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14. ABSTRACT This report results from a contract tasking Technion - Israel Institute of Technology as follows: The Grantee will use the flexible ion-implanter at the Technion (Israel) and the know-how available in Professor Kalish's group on implantation and graphitization of diamond to study the conditions of realization of free standing single crystalline diamond CVD plates. Synthetic diamond samples will be subjected to appropriate-dose, multiple-energy ion implantations to create the desired damage region. TRIM simulations of the defect profiles will be used to design the required implantation schemes. About 20 implantations will be performed (depending on required dose and number of different energy implantations required.) About 10 SIMS evaluations will be performed, if required					
15. SUBJECT TERMS EOARD, Diamond, infrared technology, thin films					
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Report on: Contract #: FA8655-03-1-3049

“Ion-Implantation into diamond for the realization of thin single crystal membranes.

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General background and Objectives:

The outstanding mechanical, chemical and electronic properties of diamond stem from the extremely strong and tight sp³ bonding. Of main interest are the electronic properties of diamond which are all related to it being a wide band gap semiconductor ($E_g=5.5$ eV) i.e. practically an electrical insulator at RT with a very high break down field) of metastable nature (the stable form of C being graphite). As a result perfect diamond has a broad optical transparency, ranging from the deep UV to the far IR. Carriers (electrons and holes) exhibit very high mobilities in perfect diamond. Diamond can be doped p-type (with Boron; $E_a=0.37$ eV) and n-type (with Phosphor; $E_a=0.56$ eV) Both these acceptor and donor levels are rather deep (in particular that associated with P) hence the RT conductivities of doped diamond are low. Native defects in diamond such as vacancies, interstitials, extended defects and combinations of different chemical dopants (co-doping effects) and combinations of dopants and defects. Broken diamond (sp³) bonds, such as resulting from ion-implantation damage, when at high enough density tend to re-grow, upon annealing, to form sp² bonds i.e. to locally change from diamond to graphite. These graphitic regions can readily be chemically etched hence preferentially removing the graphitized regions from the diamond. The diamond layer covering the graphitic regions can be thickened by CVD diamond over growth, hence permitting the realization of diamond membranes of an desired shape, depending on the implantation pattern and on the CVD over growth conditions employed.

This is the basis for the "diamond lift off technique" performed in this work.

When the unique electronic properties of diamond are combined with its exceptionally high thermal conductivity, its mechanical strength, its high break down field, its chemical inertness and its bio-compatibility it is clear that diamond offers many applications as an electronic material for unique applications.

The high carrier mobilities combined with the high thermal conductivity and high break-down field are employed in realizing high power, high frequency devices.

The high elastic constants may find application in various MEMS as Surface Acoustic Wave (SAW) devices.

Of particular interest here are the possibility to realize, in diamond membranes, high power high frequency electronic circuits and a variety of MEMS devices.

It is proposed here to take advantage of the subsurface damage layer generated in diamond, when the diamond is heavily damaged by ion-impact. Moderate dose ion-implantations into single crystal diamond create a subsurface damage region, at a depth and width that can be controlled by the implantation conditions. This damage and the expected implant profile can be simulated by the well accepted TRIM (TRansport of Ions in Matter) code. Kalish's group has studied, in the past, the implantation conditions that will lead to the graphitization of the implantation damaged layer, which can be subsequently etched by an electrochemical process.

The top layer, above the end-of-range damaged layer, remains predominantly diamond, though with some point defects, and is a sufficient template for epitaxial growth. Heating the implanted sample may enhance the conversion of the buried damaged layer to a graphitic region, and at the same time will restore the crystallinity of the top diamond layer.

Subjecting this sample to suitable chemical treatment will cause the graphitic layer to be etched away, while the diamond will resist the treatment. This results in a free standing single crystalline diamond film, the thickness of which depends mainly on the thickness of the overgrown layer. The back side of this sample may include a thin layer which contains some of the ions used in the graphitization implantation and thus be desirable for forming electrical contacts when the implants were dopants (like boron in diamond).

The Technion's task in the above proposal was to use the flexible ion-implanter at the Technion (Israel) and the know-how available in Professor Kalish's group on implantation and graphitization of diamond to study the conditions of realization of free standing single crystalline diamond CVD plates.

