AD-753 359

Studies of Superconducting Thin Film Carbides and Nitrides

Engineering and Materials Science

prepared for

**Army Mobility Equipment
Research and Development Center**

JULY 1971

Distributed By:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

UNCLASSIFIED

AD

Report No. 6

Studies of Superconducting Thin Film Carbides and Nitrides

Final Technical Report

by

Ramasubramanian Somasundaram and

Louis E. Toth

Department of Chemical Engineering and Materials Science

University of Minnesota

Minneapolis, Minnesota

July 1971

U. S. Army Mobility Equipment Research and Development Center

Fort Belvoir, Virginia 22060

Contract No. DAAK 02-70-C-0181

UNCLASSIFIED

65

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)* University of Minnesota Department of Chemical Engineering & Materials Science Minneapolis, Minnesota 55455	2a. REPORT SECURITY CLASSIFICATION Unclassified 2b. GROUP

3. REPORT TITLE

Studies of Superconducting Thin Film Carbides and Nitrides

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

Final Report

5. AUTHOR(S) *(First name, middle initial, last name)*

Louis E. Toth and Ramasubramanian Somasundaram

6. REPORT DATE July 1971	7a. TOTAL NO. OF PAGES ~~10~~ 25	7b. NO. OF REFS 13
8a. CONTRACT OR GRANT NO. DAAK 02-70-C-0181 b. PROJECT NO. 1T 061102 A34 c. d.	9a. ORIGINATOR'S REPORT NUMBER(S) None 9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*	

10. DISTRIBUTION STATEMENT

Distribution of this statement is unlimited

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY U. S. Army Mobility Equipment Research and Development Center, Fort Belvoir, Virginia, 22060

13. ABSTRACT

Thin films of niobium nitride prepared by reactive sputtering have an excellent combination of superconducting characteristics. A major problem in utilizing these nitrides has been the varied and often contradictory descriptions of how to prepare the films to obtain a desired set of superconducting properties. The problem of consistency and transferability of results can be partially resolved if one pays attention to the structure and composition of the films and not necessarily to the mechanic of sputtering. In this study we attempted to vary the sputtering conditions and correlate the superconducting properties of NbN and related alloys with the film's composition and structure. We found that relatively small changes in sputtering conditions often resulted in large changes in superconducting properties. In every case the results can be explained when film structure and composition were characterized. The study included the nitrides and carbides of niobium and tantalum. Both d.c. and a.c. sputtering techniques were used.

DD FORM 1 NOV 65 **1473** REPLACES DD FORM 1473, 1 JAN 64, WHICH IS OBSOLETE FOR ARMY USE.

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Superconducting transition temperature						
A.c. and d.c. reactive sputtering						
Niobium nitride						
carbide						
carbonitride						
Tantalum carbide						
nitride						
Crystal structure						

Studies of Superconducting Thin Film Carbides and Nitrides

Final Technical Report

July 1971

by

Ramasubramanian Somasundaram

and

Louis E. Toth

Department of Chemical Engineering and Materials Science

University of Minnesota

Minneapolis, Minnesota

U. S. Army Mobility Equipment Research and Development Center

Fort Belvoir, Virginia 22060

Contract No. DAAK 02-70-C-0181

Summary

Thin films of niobium nitride prepared by reactive sputtering have an excellent combination of superconducting characteristics. A major problem in utilizing these nitrides has been the varied and often contradictory descriptions of how to prepare the films to obtain a desired set of superconducting properties. The problem of consistency and transferability of results can be partially resolved if one pays attention to the structure and composition of the films and not necessarily to the mechanics of sputtering. In this study we attempted to vary the sputtering conditions and correlate the superconducting properties of NbN and related alloys with the film's composition and structure. We found that relatively small changes in sputtering conditions often resulted in large changes in superconducting properties. In every case the results can be explained when film structure and composition were characterized. The study included the nitrides and carbides of niobium and tantalum. Both d.c. and a.c. sputtering techniques were used.

Foreword

The work was authorized by U. S. Army Mobility Equipment Research and Development Center, Fort Belvoir, Virginia, under Contract No. DAAK 02-70-C-0181 and was carried out under the supervision of Dr. H. J. Spitzer.

The research described here will form the basis for the M. S. thesis of Ramasubramanian Somasundaram.

SUPERCONDUCTING PROPERTIES OF THIN-FILM TRANSITION METAL CARBIDES AND NITRIDES

Introduction

Thin films of niobium nitride prepared by reactive sputtering have an excellent combination of high critical temperature, magnetic field and current characteristics. Critical temperatures of 18°K, critical fields in excess of 200 kOe and current densities of 10^5 A/cm^2 at 200 kOe have been observed. Despite this unusual combination of properties, the nitride films have never been utilized in practical devices or solenoids. A major problem in utilizing these nitrides has been the varied and often contradictory descriptions of how to prepare the films to obtain a desired set of superconducting properties(1-7).

For example, Gavaler et al(1) state that high T_c's, H_{c_2}'s and J_c values were obtained only when the sputtering system is baked out to a vacuum of less than 10^{-8} torr prior to sputtering. Bell et al(2) reached a similar conclusion. Mitszuoke et al(3) and Spitzer(4), however, both obtained high T_c materials using diffusion pumped stations in which the best ultimate vacuum was not greater than 10^{-8} torr. Mitszuoke et al found that asymmetric sputtering could be used to achieve nearly maximum T_c's despite a relatively low vacuum prior to sputtering (10^{-5} torr). Investigators also disagree on the optimum conditions for nitrogen partial pressure, N_2/Ar ratios, substrate temperature, deposition rates, spacing between substrate and target. It is nearly impossible for one group of investigators to duplicate the results of another group. It is also difficult for any one group to duplicate their own results consistently.

The problem of consistency and transferability of results can be partially solved if one pays attention to the structure and composition of the films and not necessarily to the mechanics of sputtering. While a number of investigators did some characterization of their films, Spitzer was probably the first to point out the importance of the film structure on the superconducting properties of NbN.

In this study we attempted to vary the sputtering conditions and correlate the superconducting properties of NbN and related alloys with the film's composition and structure. We found that relatively small changes in sputtering conditions often resulted in large changes in superconducting properties, but in every case the results could be explained when film structure and composition were characterized.

