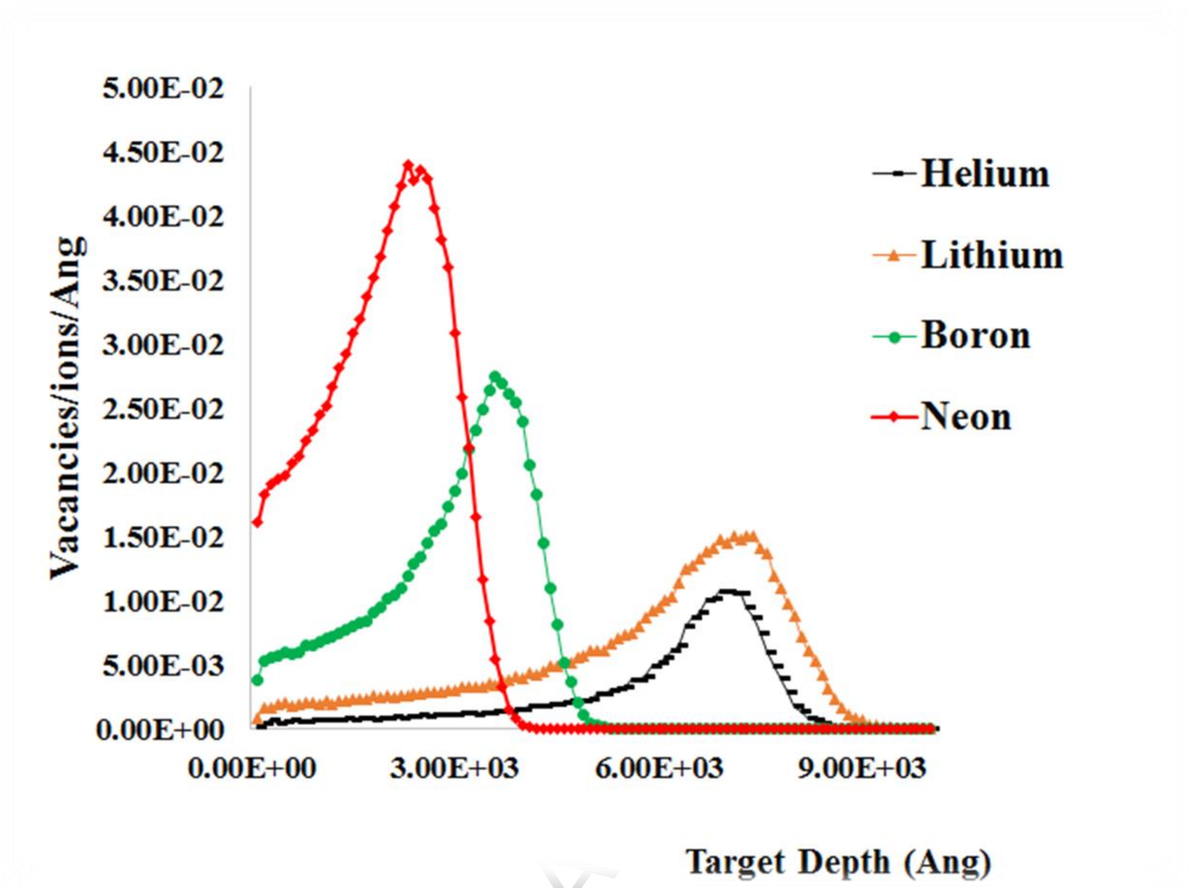
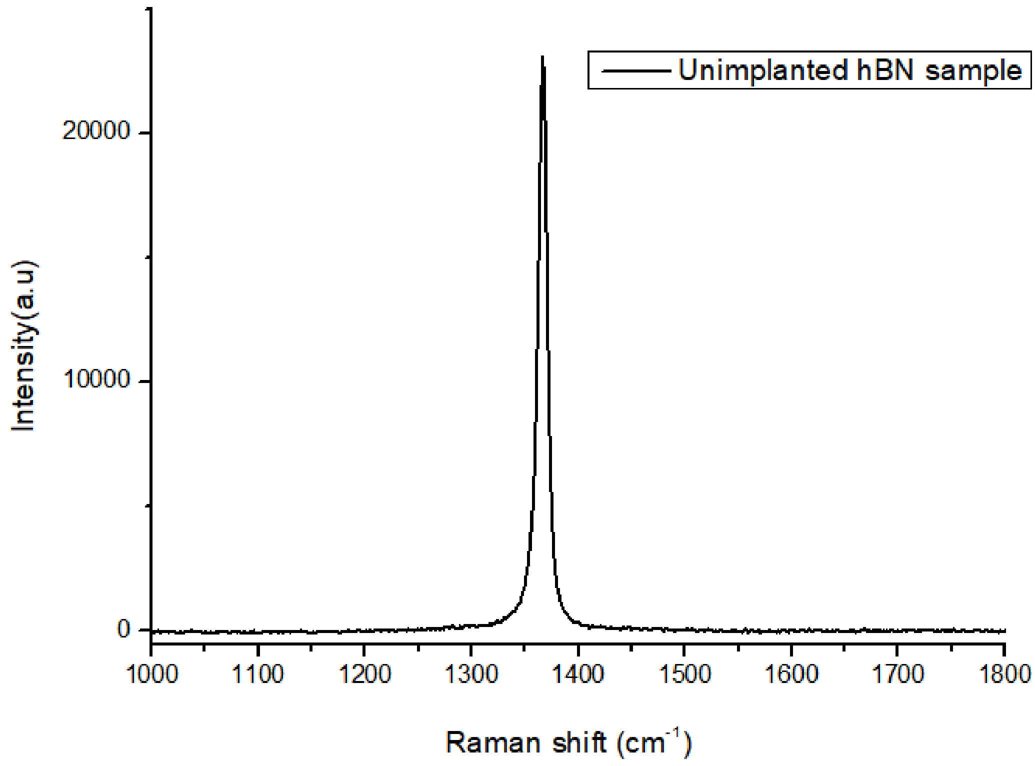
