DOE/ER/10566-1

Progress Report for the Department of Energy

Contract No. DE-AS02-80ER10566

UMass Referral No. 5-28875

Principal Investigator: Mireille T. Clapp

Department of Mechanical Engineering

University of Massachusetts

Amherst, MA 01003

Phone: (413) 545-0868

MASTER

DISCLAIMER

Mireille T. Clapp, the principal investigator, has devoted 35% of her time during the academic year and full time during the summer to this project. She will continue to devote 35% of her time to the project until its expiration date, December 31, 1980.

TABLE OF CONTENTS

I. SUMMARY

The scientific community is devoting considerable effort towards finding a superconducting material with a transition temperature (T_c) greater than 25 K. Liquid hydrogen could then be used as the coolant rather than liquid helium. The associated cryogenic expenses would be greatly reduced making engineering applications economically feasible. The highest T_c so far recorded is 23 K for A-15 Nb_3 Ge (1). Progress in high T_c superconductivity seems to involve metastable materials and in particular metastable A-15's. Our research has investigated a novel application of ion implantation to synthesize metastable A-15 Nb_3 B and Nb_3 C. Our research proposal described why it is generally thought that these compounds would have very high T_c's and why we believed ion implantation followed by epitaxial regrowth on an A-15 substrate was probably the best technique for synthesizing them.

Polished wafers of A-15 Nb_3 Al were made and were used as our substrate material. Their surfaces were depleted of Al by annealing in vacuum at 1070 C for several hours; the Al evaporated off the surface and diffused out from the bulk. The Al deficiency was then replaced with B or C ions by implanting at a sequence of energies and doses. The composition of the implanted layer thus changed gradually from the bulk Nb_3 Al to Nb_3 (Al + B) and finally to Nb_3 B at the immediate surface. (Similarly for Nb_3 C.) Four different implantation energies of 160, 120, 80 and 30 Ke V were used. These enabled us to

(1) L.R. Restardi, J.H. Wernick, W.A. Royer, Sol. St. Comms., 15 (1974).

obtain excellent cumulative dopant profiles; the (Al + B) or (Al + C) concentrations remained equal to the desirable stoichiometric composition of 25 At% throughout the entire implanted layer. This is necessary for achieving high T_c materials. The concentrations of Nb, Al, B and C were measured as a function of depth into the samples using Auger analysis. The experimentally determined profiles agreed extremely well with the theoretically predicted ones. We were consistently able to reproduce our results.

The extremely high implantation doses (up to 25 At%) produced a great deal of radiation damage and created a very disordered surface layer. This was ascertained using reflection electron diffraction which enabled us to obtain diffraction patterns of the surface structure. After implantation the diffraction rings were extremely broad and diffuse. However, after annealing for 24 hours at 750 C, the rings began to sharpen up and by 850 C, very nice clear rings were observed. This indicated that the implanted layer had indeed recrystallized. Auger analysis of the annealed surfaces showed that there was very little change in the dopant profiles before and after heat treatment. This was very encouraging. This meant that there was little enhanced diffusion of the small B and C atoms via the numerous defects created during implantation.

Superconducting transition temperatures were measured using a four point probe resistive technique. The current and voltage leads were placed from front to back of the wafers; this effectively put the

substrate and the implanted layer in series. The bulk of the Nb_3 Al wafers superconducted around 18 K, and there was a large resistivity drop at this temperature. We observed further small resistivity drops at 10 K and 11K which we believed were due to the implanted layer. We referred to these as "secondary" transitions. We are proceeding at this point to characterize these "secondary" transitions in terms of accurate structural analysis of both phase and lattice parameter. This will be done using X Ray diffraction. However, X-ray analysis of our current samples is not possible for the following reasons. X-radiation generally penetrates several microns into solids. Since the implanted layers of our samples are less than 1 micron deep, the X-rays would be measuring primarily the structure of the A-15 substrate. We are solving the problem in the following manner. New samples are being prepared. We will use a different accelerator for the implantations (2), one that is capable of achieving ion energies of 1 MeV. This will create an implanted layer of approximately 2 microns deep. Cr K α will be the radiation source because it is very strongly absorbed by Nb. In this fashion approximately 90% of the X-ray intensity will be confined to the implanted layer. We will thus be able to analyze this layer accurately in terms of phases present and A-15 lattice parameter.

