Superconducting and normal-state properties of vanadium nitride

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The near stoichiometric compound VN_x with NaCl structure has been prepared in two different forms: (1) by reacting V foils directly with pure N_2, and (2) by reactive sputtering. The magnetic susceptibility and electrical resistivity data of VN_x are consistent with the spin-fluctuation view proposed for this material. Superconducting tunneling results indicate that VN_x is a strong-coupled superconductor with $2\Delta/k_BT_c \simeq 3.92$.

INTRODUCTION

The refractory compound VN has recently stimulated intense interest because of its strongly enhanced spin susceptibility when its composition approaches stoichiometry.[1] A phenomenological theory in terms of spin fluctuation has been proposed.[2,3] The superconducting transition temperature (T_c) shows strong dependence on composition[1] and increases with increasing external pressure.[4] In this article we present the results of a systematic investigation of the preparation of VN_x and its properties in general.

EXPERIMENTAL DETAILS

Two types of VN_x specimens were synthesized: (1) foils and (2) deposited films. The foil samples were prepared in one of two ways. Ultrapure-V ribbons (0.001 or 0.002 in. thick, from the Materials Research Corporation, Marz grade) placed inside a W boat were heated at $\sim$1100 °C in a research-grade–purity N_2 atomosphere (pressure 200—600 Torr) for 10—24 h. The nitriding process was carried out in a diffusion-pump—evacuated quartz-tube furnace (background vacuum $\sim 2\times10^{-6}$ Torr). In such an arrangement, VN_x was formed uniformly throughout, but small amounts of contamination from the environment seemed unavoidable. To minimize the effects due to contaminants, in particular oxygen and carbon, a second preparation procedure was devised: A stretch of ultrapure-V ribbon 5 cm long and 0.4 cm wide was clamped between two electrodes which were situated inside an ultrahigh-vacuum system [ion and sublimation pumps, background pressure $(2-3)\times10^{-9}$ Torr]. VN_x was formed when the V ribbon was heated by an ac of 10—12 A for a few hours in a pure-N_2 atmosphere (pressure $\sim$700—2000 Torr). In this approach, VN_x was also formed readily, but only along the middle two-thirds of the length. An easy identification for the cubic VN_x of good quality is its brilliant light-gold luster.

The VN_x films were deposited on finely polished sapphire substrates at either ambient temperature or 700 °C using the technique of reactive rf sputtering. The vacuum system consisted of a diffusion pump with a liquid nitrogen trap, and an inner Meissner trap surrounding the sputtering space. The optimum total pressure of the Ar and N_2 mixture was $\sim 5\times10^{-3}$ Torr with a $[N_2]/[Ar]$ ratio of 0.5—1.0. The deposition rate was estimated to be 3—4 Å/sec.

All VN_x specimens were screened through x-ray-diffraction analyses at room temperature. Only positively identified and well-crystallized single-phase material with the NaCl structure was used for further experiments. In determining lattice parameters (a_0), the overall error was estimated to be ± 0.003 Å.

In the attempt to determine the specimen compositions, both foils and films were subjected to the analyses of electron-microprobe and Auger spectroscopy. For foils, the weight gain after nitriding was also carefully monitored.

The susceptibility was measured for crushed foil specimens with a variable-temperature superconducting susceptometer (S.H.E. Corporation model no. VTS-5) at fields up to 30 kG and at temperatures of 15, 77, 100, and 300 K. The absolute values of the measured magnetic moment were calibrated against the low-temperature saturation magnetization of pure Ni, and the overall accuracy was estimated to be within 5%.

The superconducting transition was detected inductively, and the transition temperatures were measured against a calibrated Ge thermometer. The specimen was sandwiched between two coils of a differential transformer arrangement, and an 80-cycle signal was fed to the primary. The transition was observed when the flux was shielded from the secondary by the specimen. The width of a transition was determined from the temperature range within which 10—90% of the superconducting transition signal was registered.

