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Ion-Beam Deposition of Nb and Ta Refractory Superconducting Films

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Abstract

A Kaufman ion-beam source has been used to sputter deposit high quality superconducting Nb ( $T_c = 9.1$  K) and Ta ( $T_c = 4.3$  K) films. Superconducting and electrical properties were studied as a function of deposition conditions and an optimum set of conditions was found. Nb films always had the bulk bcc crystal structure. The Nb film deposition rates ranged from 1 to 5 Å/sec with a Xe or Ar sputtering gas pressure of  $\sim 1$  to  $4 \times 10^{-4}$  Torr and a beam current density of 5-20 mA/cm<sup>2</sup>. Values of  $T_c$  above 8.3 K for Nb films were obtained with the use of Xe rather than Ar gas. In the case of Ta films, the deposition of a thin ( $\geq 3$  Å) Nb underlayer was required for the nucleation and growth of Ta in the bulk bcc crystal structure. Ta films deposited without a Nb underlayer always had high resistivity,  $\sim 150 \mu\Omega\text{cm}$ , and a tetragonal  $\beta$ -Ta crystal structure. The Nb and Ta targets and Si substrates all remained below 70°C during deposition and the films were easily patterned by standard photoresist liftoff.

I. INTRODUCTION

The use of ion-beams in thin film technology and device fabrication has received increasing attention in recent years.<sup>1</sup> Some of the major new developments include the application of ion-beams for oxidation,<sup>2</sup> for improved thin film step coverage,<sup>3</sup> and for modification of niobium film stress.<sup>4</sup> The use of an ion-beam system for sputter deposition has been explored by a number of workers.<sup>5-8</sup> Ion-beam sputtering offers a number of possible advantages for deposition of high-melting-point materials such as the refractory superconductors Nb and Ta. These advantages result from the relative absence of radiant heat and the physical separation of the deposition substrate from the plasma

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and high energy particles. Photoresist processing is one such advantage.<sup>5</sup>

Refractory superconducting films are of interest in electronic applications for their ruggedness and thermal cyclability. They are also of fundamental scientific interest in studies of the mechanisms influencing the superconducting transition temperature  $T_c$  and the effects of crystal damage and impurities. The deposition of high quality superconducting films of Nb and Ta using the methods of e-beam evaporation,<sup>9-12</sup> planar sputtering,<sup>12-14</sup> and magnetron sputtering<sup>15</sup> has been explored by other workers. Typically, very high quality vacuum systems ( $P < 10^{-7}$  Torr) and high deposition rates ( $R > 10 \text{ \AA/sec}$ ) are required. An elevated substrate temperature is also often required to achieve high quality films. These rather stringent requirements are due to the strong tendency of Nb and Ta to react with residual vacuum system impurities.

Previous work on inert gas ion-beam sputter deposition of refractory superconducting films<sup>7</sup> has demonstrated clear trends as a function of sputtering gas and crystal lattice expansion. Properties of those films, however, differed significantly from the bulk material. More recently, ion-beam deposited Nb-Ti films with properties reported to approach those of the bulk material have been produced on a heated substrate with a high-energy duoplasmatron-type ion source.<sup>6</sup>

→ In this paper we report on the electrical, superconducting, and structural properties of ion-beam deposited Nb and Ta films produced using a Kaufman ion source. We find that after careful optimization of ion gun parameters and the use of Xe gas, this technique is capable of reproducibly depositing high quality superconducting Nb films on room temperature substrates. The deposition conditions are, in fact, less stringent than for e-beam or planar sputtering systems. Importantly, we also find that by employing a multiple target capability, high quality Ta films can be produced under the same conditions by



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first depositing a thin underlayer of Nb. ↗

The dependence of  $T_c$  upon both low-temperature resistivity and lattice constant has been studied for Nb films and compared to results for bulk material.<sup>16</sup> The results of this comparison suggest that differences seen in these fundamental properties are due to the ion-beam sputtering process.