We are very encouraged by our initial results. We have consistently been able to implant very large doses of B and C (up to 25 At%) into our substrate material, and to achieve very accurate dopant

(2) Van der Graaf Acceleration - Prof. Quentin Kessel, Phys. Dept., UConn.

profiles. Auger analysis has revealed that the experimentally determined profiles agree extremely well with the theoretically predicted ones. Even after heat treatments up to 850 C there is no significant redistribution of implanted atoms; there is thus very little enhanced diffusion via the numerous defects created during implantation. We are therefore able to control very accurately the composition of our surfaces. From reflection electron diffraction we were able to ascertain that although the surface layers were extremely disordered after implantation, they did indeed recrystallize after annealing at 850 C. We observed some "secondary" superconducting transitions in the surface layers around 10K and 11K. We are proceeding to accurately characterize these transitions in terms of phase and lattice parameter analysis using X Ray diffraction.

II. EQUIPMENT ASSEMBLED

The following equipment is now installed in our laboratory.

A. A dynamic vacuum furnace has been built partly from components available in the department and partly purchased. This consists of a vacuum system assembled from mechanical and diffusion pumps, valves and gauges (vacuums in the range of 10^{-7} torr are obtainable.); an exit port coupled via o-ring seals to a closed end ceramic tube capable of being inserted into a furnace and withstanding high temperatures; a furnace that can reach and maintain a temperature of approximately 1200

degrees centigrade and remain steady for several hours to within a few degrees.

B. Metallographic polishing equipment has been assembled and a parallel sample holder has been built for obtaining smooth flat polished surfaces.

C. A dual dewar assembly has been built for holding liquid nitrogen and liquid helium needed for the T_c measurements.

D. Transfer apparatus has been assembled for transferring the liquid helium from commercial dewars to the dewars for T_c measurements.

E. A sample holder for T_c measurements has been built from the following: a glass tube that can be evacuated, a mechanism for supporting two samples so that they can be measured sequentially without having to remove and reinsert the tube into the liquid helium, a heater coil to change the sample temperature, a germanium resistance thermometer, non inductively wound leads exiting via vacuum seals to the various current supplies and recording apparati.

F. Two constant current supplies have been built to supply 1 to 10 microamps to the germanium thermistors, and approximately 20 milliamps to the samples. These currents can be monitored to four significant figures on a multimeter that was purchased from Keithley.

G. An x-y recorder to monitor the voltages from the thermistor and the samples. A nanovoltmeter that can amplify, when necessary, the sample voltages; this was purchased from Keithley.

III. EXPERIMENTAL PROCEDURE AND RESULTS

A. Sample preparation

Wafers of Nb_3Al approximately 0.5 mm thick were polished and lightly etched to obtain relatively smooth surfaces. The samples were then heat treated in a dynamic vacuum furnace at 1060 C for six to four hours. They were wrapped in niobium foil and kept at approximately 10^{-6} torr to minimize surface oxidation. During this process the Al evaporated off the surface and diffused out of the interior of the sample. A typical diffusion profile after 6 hours at 1060 C was such that there was no Al at the surface, approximately 50% Al at a depth of 2500 angstroms, and approximately 90% Al at 5,500 angstroms. The removal of Al from the immediate surface caused the A-15 structure to collapse into a somewhat disordered BCC Nb structure. This above-mentioned heat treatment was followed by an ordering anneal of 750 C for 48 hours.

B. Ion implantations

Samples were then ready to be implanted. A sample holder was fashioned from a piece of brass plate to accommodate six samples simultaneously. A copper cooling coil was soldered to the back

so that the samples could be water cooled during implantation. This prevented the extremely high ion doses that were used from overheating the samples. During implantation the samples were kept at approximately 10^{-6} torr. Accurate beam doses were recorded with an electrometer. Since both C and B are such light atoms there is very little back scattering. Even if there was some small amount of back scattering only those ions that actually penetrated into the sample were counted in the final ion dose. Ion implantations were carried out at the University of Connecticut using Prof. Howard Hayden's accelerator. This was capable of very high beam currents, approximately several hundred microamps. The maximum available beam energy was 160 Kev.