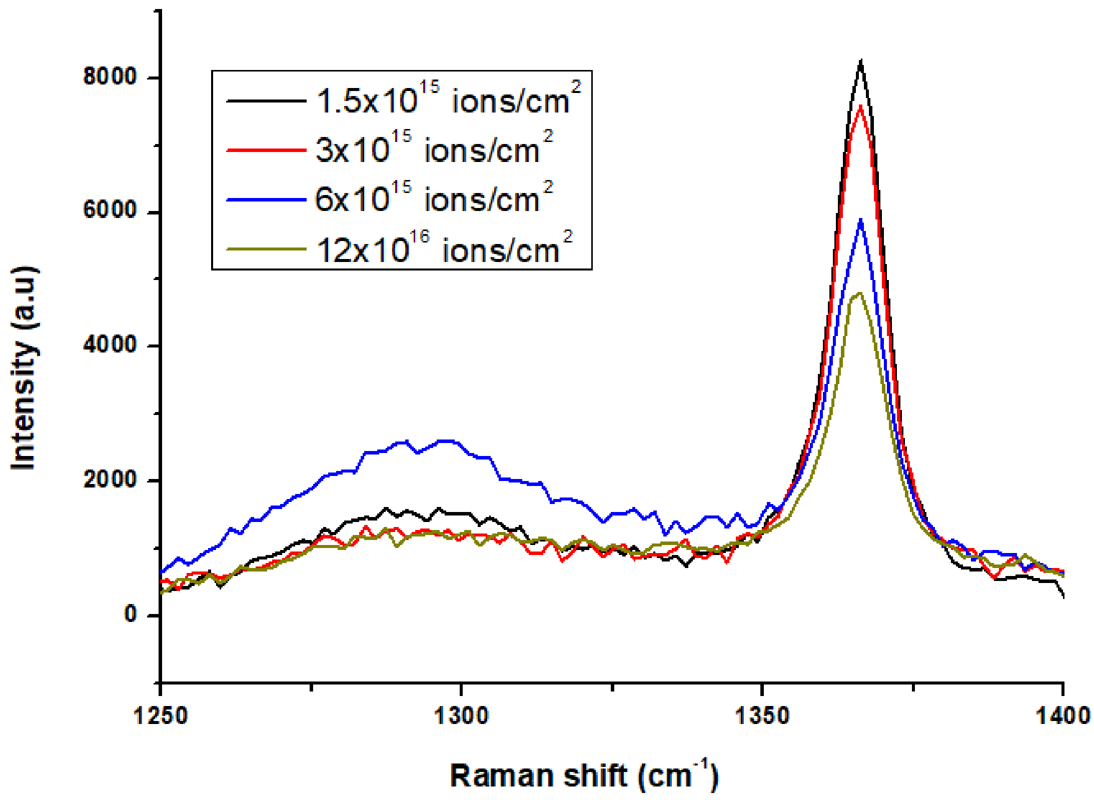