Some CVD samples grown in Dr. Butler's laboratory in the presence of boron with different concentrations of B in the plasma were to be SIMS analyzed at the Technion, to serve as reference for B doping CVD growth process at the NRL.

Accomplishments:

1. TRIM simulations:

Two kinds of implantations were simulated:

- (a) Carbon ion-implantations to create damage only.
- (b) Boron ion implantations to create damage and to introduce p-type dopants
- (c) Hydrogen ion-implantations damage and H dopants.

Figures 1a-1d below show the results obtained for C profile and damage profile for ion energies of 100 200 and 300 450 and 600 keV (the implantations at 450 and 600 keV can be done when doubly ionized ions are implanted at an acceleration voltage of 1/2 the ion energy). Figure 2a-2d shows the same for boron ions. Figure 3a-3b shows the results for 100 200 and 300 keV implantations.

2. Implantations

The following implantations were carried out and the implanted samples were delivered to Dr. Butler at the NRL:
Four single crystal samples were implanted with B⁺ ions at the following conditions: 170 keV to a total dose of 9e15 ions/cm²
140 keV to a total dose of 7e15 ions/cm²

Four single crystal samples were implanted with C⁺ ions at the following conditions: 175 keV to a total dose of 8×10^{15} ions/cm²
150 keV to a total dose of 6×10^{15} ions/cm²

The energies and doses were chosen, based on the TRIM simulations, to yield rather similar ion ranges and defect concentrations.

These samples were sent to Dr. Butler for further study, i.e. homo-epitaxial diamond overgrowth and lift off to obtain free standing single crystal diamond membranes.

3. SIMS profiling

Four CVD homo-epitaxial single crystal diamond samples, grown by Dr. Butler were sent to the Technion, for SIMS depth profiling. The aim of this evaluation was to study the boron incorporation in the grown samples, when intentionally introduced into the gas mixture as B₂H₆, to obtain quantitative information, on the B concentrations in the samples and on their thickness. Also of great interest is the unintentional nitrogen content of the samples.

Figures 3(a)- 3(d) show the SIMS profiles provided to the NRL.