Ions with a given energy will penetrate a material to an average depth R_p and will have a Gaussian distribution about R_p. The range straggling ΔR_p is given by

$$\Delta R_p = \frac{\text{full width at half maximum}}{2(2\ln 2)^{1/2}}$$

Roughly speaking R_p and ΔR_p depend on the ratio of the masses of the ion and the substrate. Values of R_p and ΔR_p were calculated for B and C ions into Nb substrates and are given in Table (I). The concentration of implanted ions is related to the ion dose by the following:

$$n = \frac{N_d}{2(2\ln 2)^{1/2}\ \Delta R_p}$$

TABLE I.

Values of penetration depths R_p and range distributions ΔR_p for B and C ions into Nb substrates.

ion beam energy Kev	R_p Å	ΔR_p Å
	B+	
160	4000	1760
100	2500	1300
90	2250	1210
80	2000	1120
70	1750	1050
30	750	570
	C+	
160	3500	1540
100	2200	1145
90	1950	1055
80	1700	950
70	1500	900
30	700	530

A typical profile for B in Nb is shown in figure (1). Four energies at different ion doses were used in an attempt to fill in a closely as possible the voids left by the diffused out Al. A series of implantations were carried out until we obtained what we thought were optimum profiles as measured by Auger analysis.

C. Auger analysis

Surface concentration profiles of the various elements in the samples were measured as a function of depth into the sample by Auger analysis. An area of approximately 1 mm in diameter was analyzed. By sputtering with an argon beam successive atomic layers were removed and the Auger electrons were analyzed for compositional analysis. A total scan of the elements at the beginning and end of each run was taken. Nb, Al, B and C were analyzed as a function of depth.

Compositional analyses were done at the various stages of sample preparation and heat treatment. These results proved to be amazingly reproducible. Nearly identical results were obtained for three different profiles done on the same sample several weeks apart. Composition profiles done immediately after implantation and after heat treatment at 850 C also proved to be very similar as can be seen in Figures (2) and (3). This indicated that there was very little diffusion of implanted ion during heat treatment. This was a very encouraging result because one

Figure 1

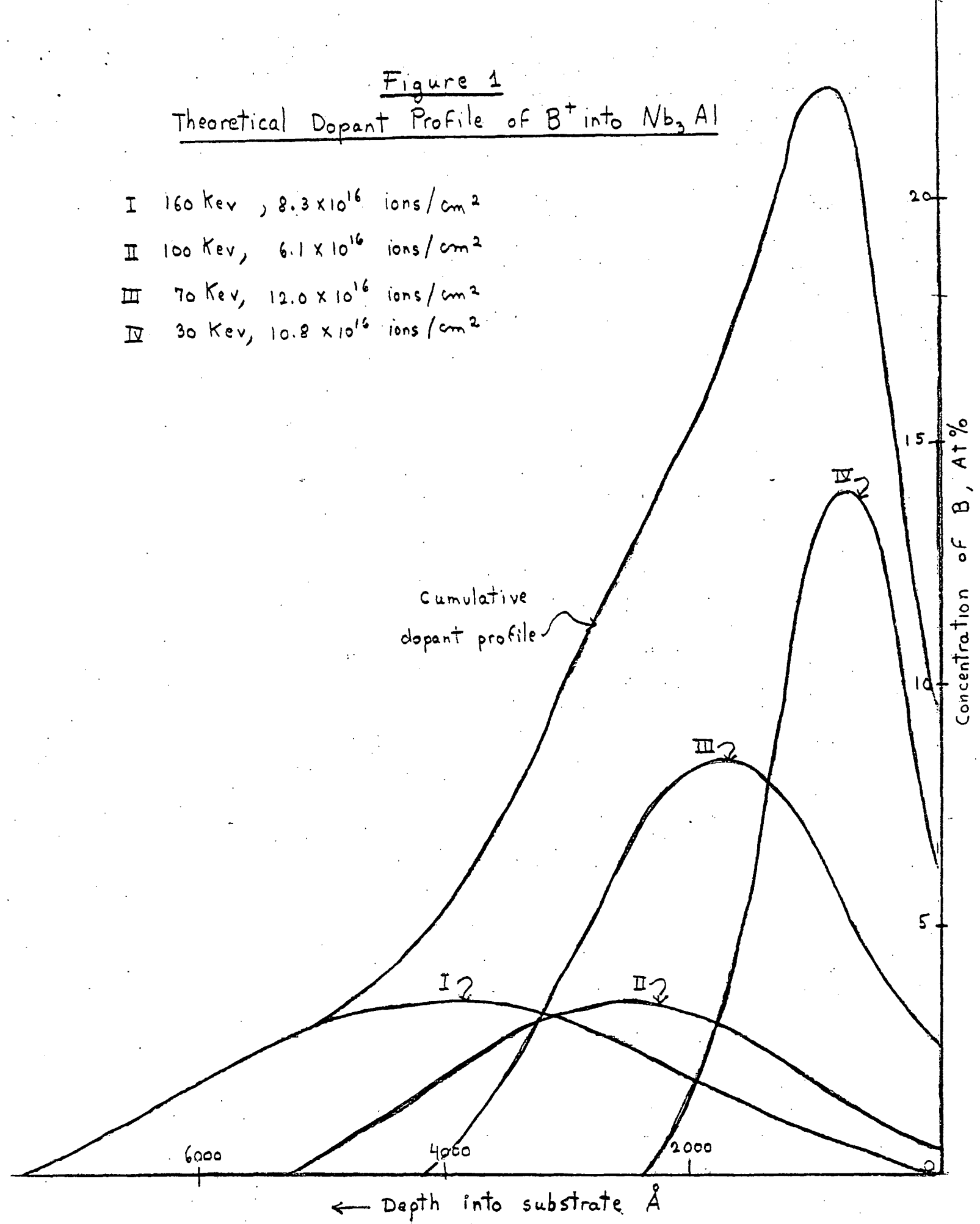
Theoretical Dopant Profile of B^+ into Nb_3Al