The resistivity measurements were carried out using a

standard four-probe arrangement with a dc of 100 μA in the temperature range of 10—300 K. Two thermometers were used to monitor the temperature variation: a germanium sensor for the range 10—75 K and a platinum resistor for above 60 K.

In order to obtain precisely defined dimensions, the resistivity specimens were prepared by either depositing films through contact masks or by etching deposited films with the conventional photoresist and lift-off techniques.

In general, the surface quality of deposited films was far superior to the foils. Therefore, tunneling experiments were carried out only with the films. Two types of tunneling junctions were fabricated: $VN_x/Al_2O_3/Al$ and $VN_x/SiO_2/Al$. Thin Al (~30 Å) or Si (~20 Å) layers were evaporated onto the freshly deposited VN_x films in an ultrahigh-vacuum environment. Tunneling barriers were formed by exposing the thin Al or Si layers to ambient laboratory air for 10—20 min. Counter electrodes of Al ~5000 Å thick were used for all junctions. As a general rule in this study, tunneling junctions with a junction resistance (R_j) in the range of 10—60 Ω usually yielded reasonable results. The I-V and (dV/dI)-V characteristics were obtained using a modified modulation technique.[5]

EXPERIMENTAL RESULTS

Among the various methods we used in determining compositions, the data do not show complete agreement. For foil samples the weight-gain measurements after nitriding were the most reproducible and the subsequent results were most reasonable. Regarding the deposited films, because of their excellent surface quality, the microprobe analyses were deemed reliable.

The Auger-electron analysis, although extremely sensitive, did not provide consistent quantitative results. Small amounts of surface contamination acquired during sample transfer and storage and the lack of a reference sample as an analysis standard contributed to the uncertainty.

The data on the lattice constant and T_c are listed in Table I. The lattice constants are also plotted as functions of composition in Figure 1 together with the data reported in the literature.[6–8]

For deposited films, the VN_x phase with the NaCl structure is stable over a wide range of sputtering-gas $[N_2]/[Ar]$ ratios, as shown in Fig. 2. The VN_x phase can be readily formed even when the sputtering gas is pure N_2.

Typical spin-susceptibility (χ_0) data are listed in Table II. The temperature dependence is minimal between 15

TABLE I. Lattice constant and superconducting transition temperature of VN_x.

(a) Foil specimens

Sample no.	x	a_0 (Å)	T_c (K)	ΔT_c (K)	Preparation conditions[a] Pressure (Torr)	Time (h)
3	0.88	4.096	9.05	0.43	700	10
6	0.94	4.121	9.10	0.34	760	12
7	0.96	4.125	9.08	0.42	750	20
8	0.97	4.127	9.25	0.20	740	22
9	0.91	4.111	9.15	0.25	750	14
F-1	0.97	4.129	9.08	0.12	1520	5.5
F-2	0.91	4.111	9.20	0.16	1900	4
F-3			8.78	0.06	2280	1.5

(b) Deposited films

Sample no.	x	a_0 (Å)	T_c (K)	ΔT_c (K)	Sputtering gas ratio $[N_2]/[Ar]$
		Group I. Substrate temperature: ambient			
27-1	0.99	4.147	8.52	0.22	1:1
26-1	0.97	4.138	8.68	0.26	1:1
02-1			8.82	0.10	1:1
22-3	0.95	4.138	8.36	0.08	2:3
22-1	0.95	4.138	8.38	0.04	2:3
18-1	0.88	4.129	8.68	0.08	2:3
04-1			8.97	0.11	2:3
21-2	0.81	4.120	5.76	0.33	1:11
28-1	0.75	4.111	6.78	0.8	1:11
		Group II. Substrate temperature: 700°C			
29-1	0.96	4.138	8.65	0.23	1:1
29-3	0.87	4.129	8.74	0.16	1:1
30-3	0.71	4.100	5.25	0.47	1:4
30-2	0.70	4.095	5.77	0.22	1:4
32-2	0.64	4.067	3.50		1:11

[a]Temperature ~1100°C for all specimens.