5.00E-02
4.50E-02
4.00E-02
3.50E-02
3.00E-02
2.50E-02
2.00E-02
1.50E-02
1.00E-02
5.00E-03
0.00E+00
Vacancies/ions/Ang
0.00E+00
3.00E+03
6.00E+03
9.00E+03
Target Depth (Ang)
Helium
Lithium
Boron
Neon

Figure 1



Unimplanted hBN sample
20000
10000
0
Intensity(a.u)
1000
1100
1200
1300
1400
1500
1600
1700
1800
Raman shift (cm-1)

Figure 2



8000
6000
4000
2000
0
Intensity (a.u)
1.5x10^15 ions/cm^2
3x10^15 ions/cm^2
6x10^15 ions/cm^2
12x10^16 ions/cm^2
1250
1300
1350
1400
Raman shift (cm^-1)

Figure 3

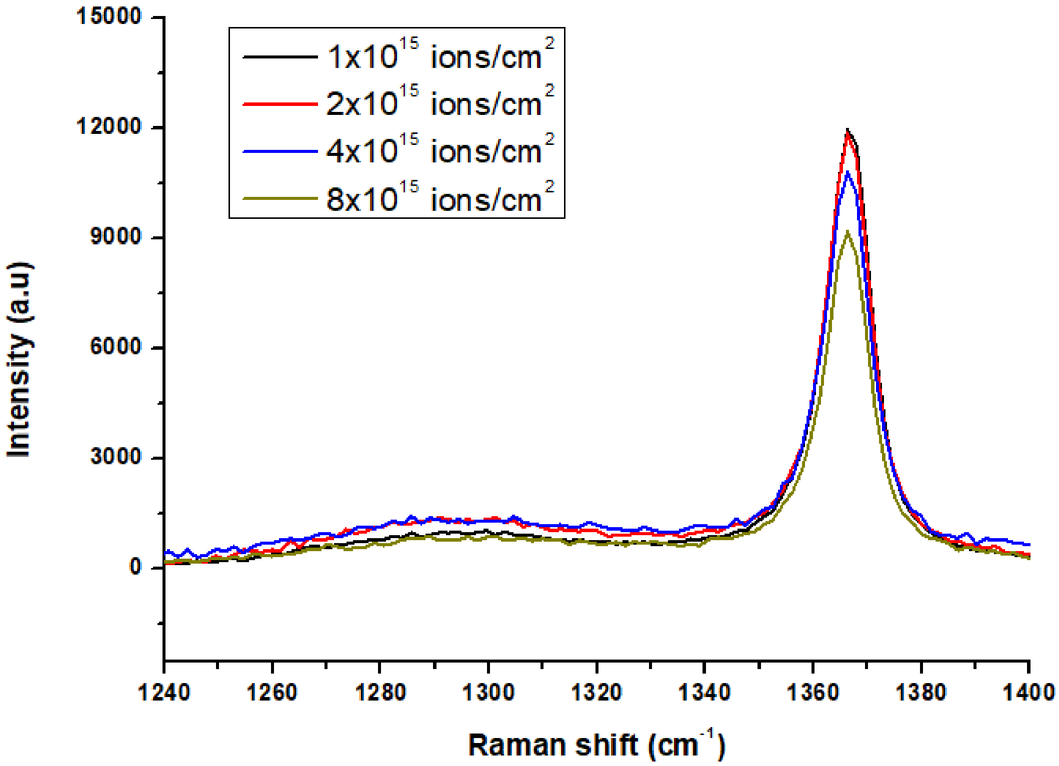

15000
12000
9000
6000
3000
0
Intensity (a.u)
1x10^15 ions/cm^2
2x10^15 ions/cm^2
4x10^15 ions/cm^2
8x10^15 ions/cm^2
1240
1260
1280
1300
1320
1340
1360
1380
1400
Raman shift (cm^-1)

