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Superconducting and normal-state properties of MoN_x thin films

Y. H. Shi, B. R. Zhao, Y. Y. Zhao, L. Li, and J. R. Liu
Institute of Physics, Academia Sinica, Beijing, China

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We report here the results of measurements of the superconducting critical temperature, the resistivity $\rho(T)$, the valence band of the electronic density of states, and $dH_{c2}/dT \mid_{T_c}$ of MoN_x thin films and discuss the variation of these experimental results with the concentration of nitrogen.

I. INTRODUCTION

On the basis of energy-band calculations[1] and from empirical relations[2] it was predicted that the $B1$-structure MoN of stoichiometric composition has higher superconducting critical temperature than NbN with an estimated T_c value around 29 K. However, the $B1$-structure MoN with stoichiometric composition does not exist in the Mo-N equilibrium phase diagram,[3] and molybdenum mononitride exists only as a hexagonal δ-MoN phase. The synthesis of $B1$-MoN is difficult by the usual equilibrium preparation technique, although several attempts have been made to prepare $B1$-MoN films by nonequilibrium or other techniques.[4–10] Saur *et al.*[9] identified a cubic phase as the $B1$ structure, but its lattice parameter is only 4.16 Å, which corresponds to that of fcc Mo_2N. Linker *et al.*[10] used the reactive sputtering method and obtained the $B1$-structure MoN_x ($x = 0.9-1.8$) with lattice parameter of 4.20-4.26 Å, but the T_c's of the films were below 5 K. Up to now, the highest T_c is of hexagonal δ-MoN, which has a superconducting critical temperature of 14.8 K. Yamamoto *et al.*[11] used an epitaxial growth method and obtained $B1$-structure MoN with $T_c = 11$ K. Using the ion-beam deposition method, Terada *et al.* obtained the $B1$-structure MoN with superconducting critical temperature of 12.8 K.[12] On the basis of our previous work on VN thin films,[13] the phase formation of stoichiometric $B1$-structure MoN and its physical properties have now been studied. Our object is to study the superconducting and normal state properties of $B1$-structure MoN and to explore the possibility of raising the superconducting critical temperature of this compound to its predicted value.

In this paper we report the results of measurement of the resistivity $\rho(T)$, the valence band of electron density of states, and $dH_{c2}/dT \mid_{T_c}$ of the MoN_x thin films and discuss the correlation of these results with the concentration of nitrogen which is most important for formation of $B1$-structure MoN_x thin films.

II. EXPERIMENTAL

The MoN_x thin films were prepared by the dc reactive magnetron sputtering method with high-purity Mo (99.999%) as the target. The background vacuum pressure of the sputtering chamber was 1×10^{-7}–5×10^{-8} Torr; the pressure at sputter deposition was $(2-5)\times10^{-2}$ Torr with a nitrogen and argon gas ratio of 0.5–0.8. The sputtering voltage was 600 V, sputtering current about 100 mA, and the temperature of the substrate 450–500 °C. The nitrogen gas was further purified to decrease the oxygen contamination during sputtering. The film was deposited on sapphire substrates and the film thicknesses were measured by a Dekatak IIA profilmeter. X-ray diffractometry was used to determine the structure of the film samples. The valence band of the electronic density of states of the MoN_x thin films was determined using VG-ESCA-Lab-type-5 equipment. The four-point method was used to determine the superconducting critical temperature and the resistivity from T_c to 300 K. $dH_{c2}/dT \mid_{T_c}$ was measured under the magnetic field from 1–7.5 T in a Nb-Ti superconducting magnet and the critical field was taken at the T_c midpoint of the sample. A Pt thermometer was used at temperatures above 60 K and a carbon resistor for temperatures below 60 K (the calibration range was 2–100 K). The nitrogen concentration was determined by the Rutherford backscattering (RBS) method, which was performed by He-beam analysis. The stopping cross section e for ions penetrating a solid compound can be approximately calculated by Bragg's additivity rule: $e = \sum_i n_i e_i$, where n_i is the concentration and e_i the stopping cross section of the ith component.

