

## Phase Transition in B1-Type $\text{Mo}_{1-x}\text{Nb}_x\text{N}$ Sputtered Films under Ammonia Annealing

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B1-type solid solution  $\text{Mo}_{1-x}\text{Nb}_x\text{N}$  sputtered films were annealed at 500–900°C for 5–100 hr under flowing ammonia, in order to investigate the stability of B1 structure and phase transition in the solid solution as a function of annealing temperature and chemical composition  $x$ . The B1 phase of the MoN films ( $x = 0$ ) transferred to a hexagonal phase above 600°C. In the Mo-rich solid solution films with  $x \leq 0.23$ , the B1 phase was converted to the  $\gamma\text{-Mo}_2\text{N}$ -type phase between 600°C and 800°C, and the transition temperature increased with increases in  $x$ . A hexagonal solid solution with WC-structure was formed in the films with  $x \leq 0.38$  at 900°C. No phase transition occurred until 900°C in the Nb-rich solid solution films with  $x \geq 0.59$ . The result indicates that the stability of B1 structure in the solid solution was increased by the addition of NbN. © 1989 Academic Press, Inc.

### Introduction

It is well known that many transition metal carbides and nitrides with B1 (NaCl) structure have excellent properties such as high melting point, extreme hardness, and metallic conductivity and superconductivity, owing to their particular chemical bonding character and electronic structure. The electronic structure of these compounds is often described by the Rigid Band Model; i.e., the position of the Fermi level and the density of states at the Fermi level [ $N(E_F)$ ] change with the number of valence electrons ( $N_{VE}$ ), independently of the constituent elements. The superconducting transition temperature ( $T_c$ ) of these compounds, therefore, was predicted to rise with an increase in  $N_{VE}$  for  $N_{VE} \geq 8$ , according to the band calculations (1, 2). It

has been observed that in fact  $T_c$  rises from 0 to 17.3 K with an increase in  $N_{VE}$  from 8 (ZrC, TiC, etc.) to 10 (NbN) (3). The  $T_c$  of 17.3 K is the highest value found so far in B1-type compounds. The  $T_c$  of B1-type MoN with  $N_{VE} = 11$ , furthermore, has been predicted to be about 30 K from both electronic band calculations (2) and empirical relationships between  $T_c$  and  $N_{VE}$  (3).

Unfortunately, the contribution of anti-bonding orbitals to the chemical bond in the B1 structure increases with an increase in  $N_{VE}$  for  $N_{VE} \geq 10$ . B1 structure of the metal nitrides with  $N_{VE} \geq 10$  has been pointed out to be less stable than WC- and NiAs-structures according to calculations on the total energy of these structures (4). There exist in practice three structure types in NbN, i.e., the B1 type and two hexagonal types, where B1-type NbN is stable only above

1230°C (5). With regard to MoN having one valence electron more than NbN, only hexagonal MoN (WC-structure) is a stable phase with stoichiometric composition, according to the phase diagram of the Mo-N system (6). Hexagonal MoN could have been obtained, moreover, by nitridation of molybdenum powder in flowing ammonia at temperatures between 700 and 1000°C, but only  $\gamma$ -Mo<sub>2</sub>N (cubic) and  $\beta$ -Mo<sub>2</sub>N (tetragonal) were formed under nitrogen pressures up to 300 atm below 1000°C, because of the lower activity of nitrogen gas compared to that of ammonia (6). It is, therefore, difficult to synthesize B1-type MoN by conventional thermal equilibrium techniques.

Recently, preparation of B1-type MoN films has been attempted by applying various nonequilibrium processing methods such as sputtering (7-9), ion implantation (10), and ion beam deposition (11). The prepared B1-type MoN films had  $T_c$ 's below 12.8 K, which were lower than the expected value. The reason for the low  $T_c$  of the MoN films prepared by nonequilibrium processing methods was considered to be due to the presence of vacancies in both metal and nitrogen sublattices. Several annealing treatments for as-prepared MoN films were attempted to reduce these vacancies. Linker *et al.* (12) annealed B1-type MoN films, which were prepared by sputtering, under atmospheric nitrogen gas, and found that the lattice parameter of B1-type MoN started to decrease at 600°C and the conversion from B1-type MoN to the  $\gamma$ -Mo<sub>2</sub>N phase took place at 700°C. Ihara *et al.* (13) made a treatment on the B1-type MoN films, prepared by sputtering, under a high pressure of 6 G Pa at temperatures between 600 and 1100°C. The result was that hexagonal MoN and  $\beta$ -Mo<sub>2</sub>N were formed at 600-900°C, and a single phase of hexagonal MoN was obtained by annealing at higher temperature. Attempts so far have not succeeded in preparing stoichiometric

B1-type MoN, and there is little information in detail about its stability.