II. EXPERIMENTAL PROCEDURE

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The ion-beam sputtering system used in this work is shown schematically in Fig. 1. The Kaufman ion source with high current density carbon grids was obtained from Ion Tech, Inc.<sup>17</sup> and has a beam diameter of 2.5 cm. Typical operating conditions with xenon (≥99.99% pure) or argon (≥99.999% pure) gas ranged from 900-1500 eV beam energy and from 25-100 mA beam current. The items shown in Fig. 1 are mechanically mounted on 3/4 inch thick metal top and bottom plates for a 18 inch dia. x 21 inch high pyrex glass cylinder. This system is pumped by a standard 6 inch diffusion pump with a liquid nitrogen cold trap.<sup>18</sup> In addition, we have constructed a liquid-nitrogen-cooled copper liner which fits just inside the pyrex glass cylinder and provides additional trapping for water vapor and other impurities. This cold shield reduces the ultimate chamber pressure from 6 to  $3 \times 10^{-7}$  Torr, the main contaminant being water vapor.

The target holder shown in Fig. 1 can be used to rotate any one of four different water-cooled targets under the beam. We use 4 inch dia. Nb and Ta (99.9+% purity) targets, the centers of which are ~15 cm from the gun when sputtering. The temperature rise during deposition is ~20°C.

The substrate holder is capable of separately exposing eight sets of substrates and is both thermally and electrically floating. During a typical deposition, the substrate temperature remains below 70°C. We have employed 1/4 inch x 1/4 inch Si(100), Si(111), and microscope cover glass (Corning 0211 glass) substrates with no distinguishable difference in deposited film proper-

ties. Substrates were cleaned ultrasonically in solvents and blown dry with nitrogen gas. The stability of the ion-beam characteristics during a deposition was always quite good (variations  $\leq 3\%$ ). An initial predeposition sputter period of typically 60 min. was always performed to allow the gun to equilibrate and to provide a layer of freshly sputtered Nb or Ta.

Resistivity measurements were made using the four-point technique due to van der Pauw,<sup>19</sup> which is independent of sample shape. Temperature measurement was made using a germanium resistance thermometer or a calibrated Allen-Bradley 220 ohm carbon resistor. The transition temperatures of high-purity bulk Pb and Nb samples have been measured to within 0.1 K of their published values.<sup>20</sup> Detection of the superconducting transition was made both resistively and inductively by an ac susceptibility measurement at  $\sim 2$  MHz. Film thickness was measured ( $\pm 100 \text{ \AA}$ ) by an optical interference technique. Most films whose properties are reported on below were thick ( $d \gtrsim 1500 \text{ \AA}$ ) to avoid the depression of  $T_c$  found in very thin films.<sup>13</sup>

Electron diffraction, transmission electron microscopy (TEM), and scanning transmission electron microscopy (STEM) were all performed on a JEOL 100CX TEMSCAN. Samples were prepared by depositing 300  $\text{\AA}$  to 400  $\text{\AA}$  of Nb or Ta onto a 300  $\text{\AA}$  carbon film which was suspended on a standard 200 mesh copper TEM grid. Energy dispersive x-ray analysis was also used to look for incorporated xenon or argon. X-ray diffraction measurements were made using a standard x-ray diffractometer with a  $\text{Cu K}\alpha$  x-ray source. Positions of the Nb and Ta peaks on the diffractometer traces were referenced to the silicon substrate peaks or a silicon powder standard, allowing an absolute accuracy of  $\pm 0.05^\circ$ .

### III. RESULTS AND DISCUSSION

#### A. Ion Beam Parameters

The initial studies of ion-beam deposition were made with argon gas.

However, the subsequent use of xenon gas, suggested by the work of Schmidt,<sup>7</sup> was found to produce our highest quality films. Using Nb as a test material, the optimum beam conditions for each gas were obtained. The ion beam was run without a neutralizer since an initial study of its use showed no beneficial effects. Grounding or applying an electrical bias of up to  $\pm 100$  V to the substrates also produced no noticeable improvements. As a result, most substrates were electrically floating with a positive self bias of about 10 volts.