I 160 Kev, 8.3×10^{16} ions/cm^2

II 100 Kev, 6.1×10^{16} ions/cm^2

III 70 Kev, 12.0×10^{16} ions/cm^2

IV 30 Kev, 10.8×10^{16} ions/cm^2



Comparison of experimental dopant profiles for

B^+ in Nb_3Al after implantation (Fig. 2) and after annealing at 850C (Fig. 3)

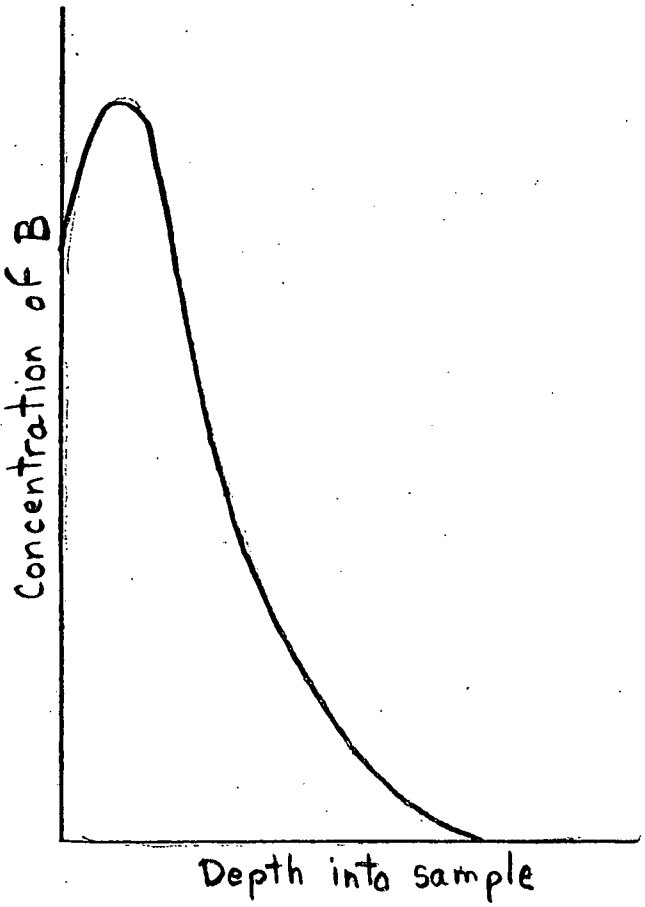


Figure 2

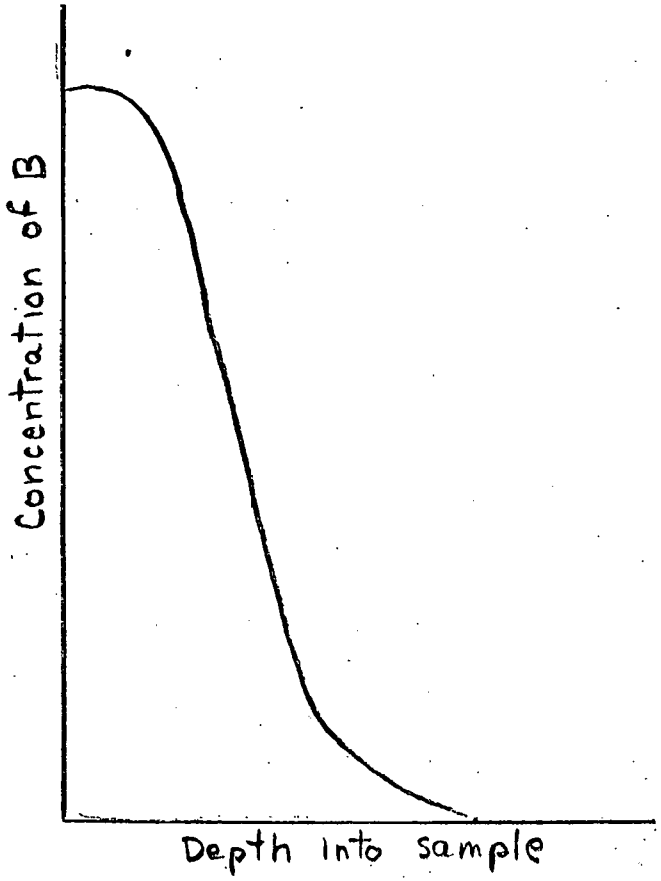


Figure 3

might have expected that the small B and C atoms would diffuse readily through the many lattice defects introduced during implantation. But apparently this was not the case. The third result which was very encouraging was that the experimentally determined profiles agreed extremely well with theoretically predicted profiles. A test sample was prepared in which the theory predicted a rather sharp bump in the curve, figure (4). This showed up beautifully in the experimental curves even after heat treatment at 850 C, figure (5). We therefore believe that we had very good control over the ion implantations and the surface composition of our samples.

D. Reflection electron diffraction

Reflection electron diffraction (RED) was used to determine the crystal structure of the implanted surface. The samples were positioned in the electron microscope such that the electron beam diffracted off the surface at a glazing angle of incidence. The electron beam penetrated to a depth of approximately 100 to 200 angstroms into the sample. The camera constant of the electron microscope was determined using an MgO standard of known atomic spacings. For our polycrystalline specimens, ring patterns were obtained and photographs were taken. From the radii we calculated the lattice spacings.

Surface structures were analyzed at the following stages: immediately after polishing and etching, after the aluminum

Comparison of a theoretical (Fig. 4) and an experimental (Fig. 5) dopant profile for B^+ in Nb_3Al