Figure 4

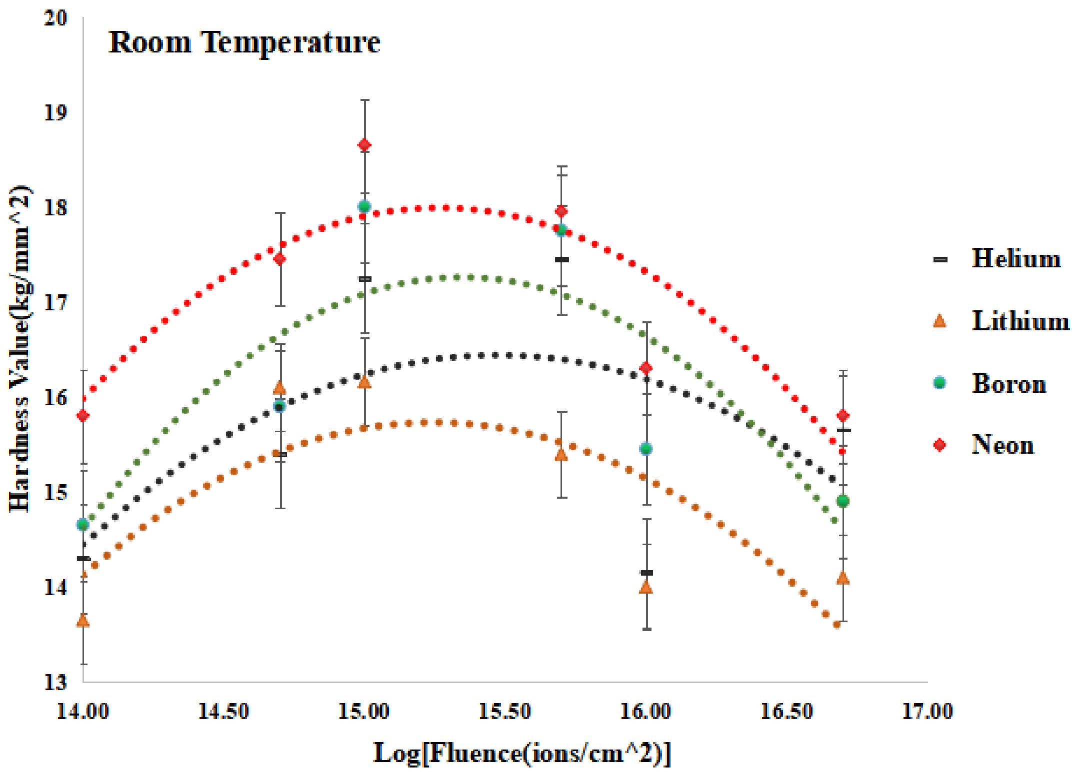