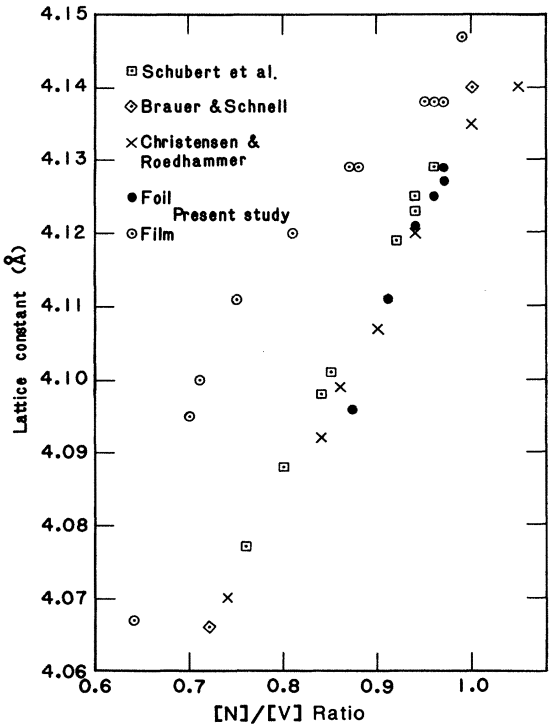

FIG. 1. Lattice constant of VN_x as a function of composition.

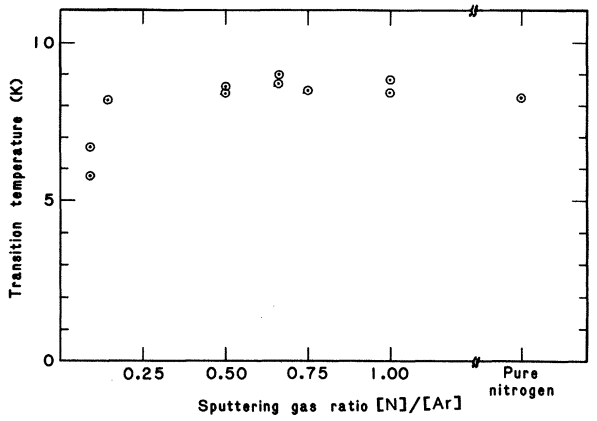

FIG. 2. Transition temperature of sputtered VN_x films.

and 300 K. However, the absolute values are high in comparison with other compounds in the same NaCl-structure family.[4]

The resistivity (ρ) of VN_x is plotted as a function of temperature (T) in Fig. 3. Near room temperature, the resistivity value for films deposited at ambient temperature is typically 50—70 $\mu\Omega$ cm, a value which is compatible with that of a reasonably good metal, which indicates that the deposited films are dense and well ordered. From 300 to 10 K, ρ decreases only 15—40 %, which reflects the fine-grain structure of the films. Despite the relatively large residual resistivity value (ρ_0), a strong negative curvature in the T dependence, typical of a high-T_c superconductor,[9] is strikingly evident.

It is also worth pointing out that the ρ value of VN_x films is much smaller than that of comparable NbN films.[10,11] This contrast may serve as the indication that VN_x films are better suited for other experiments.

In an ideal case, the discontinuity in the (dV/dI)-V curve associated with normal-metal—to—superconductor tunneling is defined as the energy gap. However, in practice, the discontinuity is usually rounded into an extremum due to a nonideal condition such as leakage current. The typical I-V and (dV/dI)-V characteristics of the tunneling junctions are shown in Fig. 4. As can be seen, the leakage current is not small. However, since the peak of the (dV/dI)-V curve is well defined, its position is taken directly to be the energy gap (Δ) without correction. The tunneling characteristics of a number of films are tabulated in Table III. The data indicate that there is no detectable difference between $VN_x/Al_2O_3/Al$ and $VN_x/SiO_2/Al$ junctions. This result suggests that any unoxidized Al below Al_2O_3, if it existed, does not exert any substantial influence on the I-V and (dV/dI)-V characteristics.