The total backscattering counts must be the same for the same amount of Mo in a pure Mo metal and a MoN_x compound. But, the He beam will lose more energy in the compound than the pure Mo metal, so for a fixed energy interval in the backscattering spectrum of the compound the count will be less than pure Mo metal. In other words, the spectrum height will be lower. Our first measurements indicate an approximately uniform MoN thin film, so we can use a more simplified formula to extract the ratios of N to Mo:

$$\frac{H_{\mathrm{Mo}}^{\mathrm{Mo}}(E)}{H_{\mathrm{Mo}}^{\mathrm{MoN}}(E)} = \left[\frac{1}{1-x}\right] \frac{[e(E)]^{\mathrm{MoN}_x}}{[e(E)]_{\mathrm{Mo}}} . \tag{1}$$

Here $H_{\mathrm{Mo}}^{\mathrm{Mo}}(E)H_{\mathrm{Mo}}^{\mathrm{MoN}_x}(E)$ are the spectrum height for pure Mo and MoN_x at the high-energy spectrum edge, e.g., at the sample surface; x is the atomic percentage of N in the compound; and $e(E)$ is the stopping cross section factor,[14]

TABLE I. The main parameters measured on the MoN_x films.

Sample no.	Composition	d (Å)	a_0 (Å)	T_{onset} (K)	T_c (K)	ΔT_c (K)	ρ_0 ($\mu\Omega$ cm)	R_R	$dH_{c2}/dT \mid_{T_c}$ (10 kG/K)
1	$MoN_{2.13}$	2691	4.22	4.2	3.4	0.2	693	0.83	9.1
2	$MoN_{1.5}$	9834	4.22	4.0	3.76	0.2	971	0.87	5.65
3	$MoN_{2.05}$	1226	4.21	5.4	3.84	0.2	436	0.89	6.85
4	$MoN_{0.61}$	7259	4.17	5.4	5.2	0.2	303	0.95	3.075
5	$MoN_{1.44}$	12064	4.20	4.75	3.92	0.15	713	0.93	4.225

$$e(E)=kE(E)_{\text{in}}+\frac{1}{\cos\theta_2}e(E)_{\text{out}} . \tag{2}$$

III. RESULTS

The main parameters measured on the MoN_x films are shown in Table I. Sample no. 4 was prepared under the condition when $[N_2]/[Ar]=0.5$, and the other samples were prepared under the condition $[N_2]/[Ar]=0.8$ with identical sputtering parameters. It can be seen in Table I that the nitrogen concentration of sample no. 4 is lower than the other samples. As an example, Fig. 1 shows the RBS spectrum of sample no. 1 and pure Mo. The backscattering spectra for a pure Mo metal sample and MoN_x compound has been measured for the same amount of accumulated charge of the incident He beam. The ratios x of MoN_x can be calculated from the spectrum heights according to formula (1). The main error of the measurement is the error of the stopping cross section and the statistics of the spectrum height. The violation of Bragg's additivity rule has been suppressed by increasing the incident He ion energy up to 4.5 MeV, and this correction was estimated as low as 4% by simple extrapolation from 2 to 4.5 MeV.[15] The stopping cross section has been taken from Ref. 16; the total error of the x value is about 10%.

Figure 2 shows the x-ray diffraction peaks of the samples compared with those theoretically predicted for the $B1$ structure and γ-Mo_2N structure. It can be seen in Fig. 2 that there are three kinds of structures: sample nos. 1 and 3 are single phase $B1$, sample no. 4 is a Mo_2N structure, and the other samples are $B1$ structures with a certain amount of the tetragonal phase. With the increase of nitrogen concentration the two-phase structure gradually transforms to $B1$ structure, and the lattice parameter increases from 4.16 to 4.22 Å. However, T_c decreases with the increase in nitrogen concentration.

The variation of resistivity ρ of MoN_x films with temperature is shown in Fig. 3. It can be seen that $\rho(T)$ shows a negative temperature coefficient for all samples, indicating that the ratio of room-temperature resistivity to the residual resistivity is less than 1. From Table I it can be clearly seen that with the increase of nitrogen concentration the negative temperature coefficient of resistivity also increases, with the exception of sample no. 3. The residual resistivities ρ_0 of the MoN_x samples are in the range of 303–971$\mu\Omega$ cm, which is larger than that of other transition-metal nitrides[17] in general.

Figure 4 shows the spectra of the valence band of MoN_x with the increase in nitrogen concentration for MoN_x films. It can be seen in the figure that the intensity of the N [2p] peak increases gradually with the increase of nitrogen concentration. When $[N]/[Mo]>1.5$, $N(E)$ of stoichiometric $B1$-MoN obtained experimentally is similar to that obtained by theoretical calculation. This result is comparable to that of Ihara *et al.*[17] From the ultraviolet photoelectron spectroscopy (UPS) spectrum of Mo, it can be seen that the valence band near the Fermi surface level originates mainly from the 4d level of Mo rather than from N 2p.