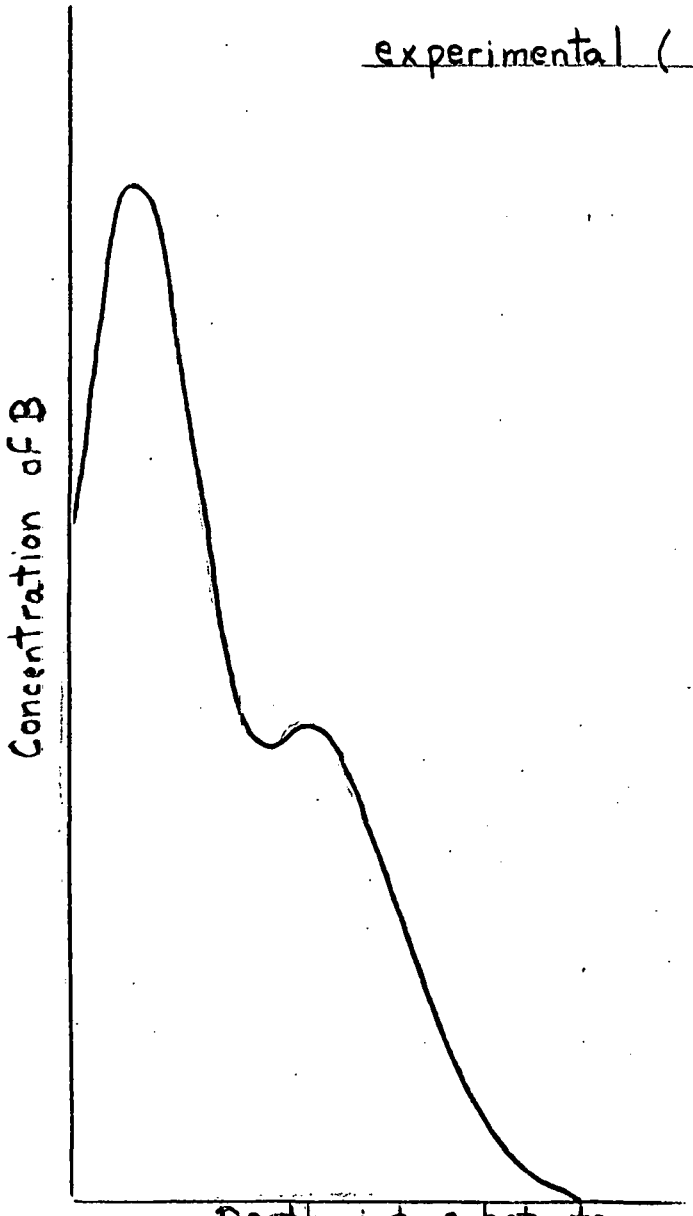


Figure 5

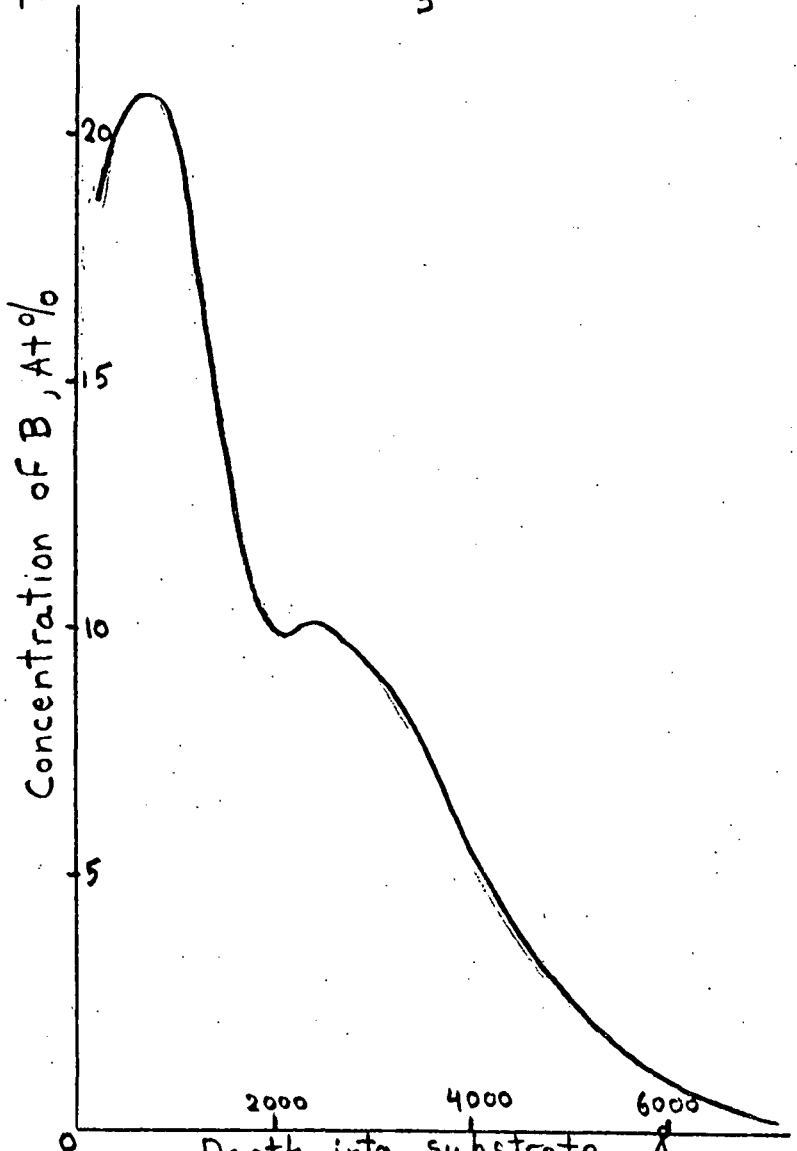


Figure 4

depletion anneal, after implantation, and after heat treatment for twenty-four hours at each of 700, 750, 800 and 850 C's. Photographs of the M_gO standard were taken regularly throughout the experiment to check for voltage drifts. Three different electron energies of 60, 80 and 100 KeV were used for each sample. It was therefore possible to have more planes in our non randomly oriented samples properly oriented towards the electron beams and to obtain more d values. The photographs at 60 Kev were not very clear and they became sharper for 80 and 100 Kev. This was probably because the electrons did not penetrate as deeply into the material at the lower energies. After the