The study included the nitrides and carbides of niobium and tantalum. Both d. c. and a. c. sputtering techniques were used.

Experimental procedure

Reactive sputtering of carbides and nitrides of niobium and tantalum was performed in an Ultek vacuum system, capable of reaching an ultimate vacuum of 10^{-9} torr. For sputtering of niobium compounds, a 2 x $\frac{1}{8}$" niobium disc of 99.98% purity was used as the target. Substrates of quartz, glazed alumina, molybdenum and copper were supported on another 2 x $\frac{1}{8}$" niobium disc. A distance of 2 inches was maintained between substrates and target in d. c. sputtering and one inch in the case of a. c. sputtering. For d. c. sputtering of tantalum compounds, a tantalum sheet of 99.98% purity, was used as the target. The substrates were cleaned ultrasonically in igepal detergent solution. The cleaned substrates were then rinsed successively in hot tap water, distilled water and reagent grade methyl alcohol and dried in a flow of nitrogen gas. After drying, the substrates were cleaned in boiling freon T. F. for five minutes followed by ultrasonic cleaning in Freon T. F. The substrates could be heated up to 500° C by a molybdenum heater.

The vacuum system was evacuated by a combination of sorption, ion and titanium sublimation pumps, followed by baking at 200°C. After cooling, the substrates were heated to 500°C by the molybdenum furnace for 24 hours to remove the absorbed gases. Except when nitrogen was required in small concentrations, argon was admitted first to the required concentration. D. C. sputtered niobium carbides were prepared with a quartz tube enveloping the target and substrates. The nitrides were prepared without the quartz envelope. During sputtering, nitrogen and methane were continuously lost; hence nitrogen and methane were continuously admitted to maintain the required pressure.

Superconducting transition temperatures were measured by monitoring the change in electrical resistance with temperature. Critical field measurements were made at 4.2°K using a pulsed field-current apparatus. Thickness measurements were made with a Leitz interferometer. Some of the films deposited on molybdenum were chemically analysed by auger electron analysis. For structural analysis, the firms deposited on quartz and alumina were stripped by dissolving the substrates in dilute solution of HF. The films deposited on copper were stripped by dissolving in ferric sulfate solution. The stripped films were mounted on a Siemens X-ray powder camera for structural analysis. Some of the samples were examined by reflection electron diffraction and transmission electron microscopy.

Experimental Results

Niobium Nitride

In asymmetric a. c. sputtered nitride films, with substrates not heated externally by the molybdenum heater, the superconducting transition temperature was found to increase with applied voltage and decrease with increasing partial pressure of nitrogen. With a gas composition of 50 m · torr of argon and 1 m · torr of nitrogen, and with an applied voltage of 2040 volts and an anode to cathode current ratio of 0.4, the transition temperature was 4.2°K. Vacuum annealing at 180°C for 48 hours led to an increase in transition temperature from 4.2 to 9.1°K. At an applied voltage of 3300 volts, the transition temperature was 10.4°K. When the partial pressure of nitrogen was increased from 1 to 3 m · torr, and the applied sputtering voltage was 2040 volts, no superconducting films were obtained. At an applied voltage of 3300 volts and a nitrogen pressure of 10 m · torr, the T_c dropped from 10.4 to 6.2°K.

In d.c. sputtered nitride films, with substrates heated to 450°C by a molybdenum heater, an increase in applied voltage resulted in an increase in T_c followed by a decrease as shown in Figure 1. Increasing the partial pressure of nitrogen was also helpful in improving the transition temperature of nitride films (Figure 2). The variations in T_c obtained by changes in substrate temperature are indicated in Figure 3. Along with the transition temperatures, the associated crystal structures are also indicated in Figs.1-3. No significant changes in results were found when different substrate materials were used. The results indicate that increasing the applied voltage, substrate temperature, and partial pressure of nitrogen led to the formation of compounds containing higher amounts of nitrogen. Auger electron alalysis of the nitride films (Table I) indicate, however, an increase in the Nb/N and Nb/O ratio (in arbitrary parameters) with increasing voltage and substrate temperature. This is similar to the observation of Sosniak (8) on the impurity contents of Nb films at different substrate temperatures. The results of both X-ray and Auger analyses seem to be contradictory. The discrepancy between the two methods probably arises from the fact that Auger analyses indicate the total nitrogen content of the film surface while X-ray analyses indicate the nitrogen that has reacted with niobium to form the nitride. Another factor is that the Auger technique analyzes the surface (1-2 surface layers) while the X-rays monitor the entire films. The H-J_c curve of NbN film having a T_c of 14.1°K is given in Figure 4.

Niobium carbide

In asymmetric a.c. sputtered carbide films, as the substrate temperature was increased from room temperature to 350°C, a superconducting carbide having a transition temperature of 5.65°K was formed at 350°C. The a.c. sputtering was carried out at an applied voltage of 3300 volts in a gas having a composition of 50 m · torr of argon and one m · torr of methane. At higher substrate temperatures, no films were obtained. By presputtering in an argon-methane atmosphere instead of a pure argon atmosphere, the T_c could be increased to 7.1°K from 5.65°K. As the methane content was increased from 1 to 5 and 10 m · torr, no superconducting films were obtained. The actual methane content during sputtering could not be determined exactly because of the dissociation of methane. Continuing experiments will utilize an RGA to determine exactly gas contents.

In d.c. sputtered carbide films, superconducting films were obtained only at substrate temperatures of 350°C (Fig. 3). Higher substrate temperatures resulted in films having no superconductivity above 3.5°K. X-ray analyses indicate the formation of Nb_2C at higher substrate temperatures as compared to the NbC at 350°. With increasing applied voltage, the transition temperature decreased and Nb_2C was found to form. Auger analyses of the film (Table I) indicate a decreasing carbon content as well as decreasing oxygen content with increasing substrate temperature. The H-J_c of 7.1°K is given in Figure 4.

