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Superconductivity of *B*1-MoN films annealed under high pressure

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*B*1-phase MoN films, prepared by sputtering, are annealed under a pressure of 6 GPa at temperatures between 600 and 1100 °C for 8 h. The *B*1-phase MoN is converted mainly to hexagonal-phase and partly to tetragonal-phase Mo_2N when annealed at temperatures above 750 °C. A residual phase was observed only at an annealing temperature of 600 °C. The T_{co} (the onset of T_c) of 1000 °C-annealed films was 14.9 K; this is the maximum value found in the literature for the Mo-N system.

MoN with *B*1-type structure has been predicted to have a higher superconducting transition temperature (T_c) than NbN.[1,2] *B*1-MoN does not appear in the equilibrium phase diagram of the Mo-N system.[3] This and the high density of antibonding states make it difficult to synthesize a perfect crystal of *B*1-MoN.

Recently some workers have succeeded in preparing *B*1-MoN films by sputter-deposition techniques.[4–6] The observed T_{co} (the onset of T_c) of the *B*1-MoN films, 12.5 K, however, is not as high as the predicted values 20–29 K. This has been explained by the occurrence of nitrogen vacancies and nitrogen defects at the interstitial sites.[5] We have attempted to improve the quality of the *B*1-MoN crystal by high-pressure annealing. It was thought that the nonequilibrium *B*1-phase MoN would be stabilized and that N vacancies would be filled by interstitial N atoms under high pressure, because the density of the *B*1-MoN is larger than that of the equilibrium hexagonal MoN.[2]

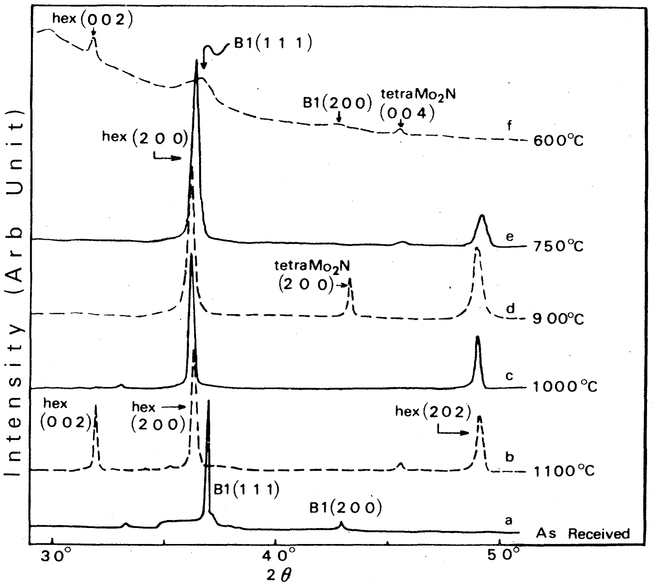

FIG. 1. (a) X-ray diffractometer traces for a starting material, and pressure-annealed films at various temperatures: (b) 1100 °C, (c) 1000 °C, (d) 900 °C, (e) 750 °C, and (f) 600 °C.

As shown in this paper, this assumption proved to be incorrect. We observed for the first time conversion from *B*1-MoN to hexagonal-phase MoN by high-pressure (6 GPa) annealing. As a result we could get pure hexagonal-phase MoN with the highest T_{co} for the Mo-N system without mixing impurities.

The original *B*1-MoN samples were prepared by dc magnetron sputtering using a cup-shaped Mo target in a nitrogen-gas atmosphere. The MoN films were deposited on sapphire substrates with a size of $5\times5\times2$ mm^3 at a temperature of 550 °C with a thickness of 7 μm.

The MoN films mainly contained *B*1-phase MoN and a small amount of another unidentified phase as shown in Fig. 1 (a). The lattice parameter of the *B*1 phase was 4.214 Å. From x-ray photoelectron-spectroscopic measurements the composition of the films was $MoN_{1.2}$, and the electronic structure of the films was *B*1 type.[1,4] The T_c of the films was below 4.2 K, as judged by resistance measurements. We selected low-T_c films as starting materials in order to observe an increase in T_c more easily.

High-pressure annealing was carried out using a belt-type apparatus. The MoN sample was covered by a sapphire plate and embedded in a pressure-transmitting medium of sodium-chloride powder. A graphite tube surrounding the sodium-chloride powder was used as a heater. The pressure

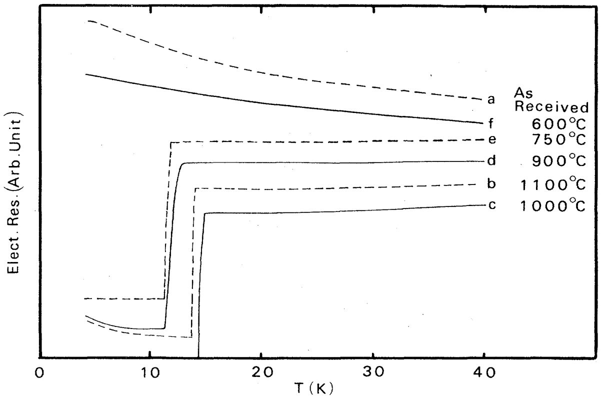

FIG. 2. (a) Electric resistance vs temperature for the starting material, and pressure-annealed films at temperatures of (b) 1100 °C, (c) 1000 °C, (d) 900 °C, (e) 750 °C, and (f) 600 °C.