Al diffusion anneal and the implantations, barely visible broad rings were obtained indicating that there was considerable disorder. By the time the heat treatments had reached 850 C the surface had obviously recrystallized because clear sharp rings were visible.

A characteristic dopant profile for B into Nb_3Al is shown in figure (1). For the maximum energy of 160 Kev the B penetrated to an average depth R_p of approximately 4000Å. For the lowest energy of 30 Kev, R_p was approximately 1000 angstroms. One also notices that the composition of the first 200 angstroms did not have the required stochiometric composition of 25 At% for the (Al + B) atoms. Since the electrons in RED penetrated no further than 200 angstroms it was impossible to

obtain an accurate structural analysis of the implanted layer. We are therefore proceeding to obtain the necessary structural analysis using X-ray diffraction; this is a far more sensitive technique for phase determinations and lattice parameter measurements.

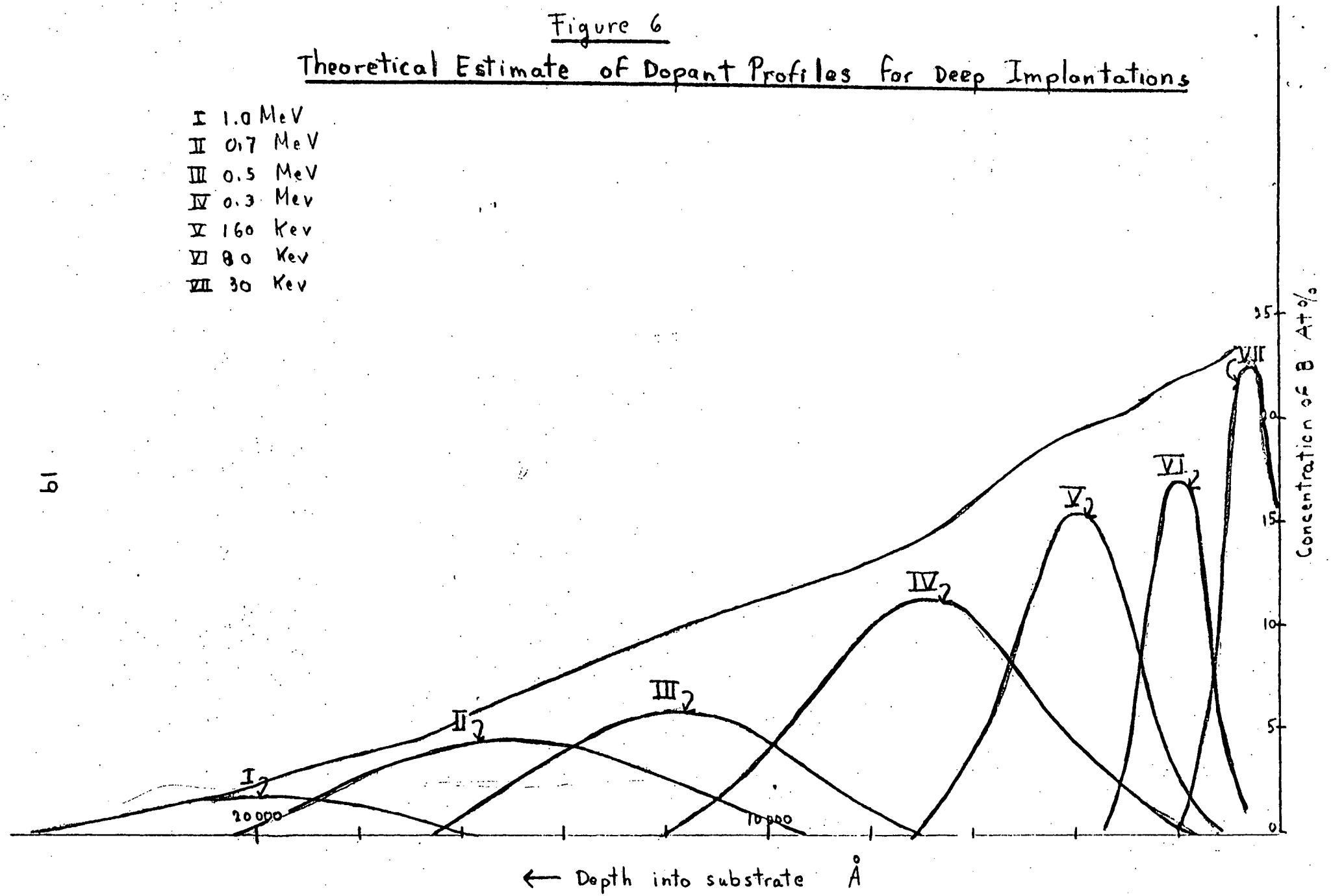
A new set of implanted samples is being prepared. A typical dopant profile for these new samples is shown in figure (6). A different accelerator is being used (2), one that is capable of accelerating ions up to 1 Mev. The corresponding penetration depth R_p for B is 2 microns. $CrK_{\alpha 2}$ radiation is very strongly absorbed by Nb atoms. By using this radiation, 90% of the X-ray intensity will be confined to the implanted layer; we will then be able to monitor accurately its phase changes and lattice parameters.