Carbonitrides of niobium

Thin films of carbonitride of niobium were prepared by reactive d.c. sputtering in an atmosphere of argon, nitrogen, and methane. At low partial pressures of nitrogen (2×10^{5} torr), superconducting films were obtained only at 400°C (Figure 3). Increasing or decreasing the substrate temperature resulted in films having no superconducting transition at 3°K. In analyzing the films by X-ray, it was not feasible to distinguish between Nb_2N and Nb_2C due to their close "d" values. Hence the films indicated in Figure 3 as Nb_2N

could also contain Nb_2C. The T_c of the films is probably associated with Nb_2N rather than Nb_2C. The latter phase did not show any superconductivity in the experiments with carbide films. Superconductivity of Nb_2N films had been observed earlier by Gravaler et al.(1) Films prepared at higher and lower substrate temperatures showed a structure very similar to ζNbC in addition to Nb_2N. Increasing the applied voltage from 4000 to 4500 volts at a substrate temperature of 400°C led to a decrease in transition temperature from 7 to 1.8°K. The transition temperature could be increased to 5.7°K by the addition of 1.5 m. torr of nitrogen. The X-ray structure obtained with increased addition of nitrogen was the same as that obtained at 400°C at 4000 v and 2×10^{-5} torr of nitrogen. At high nitrogen contents, increasing methane content resulted in an increase in transition temperature followed by a decrease (Fig. 5). The changes in T_c seem to be associated with a decreasing nitrogen content as the methane content was increased (Fig. 5).

Tantalum nitride

Sputtering conditions which gave best results for NbN also gave best results for TaN. At an applied voltage of 2800 volts, with substrates at 450°C and 500°C, a T_c of 7.4°K was obtained. Increasing the applied voltage to 3200 volts led to a small increase in transition temperature to 7.7°K. D. C. sputtering at 2000 volts and a substrate temperature of 400°C led to the formation of Ta_3N_5 with no superconductivity. The transition temperature of 7.4°K was associated with a F. C. C. structure having a lattice parameter of 4.37A°. This is similar to the results obtained by Bell laboratories(9,10) rather than the tetragonal structure suggested by Coyne et al.(11) The H-J_c curve for TaN is given in Figure 4.

Tantalum carbide

D. C. sputtering of tantalum carbide was done as a function of applied voltage, substrate temperature and partial pressure of methane. The effect of applied voltage is given in Figure 1. The X-ray structural analyses indicate the formation of TaC + Ta_2C at both low and high voltages. Only at an intermediate voltage was TaC obtained. Increasing substrate temperatures as well as increasing partial pressures of methane resulted in structures similar to that obtained with different voltages (Figs. 2 and 3.) The low superconducting temperatures of the carbides seem to be associated with the low C/Ta ratio as indicated by the lattice parameter.

Discussion

The results indicate that the transition temperature is very much affected by small changes in sputtering variables. The changes in sputtering variables seem to produce changes in crystal structure as well as changes in lattice parameter. The effect of lattice parameter (or $\frac{N}{Nb}$ & $\frac{C}{Nb}$ ratio) of thin films and bulk material on T_c is indicated in Figures 6 and 7. The variables that affect the structure are (1) presputtering (2) applied voltage (3) partial pressure of reacting gas and (4) substrate temperature.

Effect of presputtering

In a. c. sputtering of carbides, presputtering in an atmosphere of argon and methane was found to increase the transition temperature of the carbide from 5.65 to 7.1°K. For the nitrides, (no presputtering was done) the maximum transition temperature obtained was about 10.4°K after vacuum annealing at 180°C. Mitszuoka <u>et al</u>(3) however, were able to obtain a transition temperature of 15°K by presputtering in an atmosphere of argon and nitrogen. The improvement due to presputtering probably arises from purification of the gases and target and from a partial reaction of the target with nitrogen or carbon to form the compound on the target. During sputtering, further reaction can occur between niobium and the gases leading to better stoichiometry and hence to higher transition temperatures.

In d. c. sputtering of nitrides, presputtering in an argon atmosphere improved the transition temperature. The improvement resulted from the removal of oxygen in the atmosphere as indicated by the X-ray results (Fig. 3).

Effect of applied voltage

The effect of increased voltage can be explained on the basis of (1) increased deposition rate with increased voltage (2) increased thermal energy due to greater ion bombardment energy.(12) In a. c. sputtering, with the substrates not externally heated, vacuum annealing was found to improve the T_c. This indicates that sufficient thermal energy was not available during sputtering for complete reaction. Increased applied voltage improves the T_c by supplying more energy for reaction.

In d. c. sputtering, at low voltages sufficient thermal energy was not available for forming NbN as indicated by the discrepancy in the Auger and X-ray analyses. Increasing the voltage promotes compound formation and leads to higher transition temperatures. Further increased voltage led to the formation of lower carbides; however, probably due to the greater availability of sputtered Nb or Ta atoms as compared to carbon or nitrogen atoms.

Effect of substrate temperature

Increased substrate temperatures have effects similar to those of the applied voltage. At low substrate temperatures, there was insufficient energy for reaction leading the formation of Nb and Ta compounds with low carbon and nitrogen contents. At higher substrate temperatures, NbC and TaC are formed. At still higher substrate temperatures, Nb_2C and Ta_2C are formed due to a lower sticking coefficient of carbon or due to re-emission of carbon atoms as suggested by Perney.(12)

Partial pressure of reacting gases

Increasing the partial pressure of the reacting gases leads to two effects: (1) supplying enough N_2 or C atoms for the reaction with depositing atoms (2) reducing the yield and hence lower thermal energy. When there is insufficient nitrogen than required for forming NbN, the formation of a distorted Nb was observed as indicated in Figure 2. When the partial pressure of N_2 or CH_4 is about 1-10 [illegible] torr, formation of the mononitride or monocarbide is favored. At still higher pressures, the subnitrides and carbides form probably because of the lower sputtering yields and thermal energy.

Conclusion

The results here show that the superconducting properties are sensitive functions of sputtering conditions. Relatively small changes in sputtering conditions result in large changes in T_c. Optimizing the sputtering conditions for maximum T_c's is difficult because of the interrelationship of sputtering parameters. Results can be understood when the film structure a composition are known. Best T_c results are obtained when the film's structure is NaCl and the film's composition is the stoichiometric monocarbide or nitride. The T_c's of these monocarbides and nitrides varies with Nb/N or Nb/C ratio in a manner similar to that of bulk samples.