By monitoring, as a function of temperature, the (dV/dI) signal at zero bias or the (dV/dI) vs-V behavior, the T_c of the exact material at the junction can be determined. These T_c values are usually 0.2—0.3 K lower than the values recorded from the inductive measurements of the entire samples.

The Δ and $2\Delta/k_BT_c$ values listed in Table III are "raw" data. When the thermal smear is corrected for Δ (generally $\sim$7%) and the junction T_c is used, the $2\Delta/k_BT_c$ values are $\sim$0.02 lower.

TABLE II. Susceptibility of VN_x (10^{-6} emu/mol).

Sample no.	x	15 K	77 K	100 K	300 K
9	0.91	140	137	138	148
7	0.96	163	162	163	170
6	0.94	159	159	156	154
3	0.88	143	140	141	147
8	0.97	160	159	160	165
F-2	0.91	138	140	141	147

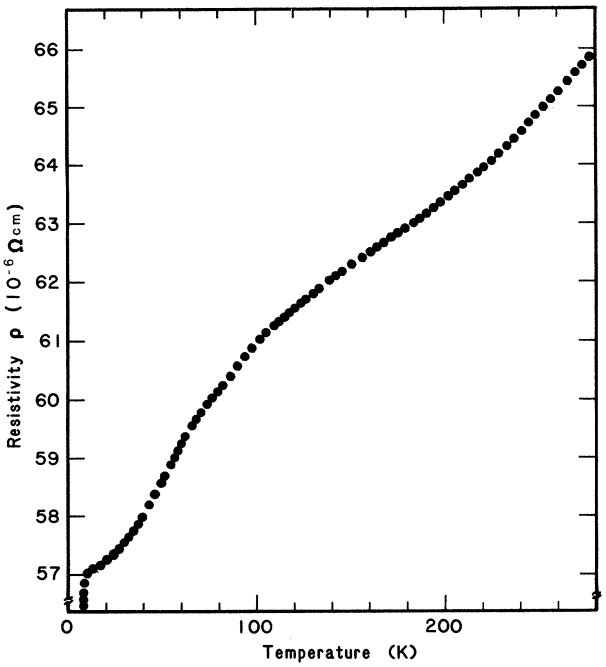

FIG. 3. Temperature dependence of resistivity for a VN_x film deposited at ambient temperature. The sample becomes superconducting at 8.6 K.

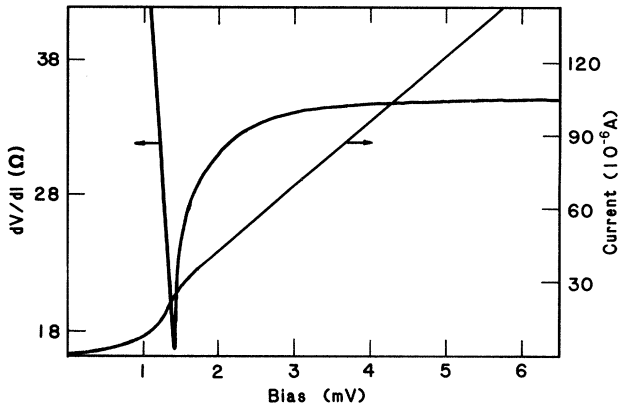

FIG. 4. Tunneling characteristics of a $VN_x/Al_2O_3/Al$ junction at 1.2 K.

DISCUSSION

The variation in lattice constant with the nitrogen content for the foil samples agrees very well with the data that appears in the literature.[6–8] However, for any given composition, the lattice constant of the deposited films is larger. This result is not unexpected because of the basic differences in sample preparation. Owing to the very nature of deposition procedures, the deposited films are more susceptible to the effects due to strain, defects, gaseous inclusions, etc. This result demonstrates the necessity for independent determination of the composition of film and bulk samples.