The optimum beam parameters were judged to be those that produced the highest  $T_c$  Nb films. For Ar gas, the optimum beam conditions were 1300 volts beam voltage and 57 mA beam current at a chamber pressure of  $\sim 1.0 \times 10^{-4}$  Torr (as measured with an ion gauge). These conditions produced a deposition rate of  $\sim 2.2 \text{ \AA}/\text{sec}$  and a  $T_c$  of 8.3 K. For Xe gas, the optimum beam conditions were 1500 eV and 35 mA at a chamber pressure of  $\sim 1.7 \times 10^{-4}$  Torr, producing a deposition rate of  $2.4 \text{ \AA}/\text{sec}$  and a  $T_c$  of 9.1 K. Deposition rates in these optimization studies for Nb films ranged from 1-5  $\text{ \AA}/\text{sec}$  and were directly proportional to ion-beam power (current x voltage). The sputtering yield for Xe gas was found to be  $\sim 50\%$  higher than for Ar gas. The  $T_c$  values for various deposited Nb films revealed a fairly broad maximum with respect to variations in ion-beam power. In general, a 25% change from the optimum values of ion-beam current or voltage given above produced a  $\sim 0.3$  K drop in  $T_c$ . In addition, fine tuning of the internal ion gun voltages and inert gas pressure has shown that a minimization of the accelerator grid current to  $\leq 3$  mA and the plasma discharge voltage (a lesser value for Xe) produced the highest  $T_c$  Nb films at a given beam power. This minimization suggests that excessive internal currents or voltages may give rise to beam contamination due to bombardment of internal gun structures.

The observed decrease in  $T_c$  with respect to decrease in beam power

(deposition rate) from the optimum value is probably due to an increased incorporation of adsorbed vacuum system impurities in the growing film. The decrease in  $T_c$  at higher rates is probably due either to increased sputtering inside of the ion gun, which could produce a contaminated beam, or to increased particle bombardment of the growing film, which could cause film damage.<sup>4,14</sup>

#### B. Niobium Films

The measurements of Nb films are more extensive than those on Ta films and represent the properties of over 100 films. Films were always observed to adhere very well to clean Si or glass substrates. The wrinkled appearance of the few films deposited on dirty substrates indicates that our films are under compressive stress, in agreement with work on low-pressure magnetron sputtered Nb films.<sup>15</sup> The electrical measurements of representative Nb films are presented in Fig. 2 and Table I. The data in these figures represent the properties of films deposited under a wide variety of beam conditions during the optimization procedure discussed above. The important feature to notice in Fig. 2 is the consistent behavior of the ion-beam-deposited films with respect to changes in deposition conditions. The decrease in  $T_c$  from  $\sim 9.1$  K at a rate of  $\sim 0.1$  K/ $\mu\Omega\text{cm}$  appears to be universal for our films and represents a rate that is less than that for bulk niobium-oxygen solid solutions ( $\sim 0.18$  K/ $\mu\Omega\text{cm}$ ).<sup>16</sup> In general, the analysis of mechanisms causing the depression of  $T_c$  in Nb films is a complicated issue and will not be discussed in detail here. In past work, it was found that the competing factors of lattice dilation, lattice damage, and inert or reactive gas incorporation all have a strong effect on  $T_c$  in Nb films.<sup>14</sup>

It is important to note that with the optimum beam conditions given above we have reproducibly prepared Nb films with a  $T_c \gtrsim 9.0$  K and a transition width  $\leq 0.03$  K. To our knowledge, this is the first report of  $T_c$  values this high for



Nb films deposited without the use of high rates ( $>10 \text{ \AA}/\text{sec}$ ), heated substrates, or a very high vacuum environment ( $P < 10^{-7}$  Torr). Because of the use of room temperature substrates, these Nb films were also easily patterned using standard photoresist liftoff techniques.

Structural data obtained from TEM and x-ray diffraction studies showed that the Nb films were bcc polycrystalline and had a grain size of  $\sim 150 \text{ \AA}$ . No significant change in  $T_c$  with grain size was observed. TEM diffraction patterns showed no preferred orientation of grains with respect to rotations in the plane of the substrate. X-ray diffractometer scans, however, indicated a strong preference for the (110) lattice planes to be parallel to the substrate. This (110) texturing was found for all substrates. A plot of  $T_c$  vs. lattice constant  $a_0$ , as determined by the position of the (110) lattice reflection, is given in Fig. 3 and is compared with previous work on bulk<sup>16</sup> and ion-beam deposited Nb.<sup>7</sup> The data in Fig. 3 suggest that a mechanism other than oxygen gas incorporation, possibly inert gas incorporation, may be expanding the lattice in the case of ion-beam deposited films. The absence of any detectable levels of xenon or argon by standard energy dispersive x-ray analysis, however, indicates that concentrations of Xe or Ar must be less than  $\sim 0.5$  atomic %. In addition, a SIMS analysis of our best films reveals that oxygen and carbon impurity concentrations are  $\sim 0.1$  at. %. The results of tunnel junction fabrication on Nb and on Nb with Ta overlayers are presented elsewhere.<sup>30</sup>