References

1. J. R. Gavaler, J. K. Hulm, M. A. Janocko, and C. K. Jones, J. Vac. Sci. and Tech., 6, 177(1969).
2. H. Bell, Y. N. Shy, D. E. Anderson and L. E. Toth, J. Appl. Phys., 39, 2797(1968).
3. T. Mitszuoka, T. Yamashita, T. Nakazawa and Y. Onodera, J. Appl. Phys., 39, 4788(1968).
4. H. J. Spitzer, J. Vac. Sci. and Tech., 9, 333(1972).
5. E. I. Alessandrini, V. Sadagopan and R. B. Laibowitz, J. Vac. Sci. and Tech., 8, 188(1971).
6. J. R. Gavaler, M. A. Janocko and C. K. Jones, Appl. Phys. Letters, 19, 305(1971).
7. Y. M. Shy and L. E. Toth, Report No. 4, Studies of Thin Film Superconductors.
8. Sosniak, J. Appl. Phys., 39, 4157(1968).
9. D. Gerstenberg and C. J. Calbick, J. Appl. Phys., 35, 402(1964).
10. D. Gerstenberg and P. M. Hall, J. Electrochem. Soc., Aug. 1964, p.936.
11. H. J. Coyne, Jr. and R. N. Tauber, J. Appl. Phys., 39, 5585(1968).
12. L. I. Maissel, Physics of Thin Films, vol. 3, ed. by G. Hass and R. Thun, Academic Press, New York and London, 1966.
13. G. B. Perney, Comp. Rend. Oct. 1966, p. 106.

TABLE I

Auger Analysis of Thin Films

	Conditions of Preparation	$\frac{Nb}{C}$ or $\frac{Nb}{N}$	$\frac{Nb}{O}$	T_c °K	X-ray results
NbC					
1.	3300 volts, A = 50 m · torr, CH_4 1 m · torr, substrate 350°C	3.2	0.85	8.5	NbC(a = 4.45)
2.	3300 volts, A = 50 m · torr, CH_4 1 m · torr, substrate 475°C	3.61	1.01	---	Nb_2C
3.	NbC single crystal (bulk)	2.12	1.80	not measured	NbC(a = 4.46)
NbN					
1.	2000 v, A = 50 m · torr, N_2 = 7 m · torr, 450°C	0.78	0.69	---	Nb(N, O) a = 4.416
2.	2800 v, A = 50 m · torr, N_2 = 7 m · torr, 450°C + presputtering	0.91	0.81	14.1	NbN(a = 4.39)
3.	2800 v, A = 50 m · torr, 500°C + presputtering	0.97	0.90	13.25	NbN(a = 4.386) + Nb_4N_5