The temperature variation of the critical field H_{c2} with critical temperature is shown in Fig. 5. It can be seen that $dH_{c2}/dT \mid_{T_c}$ increases with the increase in nitrogen

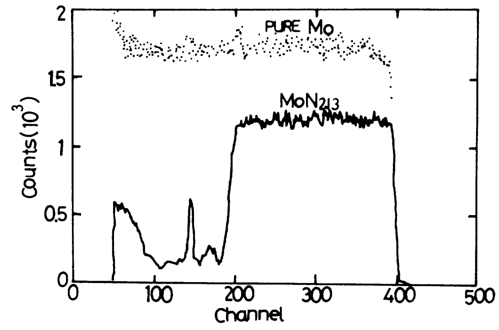

FIG. 1. The backscattered spectrum of sample no. 1.

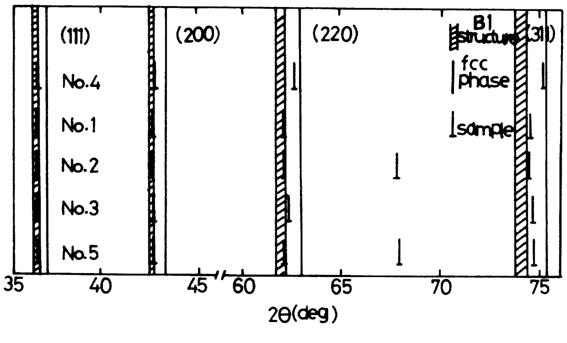

FIG. 2. The diffraction peaks of the samples compared with those of the theoretically prediced $B1$ structure and γ-Mo_2N structure.

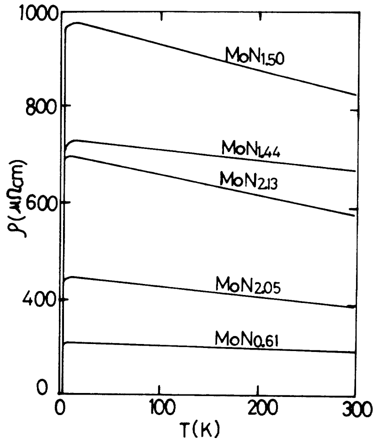

FIG. 3. The variation of resistivity curves with temperature.

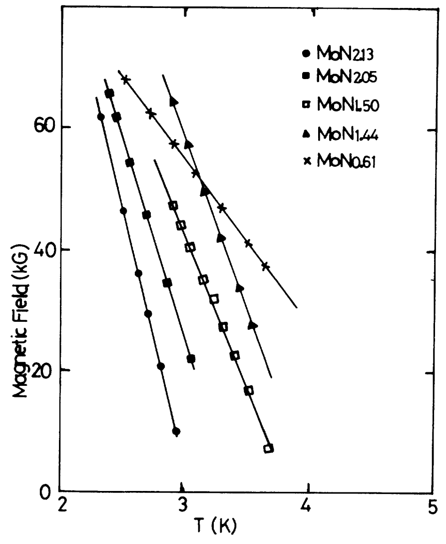

FIG. 5. The temperature variation of the critical field H_{c2} with critical temperature.

concentration. For sample no. 4, when [N]/[Mo] = 0.61, a typical fcc structure γ-Mo_2N is obtained; the value of the slope $dH_{c2}/dT \mid_{T_c}$ is smallest and equals 3.07 T/K. For sample no. 1, [N]/[Mo] = 2.13, $a_0 = 4.22$ Å, showing a $B1$ structure; the measured slope $dH_{c2}/dT \mid_{T_c}$ is largest and equal 9.1 T/K. The slope $dH_{c2}/dT \mid_{T_c}$ is proportional to both the electronic density of state N(0) and normal-state resistivity. From Table I, comparing $dH_{c2}/dT \mid_{T_c}$ and ρ, it is most probable that $B1$-structure $MoN_{2.13}$ has a higher electronic density of states than that of all the other samples except sample no. 3. Similarly, it is also probable that samples nos. 2 and 5 have a comparable electronic density of state and are consistent with the results obtained with UPS (Fig. 4). For NbN thin films with $T_c = 15.5$ K, $\rho_0 = 643$ $\mu\Omega$ cm, and the ratio of room-temperature resistivity to the residual resistivity equals 0.9, while the measured $dH_{c2}/dT \mid_{T_c}$ is only 2–4 T/K.[18] This experimental result proved the energy band state of the theoretical calculated $B1$ MoN is 1.5–2 times higher that of the predicted value of NbN. However, T_c decreased with the increase of nitrogen concentration.