### C. Tantalum Films

All investigations of Ta film deposition were performed with a xenon ion-beam using the optimum beam conditions for Xe gas given above for Nb. These conditions produced a Ta deposition rate of  $2.7 \text{ \AA}/\text{sec}$ . It was found that room temperature glass or silicon substrates always produced high resistivity (150-200  $\mu\Omega\text{cm}$ ) films characteristic of the well known  $\beta$  phase of Ta.<sup>21-26</sup> This is consistent with previous work<sup>5,8</sup> on ion-beam deposited Ta films. (Note, how-

ever, that bcc Ta has been obtained<sup>11,26</sup> by substrate heating or the use of particular substrates such as gold.) The residual resistance ratio ( $\rho_{298K}/\rho_{10K}$ ) of these films was always  $\lesssim 1$ . X-ray diffractometer scans confirm the existence of the  $\beta$ -Ta tetragonal crystal structure and a strong degree of (100) texturing. Although there can be difficulties in interpreting diffractometer scans without the use of off-axis information,<sup>25</sup> our data do suggest that little or no Ta in the bcc phase exists in our  $\beta$ -Ta films. The  $\beta$ -Ta films did not superconduct above 1.5 K, which is consistent with the published  $T_c$  of 0.5 K<sup>21</sup> for the  $\beta$ -Ta phase.

In order to promote the formation of Ta in the bcc phase (bulk  $T_c \approx 4.4$  K) we have ion-beam deposited a layer of Nb onto the Si substrates just before depositing the Ta. This was accomplished by depositing a layer of Nb 3 Å to 600 Å thick and then immediately (within  $\sim 1$  sec.) rotating the target holder to the Ta position without turning off the beam or closing the shutter. Nb underlayers of 3 Å and 10 Å showed a dramatic decrease in the amount of  $\beta$ -Ta, by a factor of more than 100. Ta films on Nb underlayers thicker than 10 Å showed no detectable amount of  $\beta$ -Ta. Nb underlayers of all thicknesses produced a large increase in the amount of bcc Ta as inferred from  $T_c$ , low temperature resistivity, and x-ray diffractometer scans. X-ray data also showed a strong degree of (110) texturing. The Ta film data are summarized in Table I. Consistent with the proximity effect theory,<sup>27</sup> Ta films on Nb underlayers with thicknesses  $\lambda \xi(0) (\sim 100 \text{ Å})$ <sup>28</sup> appear to have enhanced values of  $T_c$ .

The strong influence of the substrate on the nucleation of  $\beta$ -Ta has been previously observed by other workers.<sup>23,26</sup> Our findings suggest that the thin Nb underlayer is modifying the substrate surface to provide a surface that favors the formation of the bcc phase of Ta. These findings are consistent with the hypothesis of Feinstein<sup>26</sup> that the presence of O or OH, formed by the reaction of  $H_2O$  with the surface oxide, favors the nucleation of  $\beta$ -Ta. There

may also be a propensity for bcc Ta growth due to the close lattice match of bcc Ta and Nb.<sup>29</sup> The use of a Nb underlayer, in any case, is a particularly convenient method for obtaining bcc Ta films. Further investigations of Ta films are in progress.

#### IV. CONCLUSIONS

In summary, we find that the ion-beam deposition technique is capable of producing high quality superconducting films of Nb and Ta. While high quality films may be produced by other techniques, ion-beam deposition offers some special advantages. Importantly, Nb and Ta films can be produced on room temperature substrates, in a moderate vacuum system and with moderate deposition rates. These ion-beam deposited films are compatible with standard photoresist liftoff techniques, which is an important advantage for electronic device applications. In addition, the ability to sequentially deposit different materials, using a multiple target holder, is of general utility and is helpful in conveniently obtaining the bulk bcc crystal structure in Ta films.