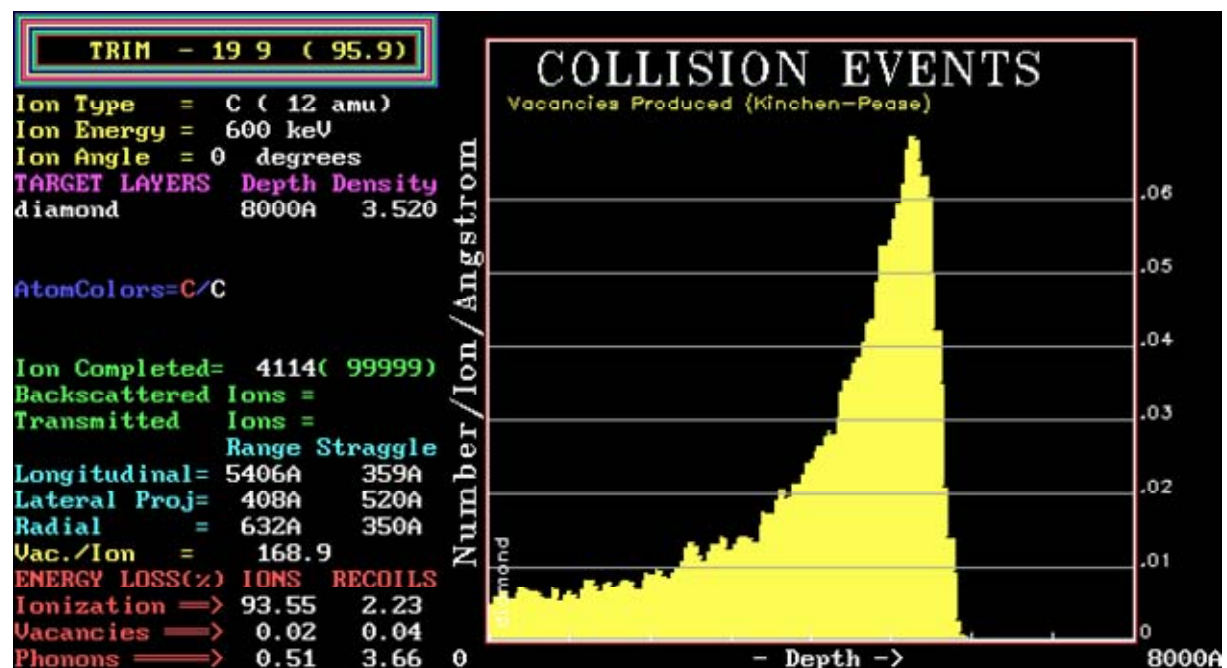
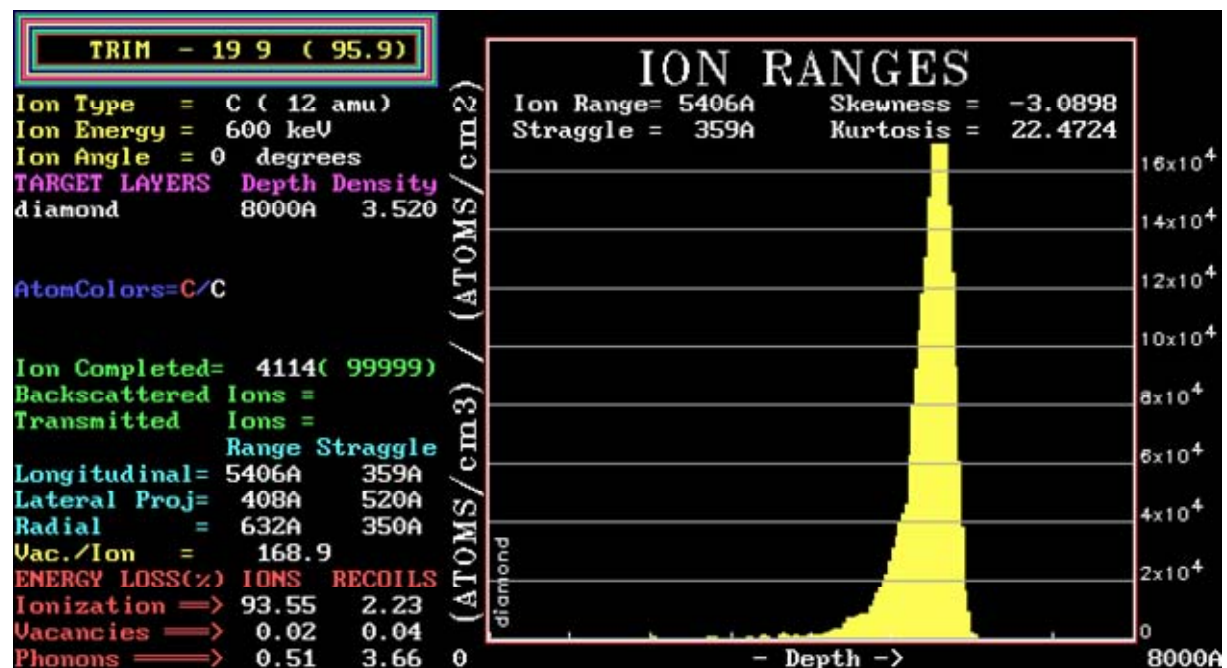
Table 1 (provided by Dr Butler) correlates the growth conditions with the boron content in the samples. It is worth mentioning that the nitrogen content of the samples exceeds the detection limit of the SIMS (being $\sim 5 \times 10^{18}$ /cm³ which is rather high, but common for UHV SIMS due to the unavoidable nitrogen in the residual gas) in the B containing samples.