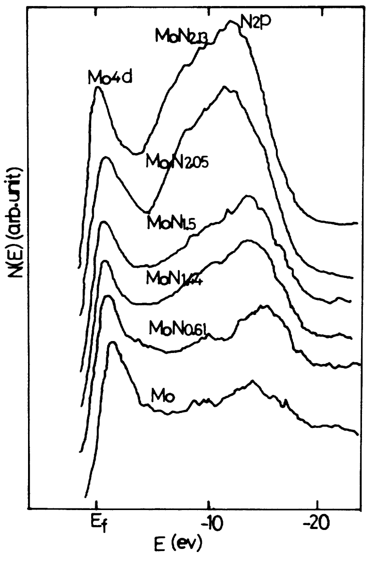

FIG. 4. The spectra of valence band of MoN_x with increase in nitrogen concentration.

IV. DISCUSSION

The resistivity of MoN_x thin films becomes closer to the semiconductor state with the increase in nitrogen concentration. The following model may be able to explain this kind of phenomenon: When the nitrogen concentration is high enough ([N]/[Mo] > 1) and with an appropriate deposition temperature, $B1$ MoN is easy to form in the Mo-N film matrix (i.e., the free energy is lowest for $B1$ MoN). With an excess of nitrogen and with the formation of a large amount of $B1$-structure crystals, the nitrogen-vacancy concentrations in the crystal could be reduced. On the other hand, the Mo vacancy might appear in some of the crystals. From the electron transport point of view, when there are nitrogen vacancies the bonds of Mo with nitrogen are partially empty. As a whole, it is not possible to obtain complete charge transfer, which is beneficial for conductance. If there are vacancies at the Mo sites, there probably is a potential well in the electron transport path, especially for thin films, because the conductance path is nearly two dimensional. The potential well could lead the electron transport process to have a hopping behavior, thus leading to a negative temperature coefficient of resistance. If there are excess nitrogen atoms or atomic clusters in the film matrix (from the energy point of view) they might occupy Mo sites in the crystal, when an apparent $B1$ structure will be formed. This is not actually a $B1$ structure however; not only is it impossible to obtain a high T_c, but also the conductance electrons are localized. Besides, the oxygen and carbon impurities in the thin film will also lead to the electron transport properties and low superconducting critical temperatures discussed above. The conductance could also be influenced by the microstructure of the films, especially when this is columnar.

The slope $dH_{c2}/dT \mid_{T_c}$ and the UPS spectra indicate that with the increase in nitrogen concentration, both the valence band and $dH_{c2}/dT \mid_{T_c}$ will increase. When $[\mathrm{N}]/[\mathrm{Mo}]=1.5$, the valence band is similar to that of the theoretical calculated $N(E)$, and at the same time the $dH_{c2}/dT \mid_{T_c}$ of $B1$ MoN is 1.5–2 times that of NbN, which means that the electronic density of state $\mathrm{MoN}_{1.5}$ is higher than that of NbN. This explains the reason why stoichiometric $B1$ MoN can only form in the case of excess nitrogen concentration. However, the excess nitrogen atoms will cause the $B1$ MoN to have lattice defects, and these defects might be the direct cause leading to the deviation of the T_c from the theoretical value. Therefore in the synthesis of MoN_x, it is crucial to obtain high-quality thin films with the stoichiometric $B1$-structure MoN.

Yamamoto *et al.*[11] reported the epitaxial growth of the $B1$-MoN film on a MgO substrate, with a T_c onset of 11 K. Terada *et al.*[12] used the ion-beam deposition method and prepared single crystal $B1$ MoN, with $T_c=12.8$ K. These results indicate that a high-T_c phase might exist in the MoN_x compound.

V. CONCLUSION

Experimental results showed that the conductance electrons are localized in the MoN_x thin films, resulting in a negative temperature coefficient of resistivity. The main cause may be the excess of nitrogen atoms. However, the large lattice parameter (4.21 Å), high value of $dH_{c2}/dT \mid_{T_c}$, and high density of states of the $B1$-structure MoN are only obtained when the ratio of nitrogen atoms to molybdenum atoms is larger than one. Therefore we can conclude that the $B1$-structure MoN can only be formed under the nitrogen-excess condition. If it is possible to overcome this problem, it might be possible to prepare high-T_c stoichiometric $B1$-structure MoN thin films.

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