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Table I Representative Nb and Ta Film Properties

Film No.	Sputtering Gas	Film Thickness <sup>a</sup>		bcc Lattice Constant (Å)	$\rho_{10\text{ K}}$ ( $\mu\Omega\text{cm}$ )	$\frac{\rho_{298\text{ K}}}{\rho_{10\text{ K}}}$	$T_c^b$ (K)
		Nb (Å)	Ta (Å)				
bulk Nb				3.301	-	-	9.3
25-2	Xe	2500		3.335	4.0	3.86	9.1 <sup>c</sup>
28-3	Xe	2000		3.335	5.2	3.56	8.9
26-1	Xe	2500		3.343	7.3	2.88	8.7
24-7	Xe	2700		3.367	13.5	2.00	8.4
24-4	Xe	2300		3.367	18.8	1.63	7.5
112-6	Ar	1900		3.353	11.5	2.00	8.3 <sup>c</sup>
18-6	Ar	1900		3.362	21.4	1.64	7.6
19-1	Ar	2200		3.380	27.3	1.43	6.7
18-3	Ar	1800		3.405	43.8	1.28	5.8
15-1	Ar	1600		-	53.4	1.24	5.3
bulk Ta				3.303			4.4
210-8	Xe	600	2400	-	5.2	5.32	7.9
28-1	Xe	300	2400	-	6.2	3.35	6.6
210-5	Xe	70	2400	3.328	5.6	3.25	4.5
210-4	Xe	30	2400	3.324	6.1	3.23	4.3
210-2	Xe	10	2400	3.324	5.5	3.75	4.3
210-1	Xe	3	2400	3.324	7.2	3.45	4.2
28-8	Xe	0	2400	$\beta$ -Ta	151	0.95	-

<sup>a</sup> Ta films were deposited on Nb underlayers to nucleate bcc Ta (see text).

<sup>b</sup> Different Nb film  $T_c$ 's were produced under different deposition conditions (see text).

<sup>c</sup> Optimum values for sputtering gas used.

## FIGURE CAPTIONS

- Fig. 1 Schematic of ion-beam sputter deposition system (dimensions given in the text). A shutter (not shown) is located between the target and the substrate holder.
- Fig. 2 Superconducting transition temperature,  $T_c$ , of ion-beam deposited Nb films vs low temperature (10 K) resistivity. Film thickness ranged from 1000 Å to 3000 Å. Other data from Koch et. al., Ref. 16.
- Fig. 3 Superconducting transition temperature,  $T_c$ , of ion-beam deposited Nb films vs crystal lattice constant,  $a_0$ . Data from this work given in Table II. Other data from Schmidt, Ref. 7 and Koch et. al., Ref. 16.