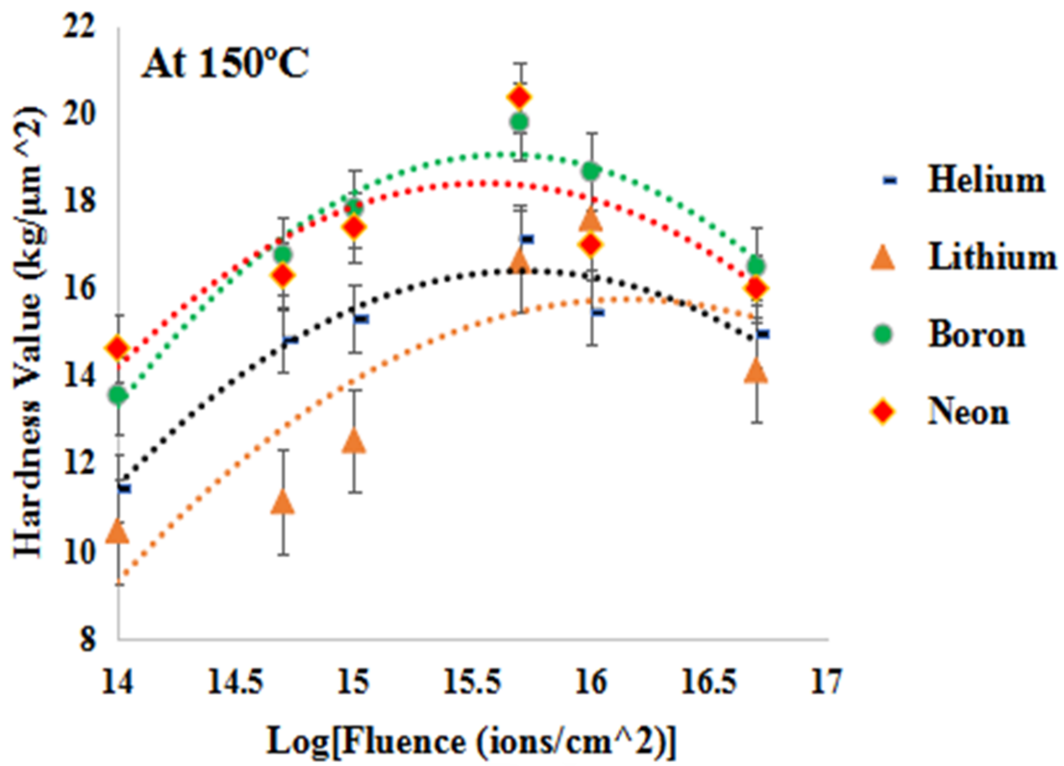
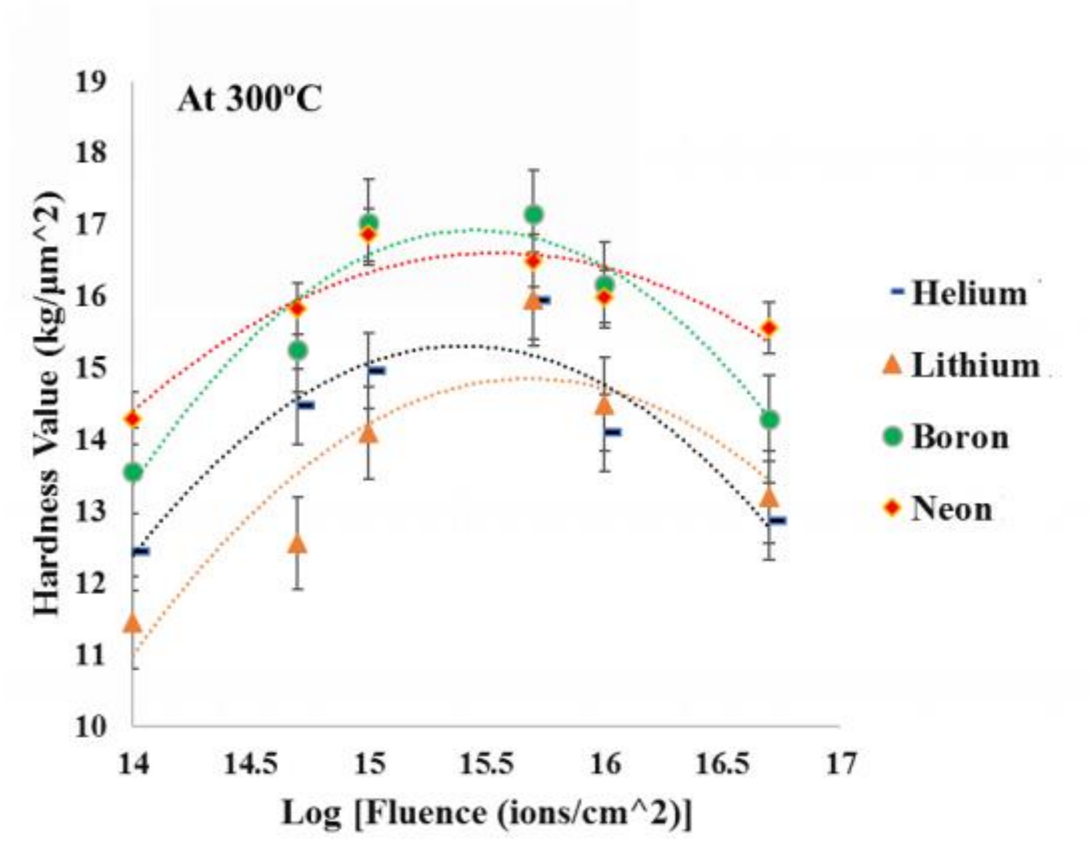