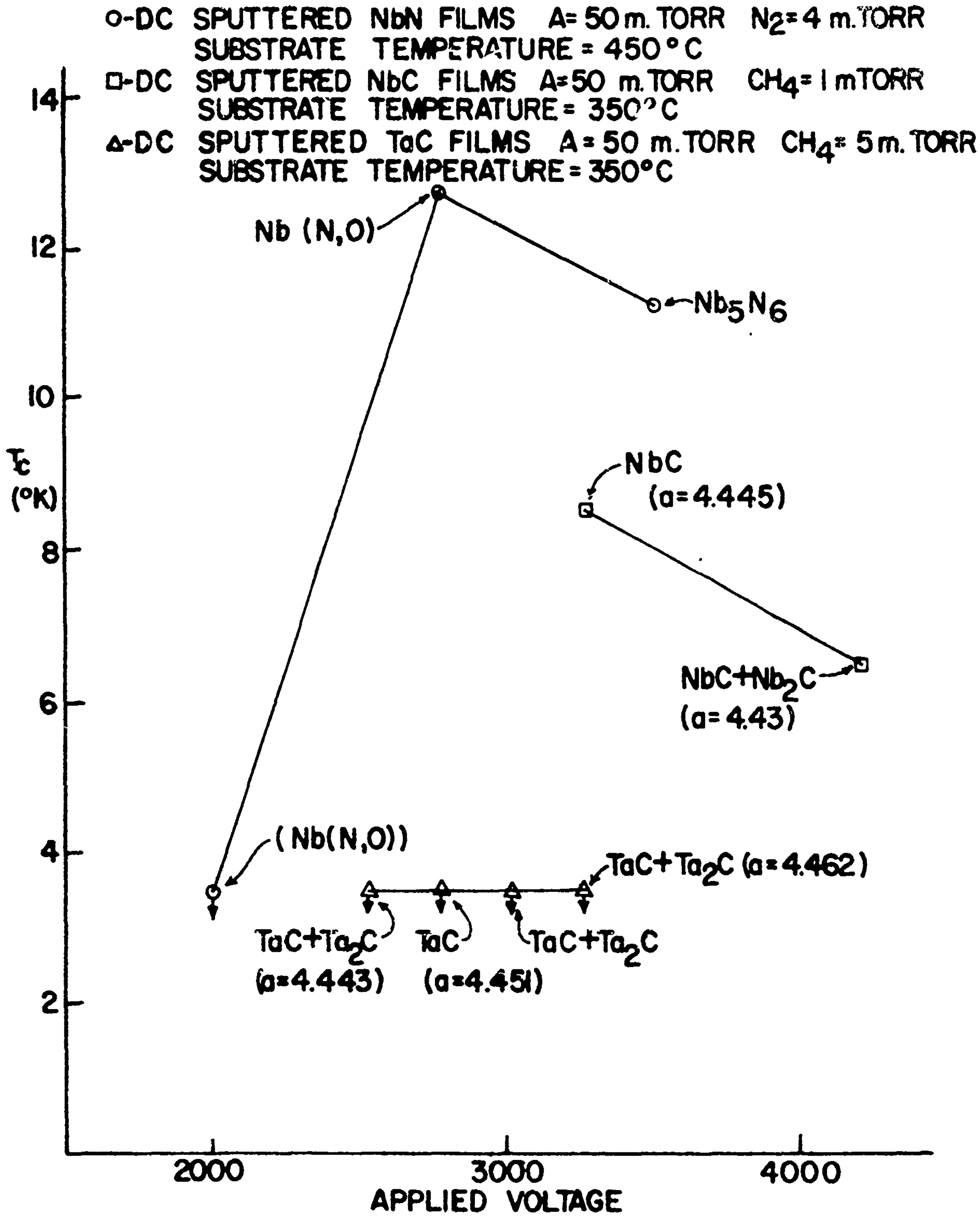

FIGURE 1. EFFECT OF APPLIED VOLTAGE ON TRANSITION TEMPERATURE AND STRUCTURE

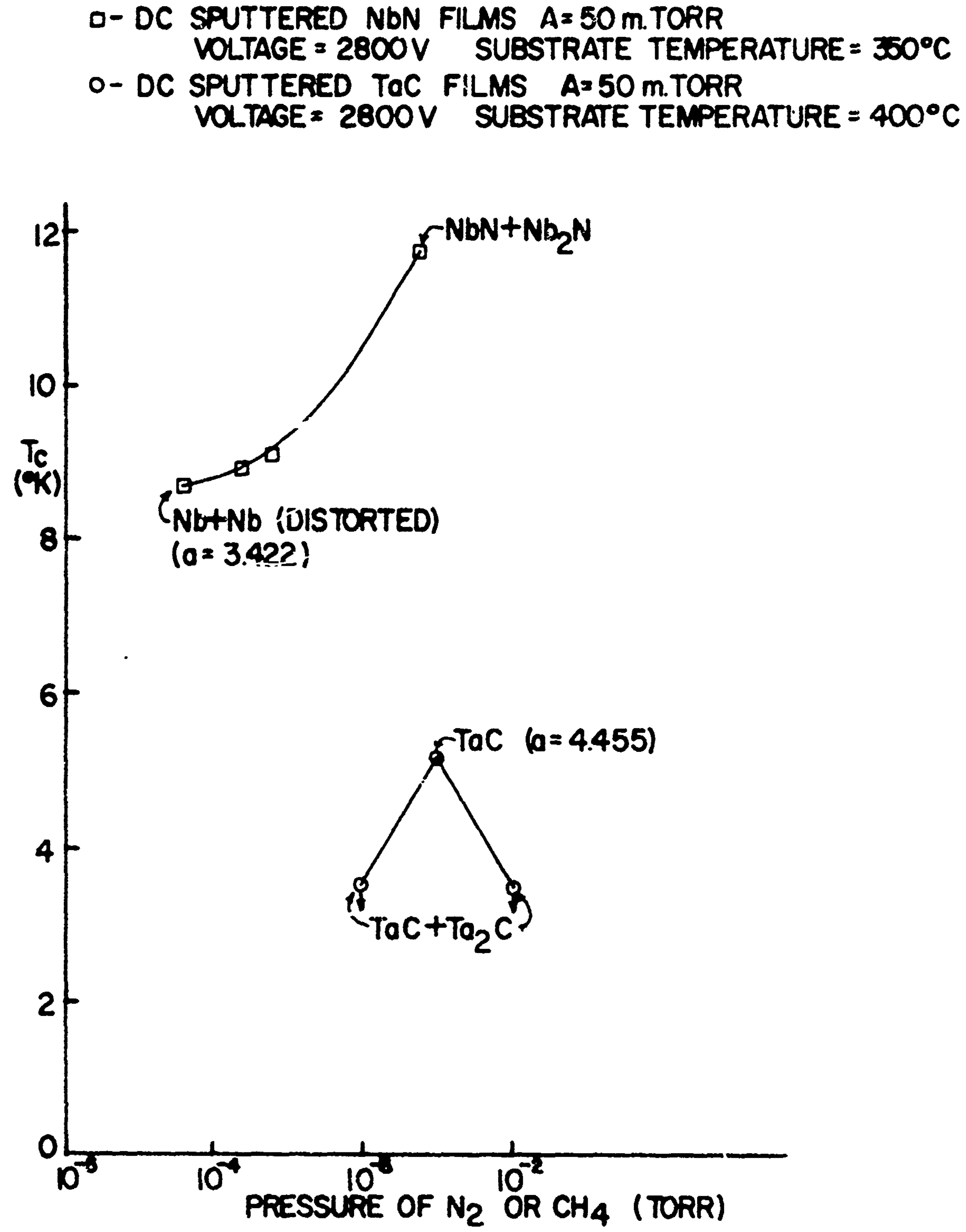

FIGURE 2. EFFECT OF PARTIAL PRESSURE OF