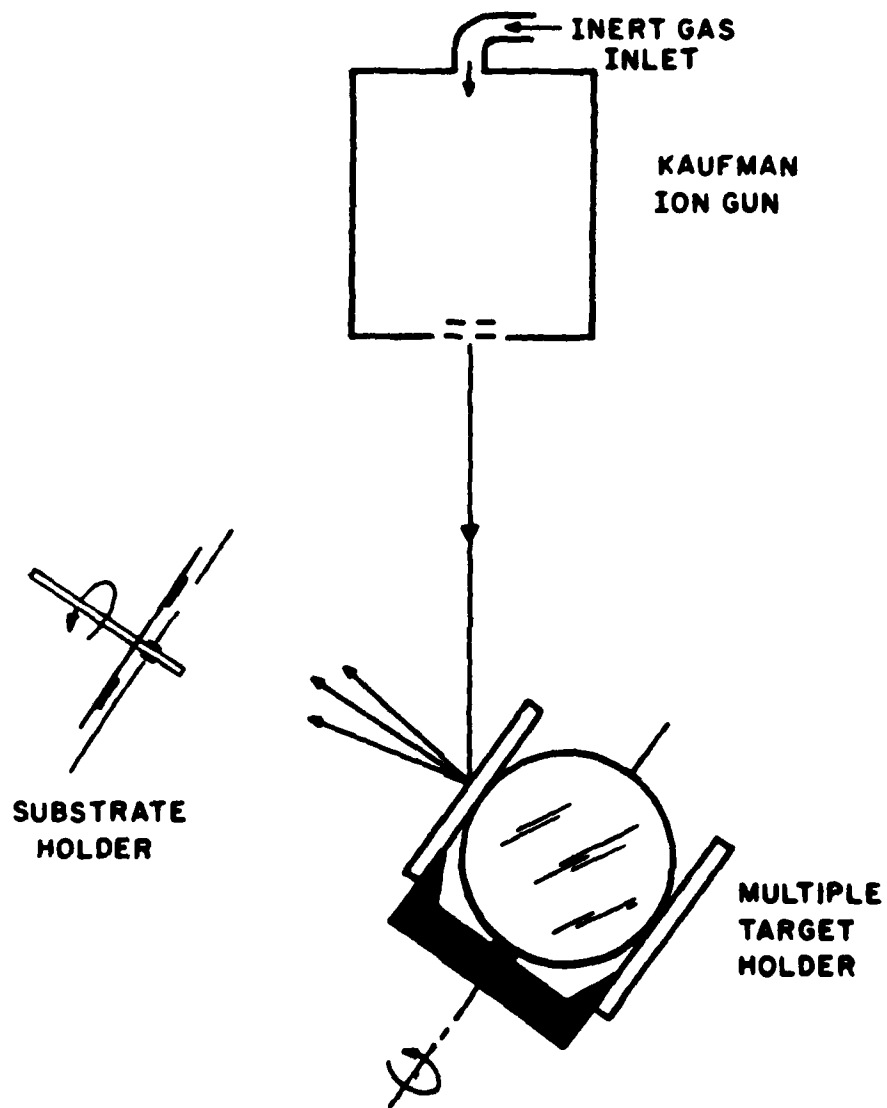


Fig. 1



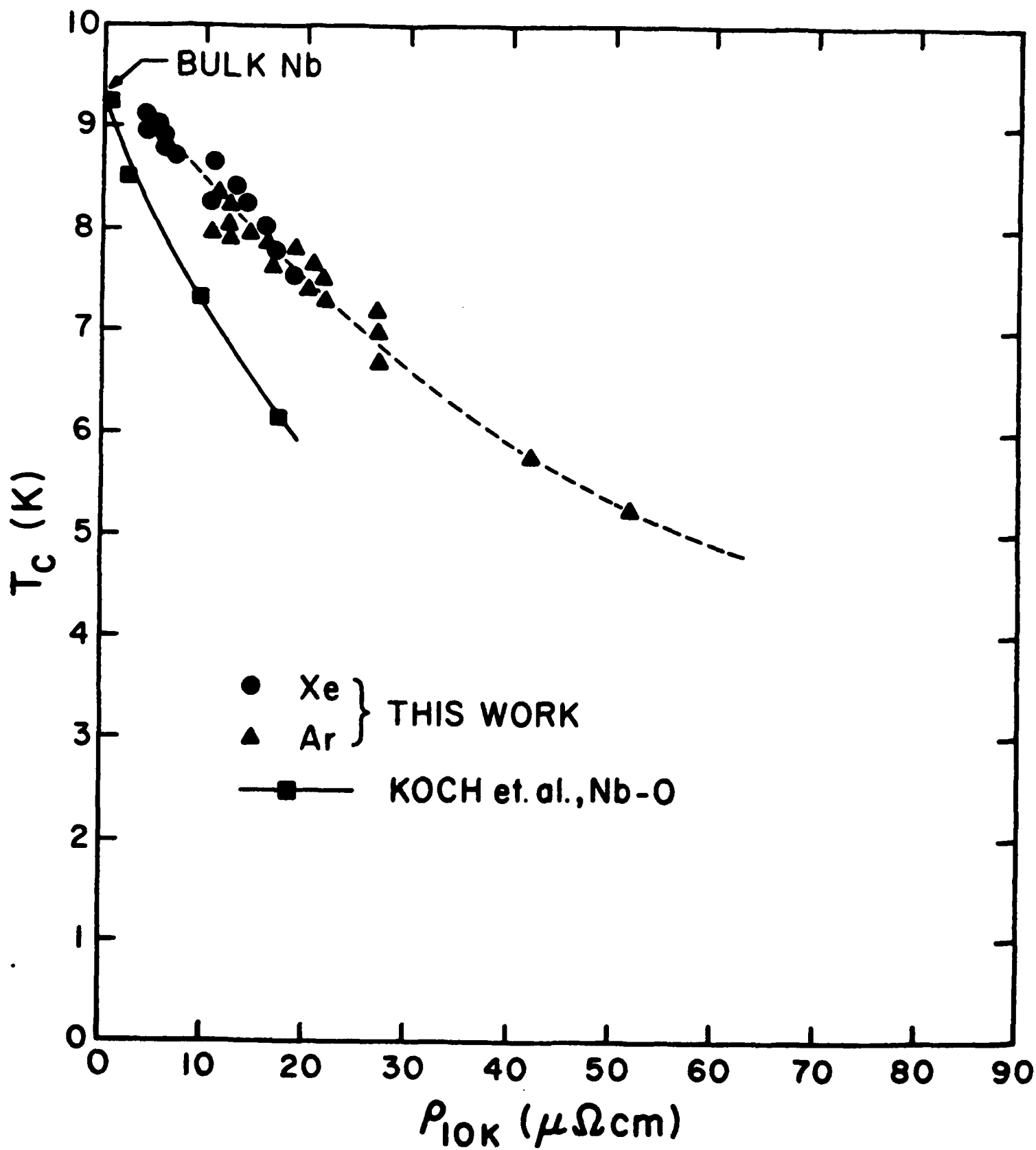