TABLE I. Characteristics of pressure-annealed *B*1-MoN films.

Pressure (GPa)	Temp (°C)	Phase	Lattice constant of hex.-MoN (Å)		T_{co} (K)	T_c (K)	T_{ce} (K)	ΔT (K)
			a	*c*				
60	600	*B*1, hex., tet.	5.735	5.640				
60	750	hex.	5.721	5.647	11.8	11.3	11.3	0.5
60	900	hex., tet.	5.726	5.613	12.7	11.7	11.3	1.4
60	1000	hex.	5.726	5.608	14.9	14.5	14.3	0.6
60	1100	hex.	5.710	5.606	14.1	13.8	13.7	0.4

was first raised to 6 GPa, and then an ac current was passed through the heater. The annealing temperature was varied from 600 to 1100 °C in the different runs. After annealing for 8 h, the sample was quenched to ambient conditions.

Figure 1 shows x-ray diffractometer traces taken with Cu$K\alpha$ radiation for five samples annealed at different temperatures and an as-received sample. Above 750 °C annealing temperature (Fig. 1, curves b–e), the *B*1 phase is completely converted, mainly to hexagonal-phase MoN and partly to tetragonal-phase Mo$_2$N. The lattice consants of hexagonal-phase MoN vary, depending upon annealing conditions. Maximum lattice constants are obtained at 1000 °C (c). A residual *B*1 phase is observed only at 600 °C (f). The quality of the *B*1 crystal was not improved but worsened after the annealing. Even at 600 °C part of the *B*1 phase was converted to hexagonal MoN and tetragonal Mo$_2$N phases.

The T_c values were measured resistively by a four-probe technique using a calibrated Ge-resistance-thermometer within a maximum experimental error of ±0.1 K. Electrical resistance versus temperature curves are shown in Fig. 2. The highest T_c was obtained in the 1000 °C-annealed sample. T_{co}, T_c, T_{ce} (the end of T_c), and ΔT (transition width) are listed in Table I with crystal phases and lattice constants of hexagonal MoN for each sample. T_{co} and T_{ce} are defined as the 1% and 99% points of the resistance transition.

The T_{co} of 14.9 K in the 1000 °C-annealed sample is the maximum value in the literature for the Mo-N system. Though the hexagonal-phase MoN phase with 14.8 K in T_c has been synthesized under 4 GPa pressure at the temperature of 1000 °C by Vanderberg and Matthias,[7] their T_c value is assumed to correspond to the present T_{co}, for historical reasons. Moreover, their sample was not purely MoN, because it was synthesized from a mixture of MoS and BN in equal amounts by high-pressure annealing. B and S must have been in their samples in abundance.

On the other hand, the present MoN sample originated from pure Mo-N material, and moreover, the sample consists of almost a single phase of the hexagonal MoN as determined for x-ray measurements. All MoN samples except that annealed at 1000 °C have a tendency to increase in electrical resistance with decreasing temperature. The tendency is clearest in the as-received *B*1-MoN sample. The tendency became stronger when the N concentration in the *B*1-MoN$_x$ phase increased.

This phenomenon could be caused by Anderson localization[8] owing to such disorders as N vacancies and N interstitial defects or Mo vacancies and N clusters around the Mo vacancies. Such disorder is thought to remain locally even in the pressure-annealed samples except for that annealed at 1000 °C. The density of states at the Fermi level [$N(E_F)$] of *B*1-MoN is 1.3–1.5 times larger than that of hexagonal MoN from the x-ray photoelectron-spectroscopic measurement.[5] From this result we can estimate T_c of a high-quality *B*1-MoN crystal as 20–28 K by using McMillan's formula[9] and the present T_c value of hexagonal MoN. In this estimation we assumed that the Debye temperature, effective Coulomb repulsion, phonon density of states, and electron-phonon matrix element, in fact, all parameters except the $N(E_F)$ term in McMillan's formula, are the same in both *B*1-phase and hexagonal-phase MoN. This assumption would be an underestimation of T_c for *B*1-MoN, because we neglected the effect of the soft phonon usually existing in the *B*1 phase and the increase of the Debye temperature with the transition from hexagonal to *B*1 phase.

The present pressure annealing did not succeed in retaining the *B*1-phase MoN. The present work, however, is important in revealing the existence of the pure hexagonal-phase MoN with high T_c and the need of a pressure higher than 6 GPa to obtain the nonequilibrium *B*1-phase MoN.

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