Room Temperature
Hardness Value(kg/mm^2)
20
19
18
17
16
15
14
13
14.00
14.50
15.00
15.50
16.00
16.50
17.00
Log[Fluence(ions/cm^2)]
Helium
Lithium
Boron
Neon

Figure 5



At 150°C
Hardness Value (kg/μm ^2)
22
20
18
16
14
12
10
8
14
14.5
15
15.5
16
16.5
17
Log[Fluence (ions/cm^2)]
Helium
Lithium
Boron
Neon

Figure 6



At 300°C
Hardness Value (kg/µm^2)
Log [Fluence (ions/cm^2)]
19
18
17
16
15
14
13
12
11
10
14
14.5
15
15.5
16
16.5
17
Helium
Lithium
Boron
Neon

Figure 7

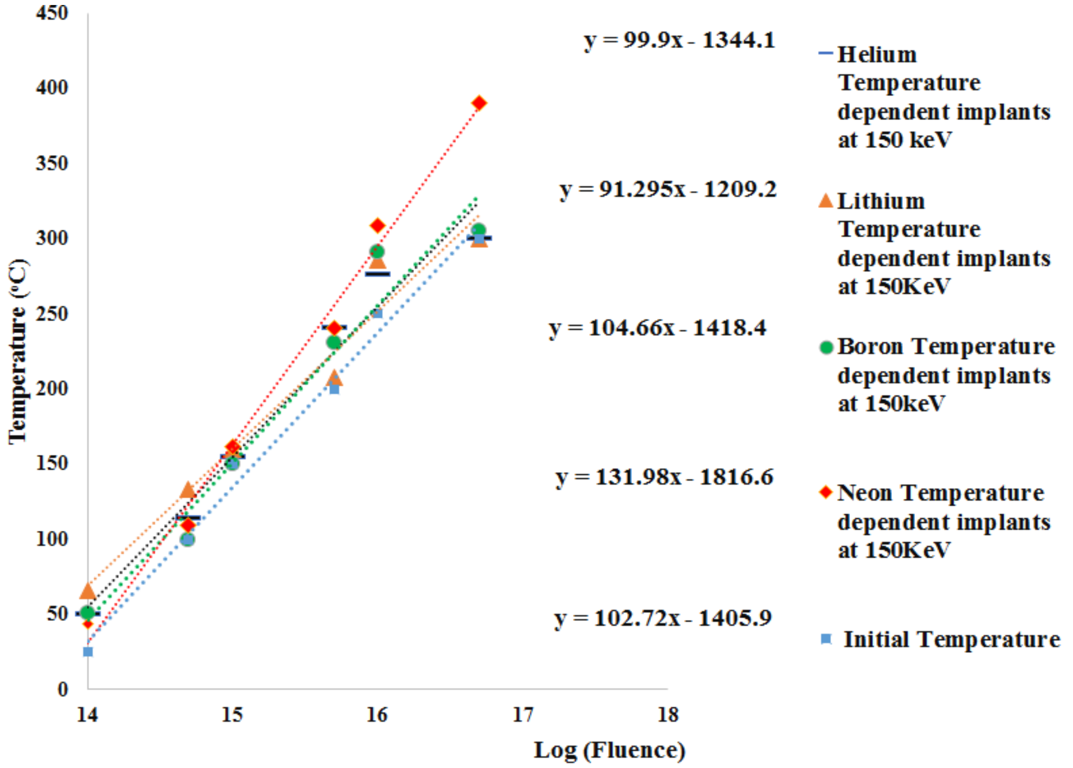

450
400
350
300
250
200
150
100
50
0
Temperature (°C)
14
15
16
17
18
Log (Fluence)
y = 99.9x - 1344.1
y = 91.295x - 1209.2
y = 104.66x - 1418.4
y = 131.98x - 1816.6
y = 102.72x - 1405.9
Helium Temperature dependent implants at 150 keV
Lithium Temperature dependent implants at 150KeV
Boron Temperature dependent implants at 150keV
Neon Temperature dependent implants at 150KeV
Initial Temperature

Figure 8

Highlights

- Implantation of light ions in h-BN induces a thin-layer transformation into c-BN.
- An increase in micro-hardness can be clearly measured by micro-indentation.
- The hardness increases up to an optimum ion fluence which depends on the ion.
- The temperature of the substrate needs to be controlled during these implantations.