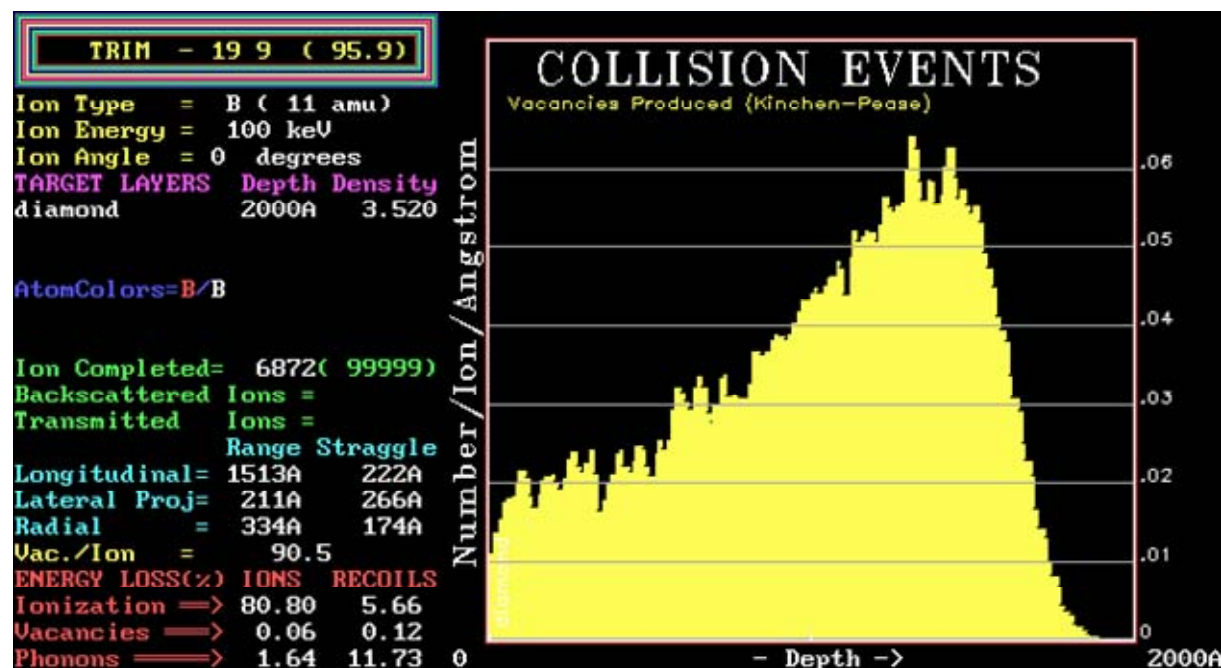
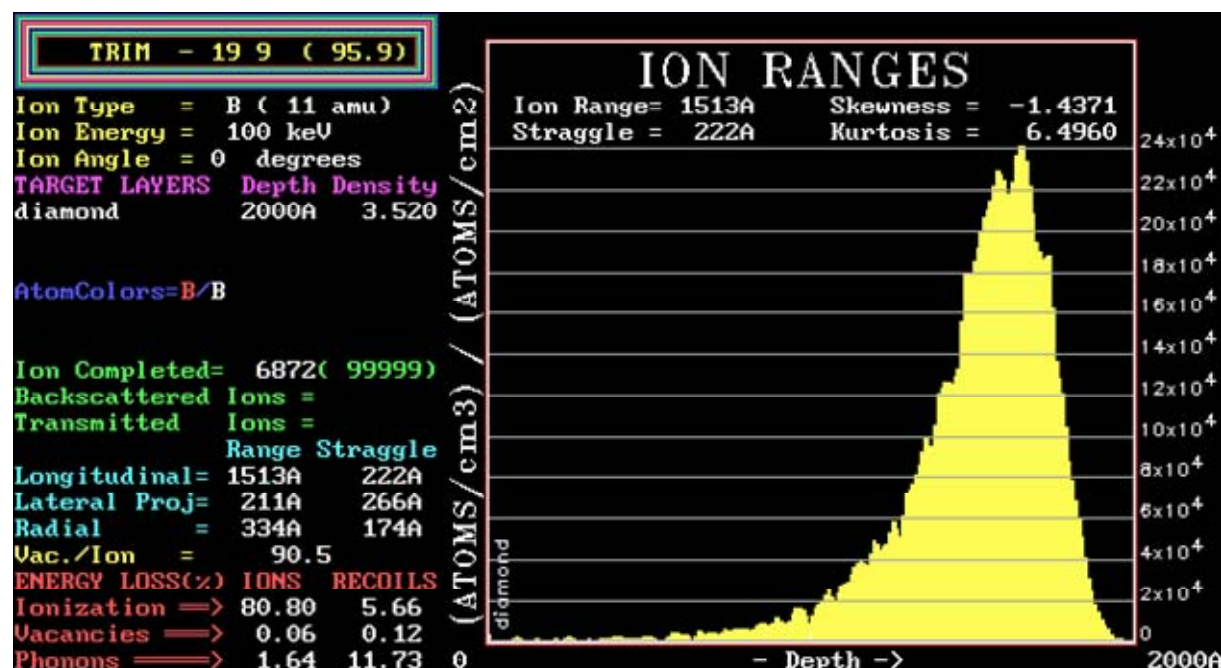
Conclusions:

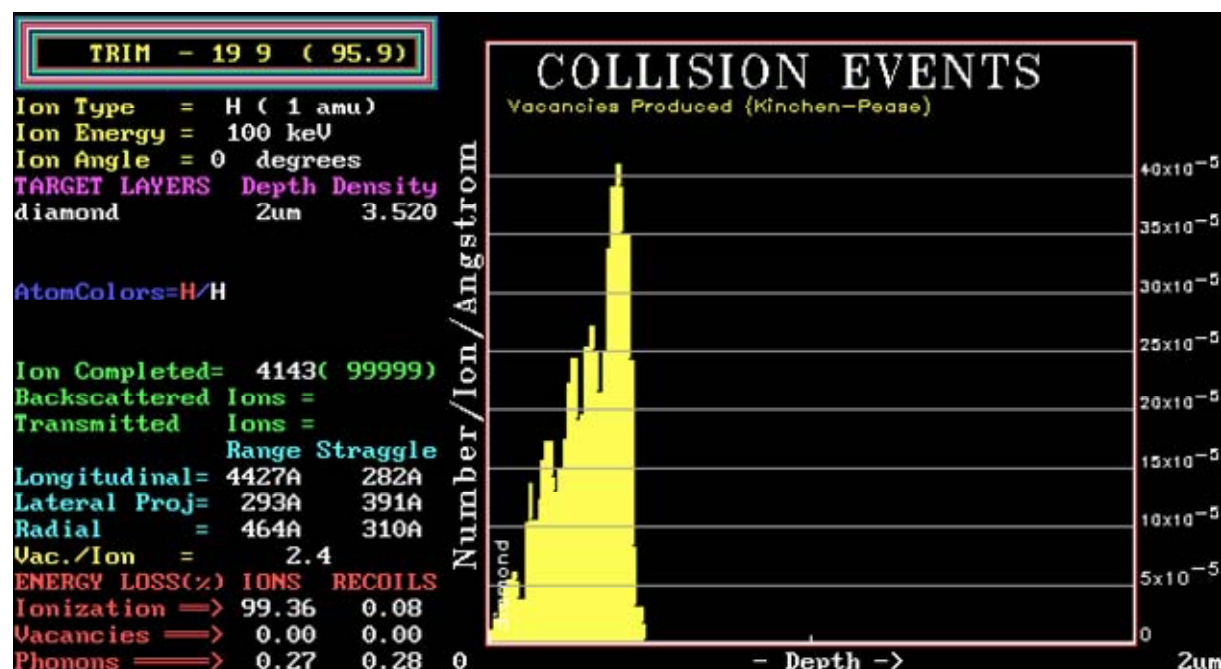
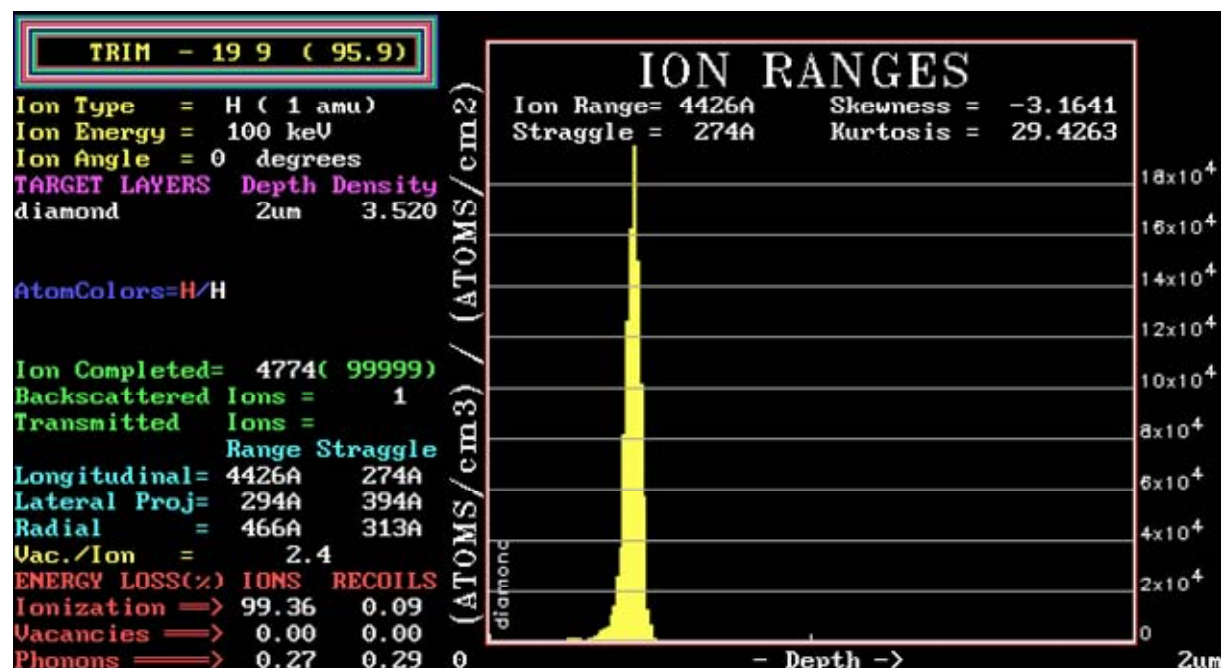
This project was meant to provide unique samples and information to Dr Butler's diamond growth and applications at the NRL.