REACTING GAS ON TRANSITION TEMPERATURE AND STRUCTURE

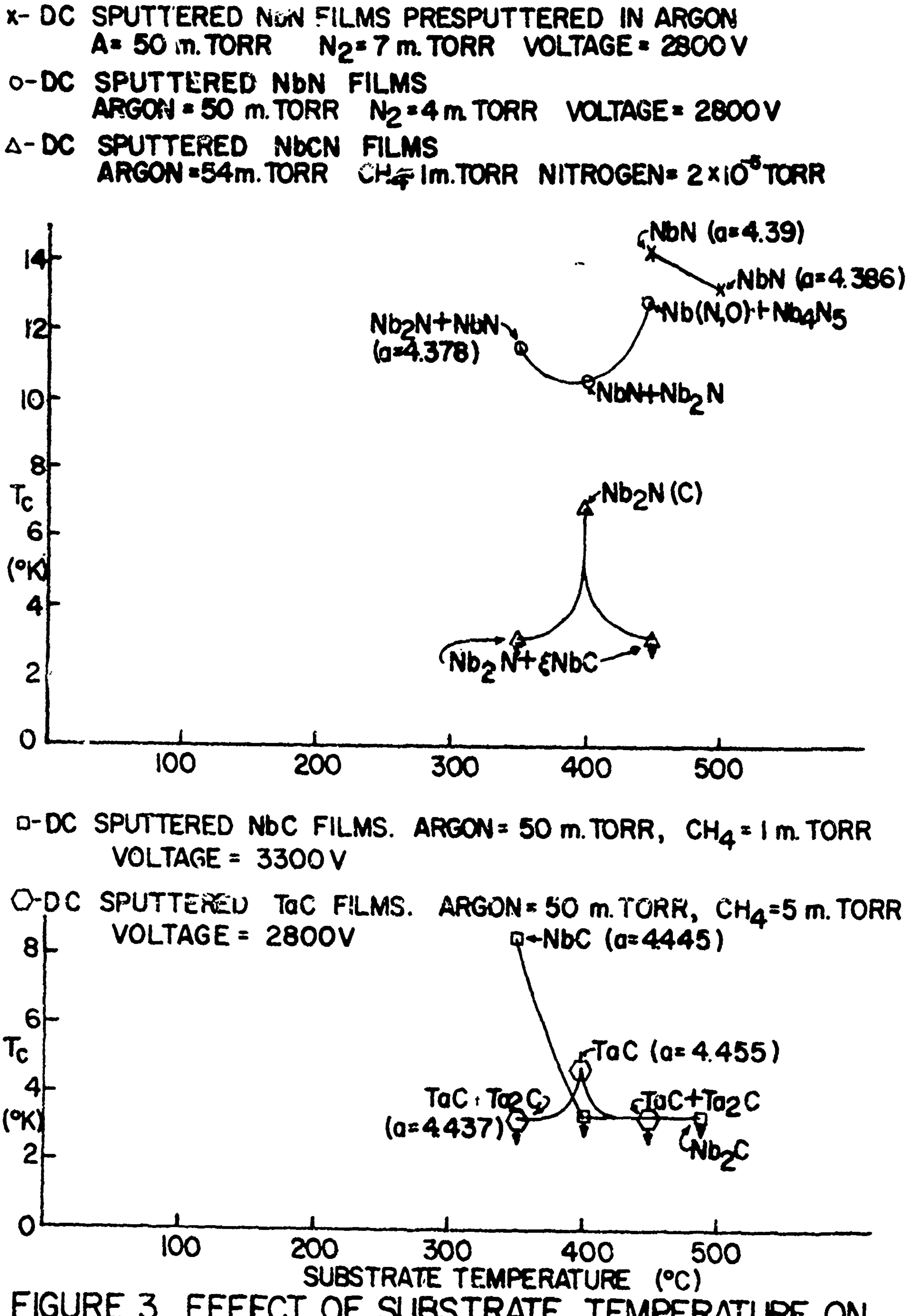

FIGURE 3. EFFECT OF SUBSTRATE TEMPERATURE ON TRANSITION TEMPERATURE AND STRUCTURE

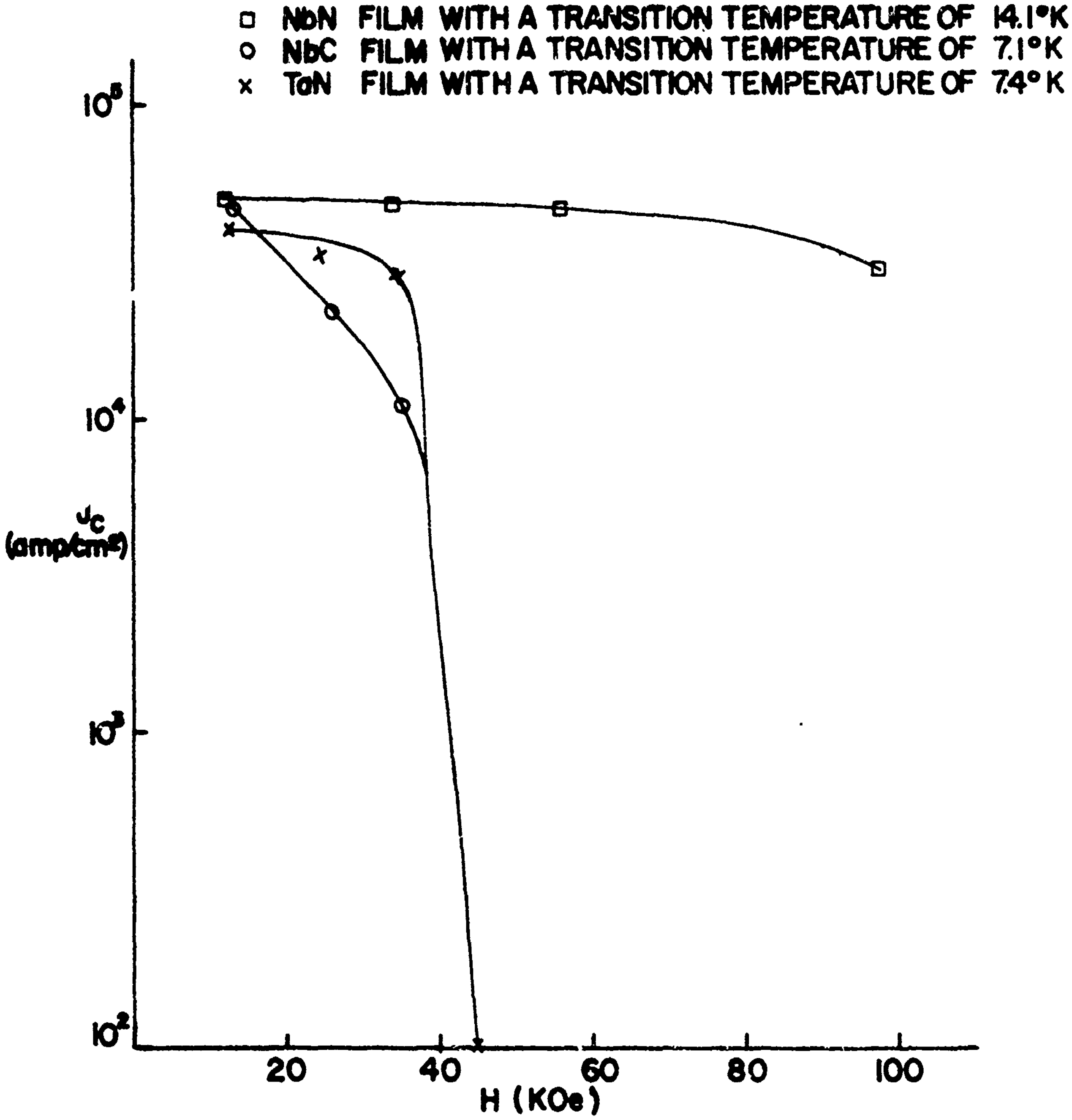