E. Superconducting transition temperature measurements

The T_c's were measured using a four point probe resistive technique. The voltage and current leads were placed from front to back of the sample so that the implanted surface was effectively in series with the substrate. Different resistivity drops could thus be obtained if the implanted surface and the substrate had different T_c's. A nanovoltmeter was used to pick up very small resistivity drops that might correspond to small portions of the samples going superconducting at different temperatures. T_c measurements were done on the

Figure 6

Theoretical Estimate of Dopant Profiles for Deep Implantations



samples at various stages of heat treatment. The substrate material superconducted around 18 K. A corresponding large resistivity drop was detected. After the recrystallization anneals some small resistivity drops were observed around 10 K and 11K. We are currently trying to correlate these with phases in the implanted layer and with accurate lattice parameter measurements. As mentioned previously we will be doing this using X-ray diffraction.

IV. DISCUSSION AND CONCLUSIONS

Large doses of B and C (up to 25 At%) were implanted into Nb_3Al substrates. The experimentally determined compositional profiles from Auger analysis agreed very well with theoretically predicted profiles. There was also no significant redistribution of the B and C after heat treatments up to 850 C. The high doses involved produced a very disordered surface layer. From reflection electron diffraction analysis it was ascertained that this layer recrystallized at 850 C. The samples were subjected to a variety of heat treatments and superconducting transition temperatures were measured. After the recrystallization anneals, transitions in the implanted layer were observed around 10 K and 11K. We are currently trying to relate these to structure and lattice parameter of the implanted layers. As is well known the T_c of A-15's is strongly dependent on lattice paramter. The smaller a_o the higher the T_c. A difference in a_o of 0.5 percent can make a dramatic change in T_c. T_c's are also very sensitive to the degree of order in

A-15's. The high implantation doses used created a great deal of disorder. It was hoped that annealing removed the effect of this disorder on T_c. However it may be necessary to use a much more dramatic means of annealing, such as laser melting of the implanted layers. It has been found in ion implanted semiconductors that laser melting is a very effective way of removing the defects associated with radiation damage.