These were provided to the full satisfaction of Dr. Butler.

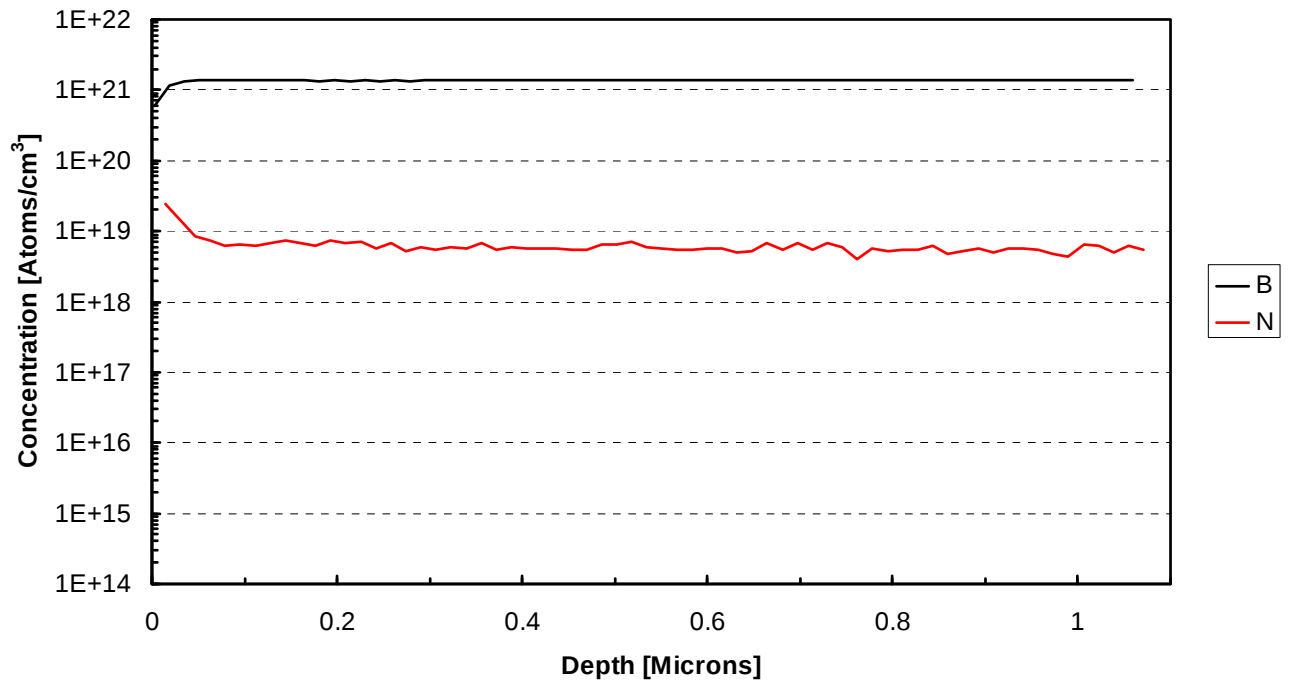
No information of "new findings", "publications", "inventions" or "awards" related to this work is available to Professor Kalish, being the sample and diagnostic provider only.