Fig. 2

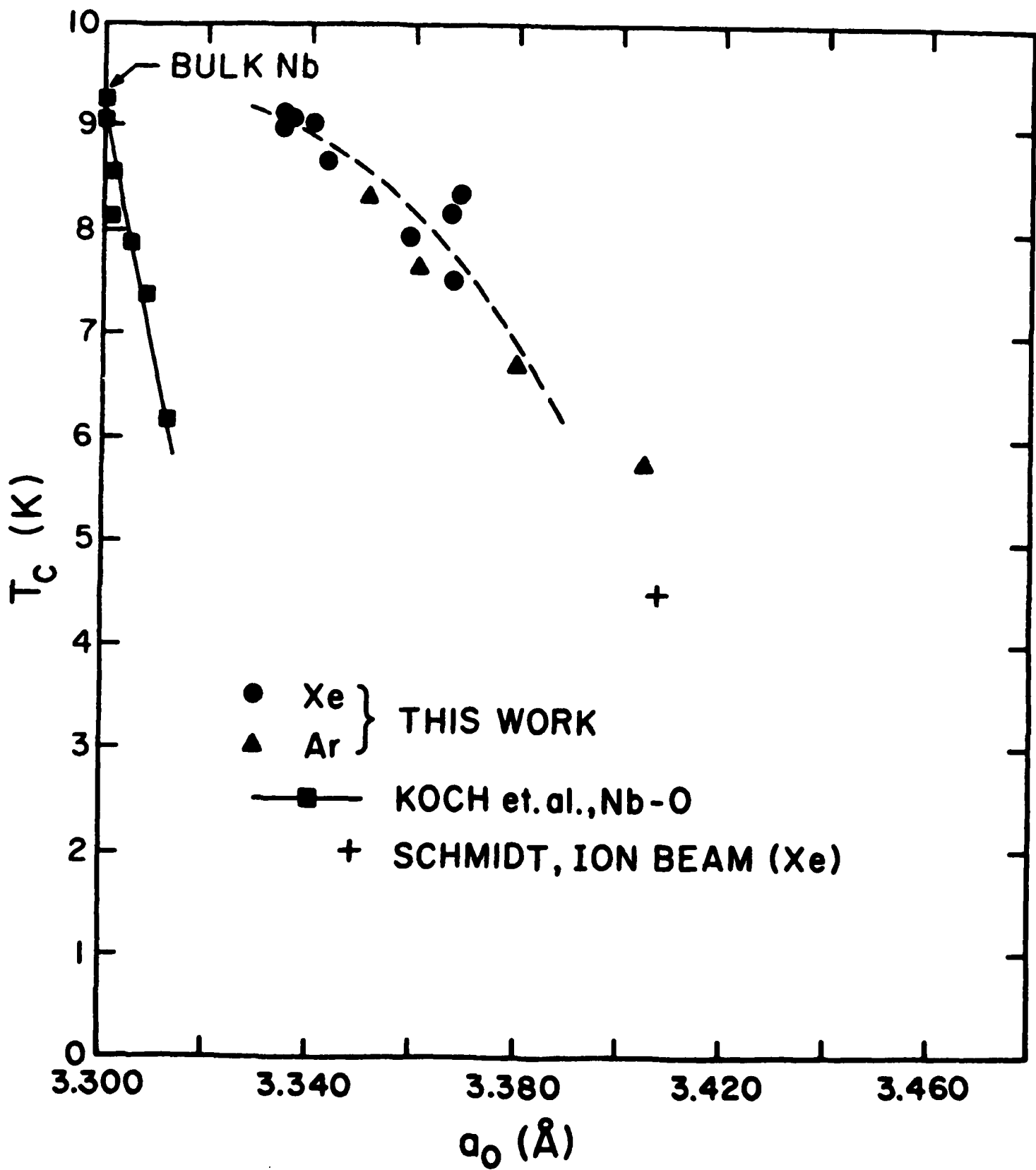


Fig. 3