FIGURE 4. J_c vs H CHARACTERISTICS FOR THIN FILMS

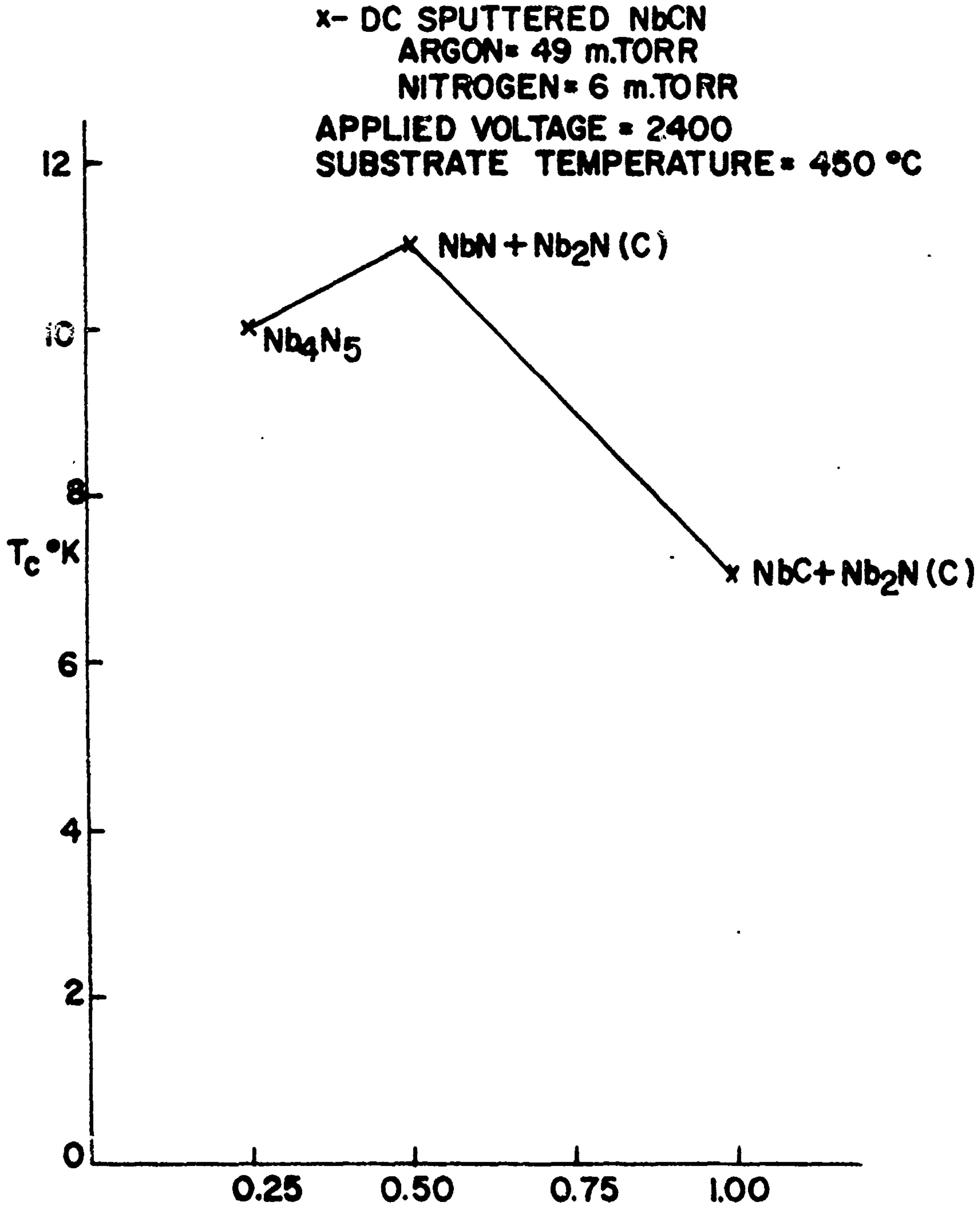

FIGURE 5. EFFECT OF PARTIAL PRESSURE OF METHANE ON TRANSITION TEMPERATURE OF NbCN FILMS