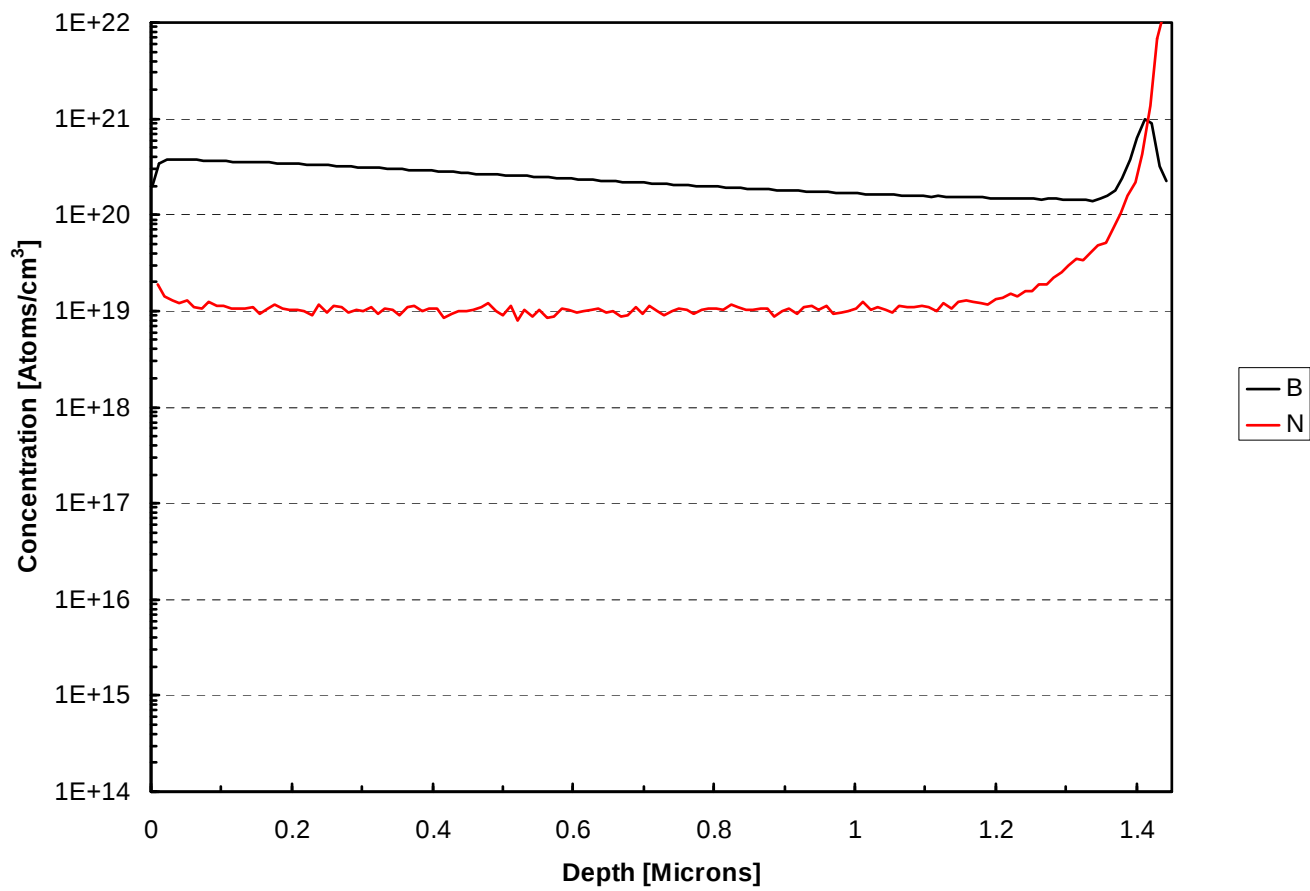




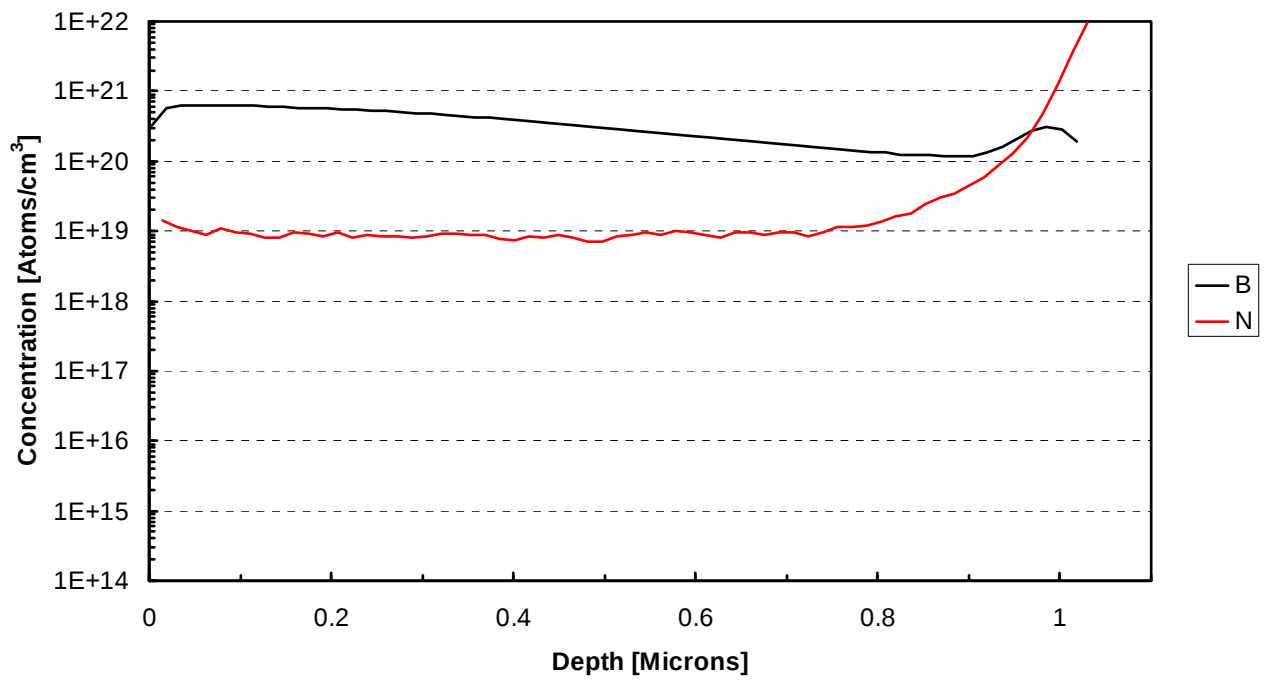
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Run Date	H2 flow	CH4 flow	B2H6 flow 0.1% in H2	H2S flow 0.518% in H2	Press	Substrate Temp.	thickness	C/H gas phase	B/C gas phase	Technion SIMS
	sccm	sccm	sccm	sccm	torr	C	microns	atom %	atom ppm	
4/10/02 (N3S0011)	900	3	0	0	15	800	0.53	0.166	0	
4/15/02 (N3S0014)	900	3	0	12	15	800	0.53	0.166	0	
10/5/2001	900	3	0	0	15	750	1.57	0.166	0	
10/7/2001	900	8	0	0	15	750	3.3	0.437	0	1.00E+20
11/1/2001	900	9	0.6	0	15	830	1.31	0.490	133	3.00E+20
12/7/2001	900	3	1	0	15	750	0.53	0.165	667	5.00E+20
3/20/2001	500	1.5	1	0	15	800	2	0.148	1333	1.50E+21