The most intriguing observation in the VN_x system is the strong paramagnetism exhibited by its high spin susceptibility (χ_0). This study reconfirms this point, although the recorded χ_0 values were not as high and the dependence on the N content is not as strong as first reported in the literature.[1] It is true that full stoichiometry of VN at which χ_0 reaches its highest value is difficult to achieve. However, judging from the data on the lattice constants and T_c's of this investigation and an independent study,[12] the χ_0 value of stoichiometric VN must be close to what is reported here.

A minor point involves the T dependence of χ_0. As indicated in Table II, the χ_0 values are generally higher at 300 K. Below 100 K, within experimental error, χ_0 is virtually T independent, in contrast with the monotonic decreasing from 300 K to low temperatures reported in the literature.[1]

As pointed out, immediately above T_c the T dependence of ρ is reminiscent of those of high-T_c β-W compounds. A closer analysis actually indicates that a T^2 dependence also exists, as shown in Fig. 5. Since the T^2 dependence of ρ is quite common among high-T_c superconductors,[13,14] its origin has been suggested in different ways. In the case of β-W compounds, the T^2 dependence of ρ was accounted for solely on the basis of electron-phonon scattering using a modified Debye phonon spectrum.[9] However, this line of reasoning has been disputed.[12] Since VN_x is a strong paramagnetic system, the most legitimate explanation for the T^2 behavior is electron-electron scattering.[15] To enhance this view, the coefficient A in the expression $\rho-\rho_0=AT^2$ is calculated to be 5.8×10^{-4} $\mu\Omega\,\mathrm{cm/K^2}$, which falls in between the corresponding values of β-W compounds and Pd metal.[16]

TABLE III. Tunneling characteristics of VN_x films.

Sample no.	Δ (meV)[a]	T_c (K)[b]	$2\Delta/k_BT_c$	Barrier
24-3	1.45	8.50	3.95	SiO_2
24-2	1.35	8.00	3.92	SiO_2
21-1	1.35	7.98	3.93	Al_2O_3
29-2	1.43	8.40	3.94	Al_2O_3
29-1	1.40	8.30	3.92	Al_2O_3
28-1	1.45	8.42	3.99	SiO_2

[a]Determined from the peak position of the (dV/dI)-V curve without correction at 1.2 K.
[b]From inductive measurements of the entire films.

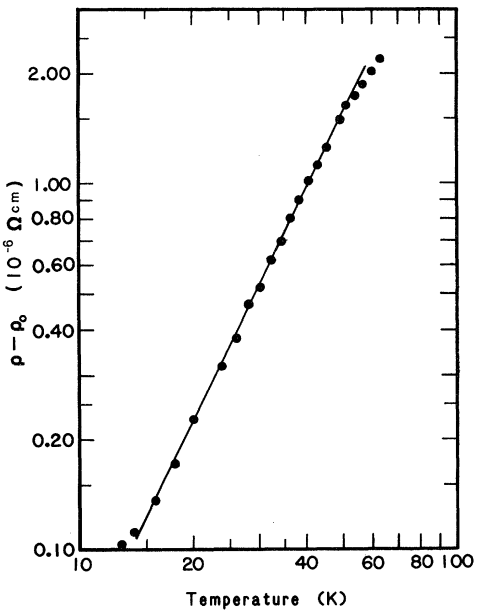

FIG. 5. Resistivity of VN_x in the temperature range 15—60 K. Slope of the solid line is 2.1. Because of the superconducting transition, the resistivity value at 10 K is taken to be ρ_0.

From Table III it is clear that VN_x is a strongly coupled superconductor. This result is in good agreement with a recent study[17] except that the present $2\Delta/k_BT_c$ values are generally higher. When the leakage current is low in the tunneling I-V characteristics (less than 10% of the normal-state resistance), reproducible structures are detectable in the junction resistance.[18]

Currently, NbN, a compound from the same NaCl-structure family, draws considerable attention as a good material for superconducting tunneling investigations.[19–21] However, this study indicates that there are certain advantages in working with VN_x. For example, VN_x can be formed much more readily. The quality of VN_x films deposited at ambient temperature is not inferior to the bulk material, as evidenced by the T_c value.

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