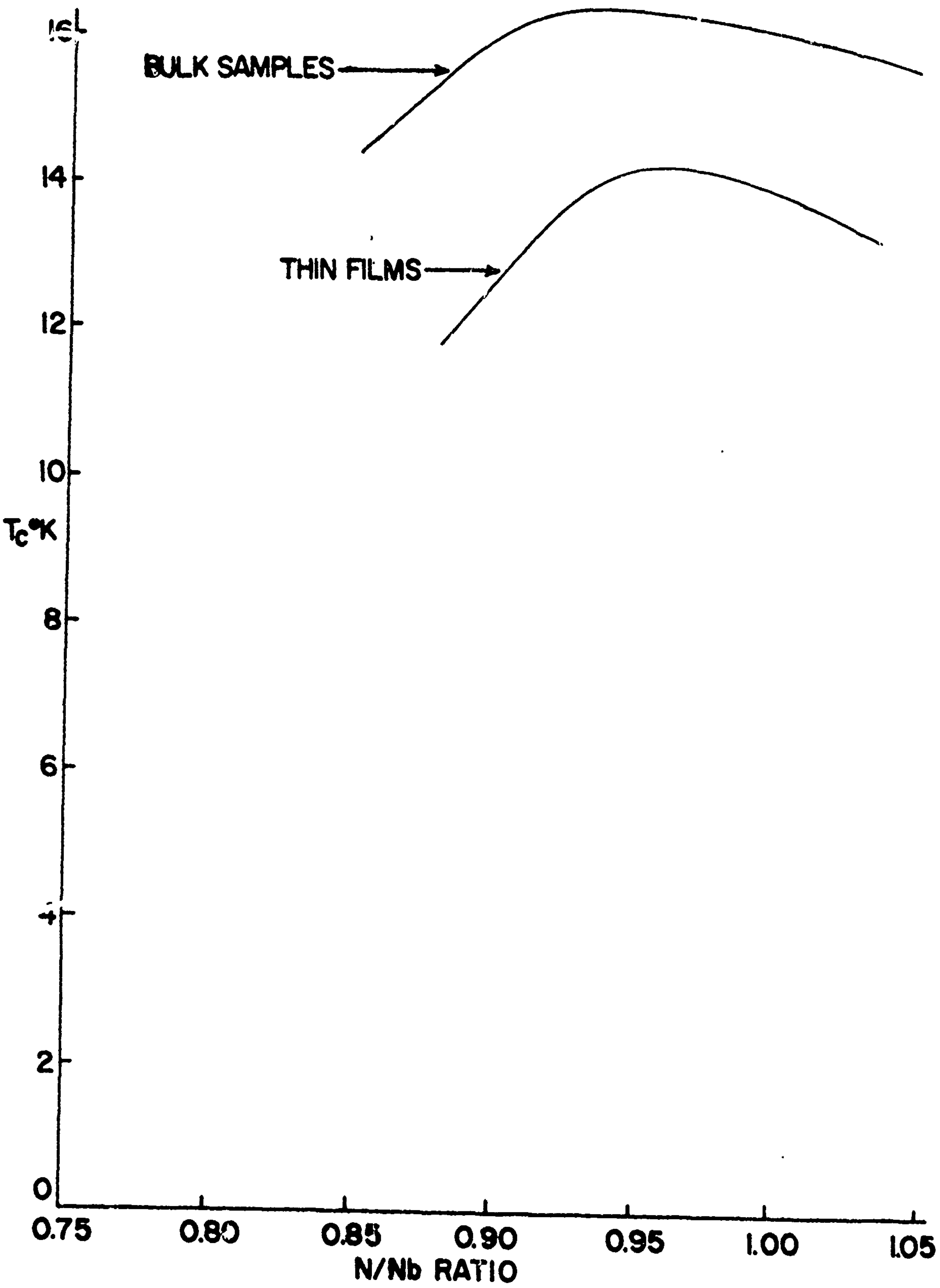

FIGURE 6. VARIATION OF T_c WITH N/Nb RATIO

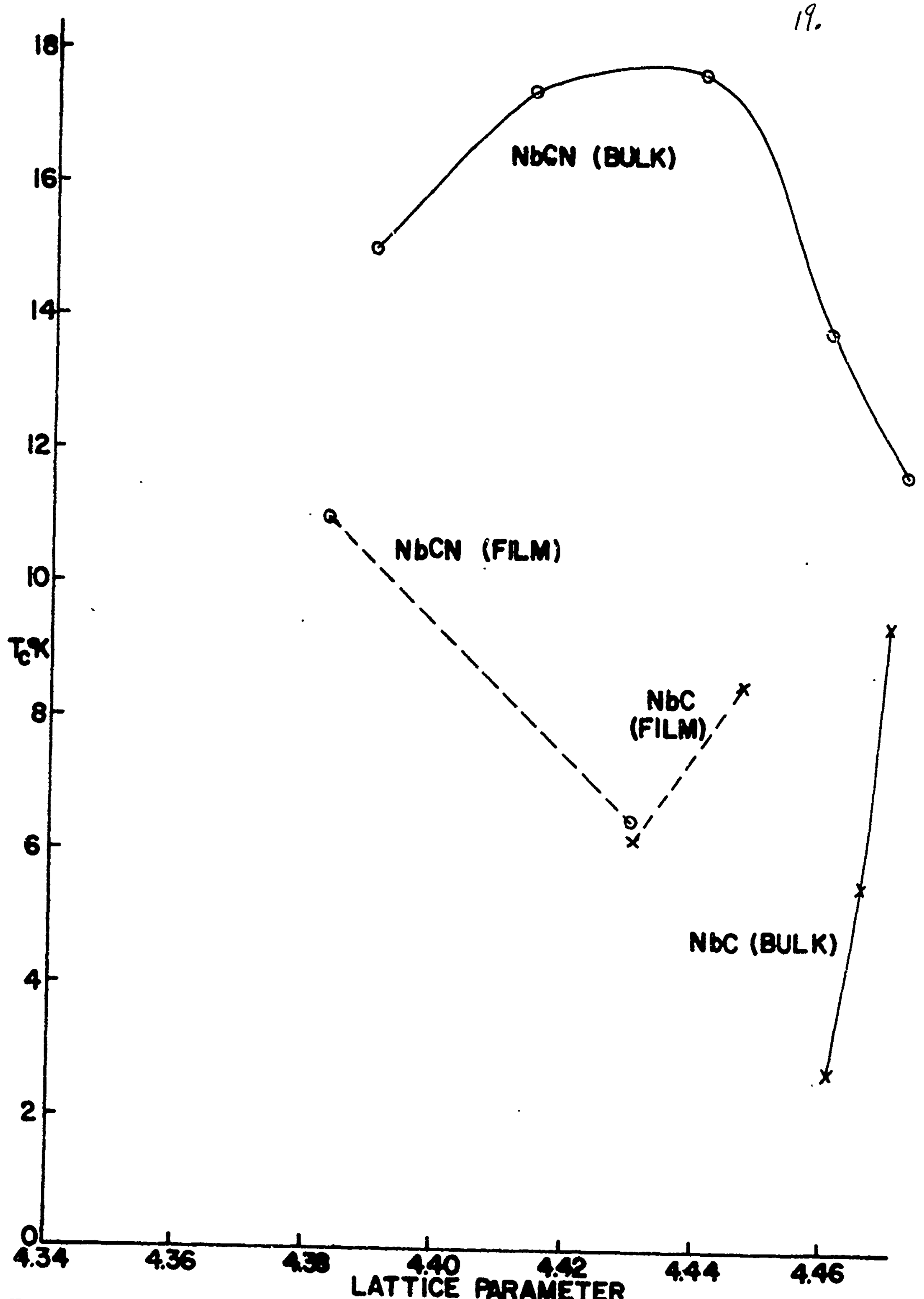

FIGURE 7. VARIATION OF T_c WITH LATTICE PARAMETERS IN NbC AND NbCN FILMS