We are interested in the relation between  $N_{VE}$  and  $T_c$  as well as in the stability of the B1 structure for transition metal nitrides. We previously prepared by reactive sputtering B1-type Mo<sub>1-x</sub>Nb<sub>x</sub>N solid solutions, whose  $N_{VE}$  varied continuously from 10 to 11, and investigated their superconducting properties (14). In this paper, we report the results of annealing such solid solutions under flowing ammonia at 500-900°C for 5-100 hr. The effects of both annealing temperature and chemical composition on the phase transition in the solid solution have been investigated, and the conditions under which the B1 type solid solution is stabilized are discussed.

### Experimental Details

The samples used for the annealing experiments were solid solution films, Mo<sub>1-x</sub>Nb<sub>x</sub>N, with B1 structure. The films were deposited on fused silica substrates by reactive sputtering of Mo/Nb-composite targets in an Ar/N<sub>2</sub> equimolar mixing gas at a substrate temperature of 450°C. The deposition rate was 10-20 nm/min, and the thickness of the films was controlled to 1.5-2.5  $\mu$ m. The films had a strong preferred orientation with the (100) plane parallel to the film surface. Annealing treatment was carried out in such a way that the samples were put in a silica glass tube with an inlet and an outlet for ammonia gas flow. The samples were subjected to flowing ammonia gas for 2 hr at room temperature, and then the temperature was raised at a rate of 10°C/min in ammonia gas flow. The samples were annealed at the given temperature for 5-100 hr, and then quenched to room temperature in the same atmosphere.

The atomic ratio of metal atoms in the samples was determined by the intensity ratio of Mo<sub>L $\alpha$ 1</sub> to Nb<sub>L $\alpha$ 1</sub> radiation by EPMA measurement. Identification of the crystal

phases in both the sputtered films and the annealed films was carried out by X-ray diffractometry. The lattice parameter of the samples was determined from 200 and 400 reflections for the B1 phase and 200 and 202 reflections for the hexagonal phase. The Bragg angle  $2\theta$  was calibrated using silicon powder as a standard.

## Results

### 1. Annealing of B1-Type $\text{MoN}$ ( $x = 0$ )

Figure 1 displays the X-ray diffraction patterns of the  $\text{MoN}$  films ( $x = 0$ ) annealed in flowing ammonia at 500–900°C for 5 hr. No change was observed in the X-ray diffraction pattern after annealing the sample at 500°C, but at 600°C a hexagonal phase was formed, and the peak intensity of this phase increased relatively with increase in annealing temperature up to 700°C. The B1 phase converted completely to the hexagonal phase at 800°C within 5 hr, and the hexagonal phase remained stable up to 900°C.

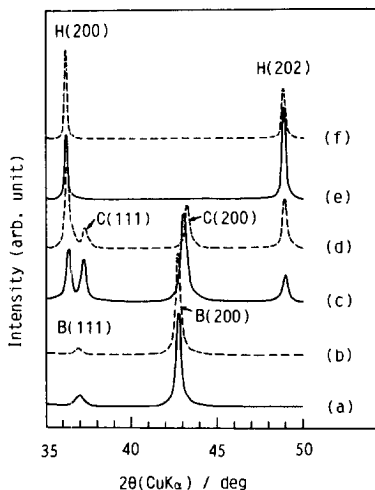


FIG. 1. XRD patterns of the  $\text{MoN}$  films annealed at 500–900°C for 5 hr. (a) Before annealing, (b) at 500°C, (c) 600°C, (d) 700°C, (e) 800°C, and (f) 900°C.  $H(hkl)$ , for hexagonal  $\text{MoN}$ ;  $C(hkl)$ ,  $\gamma\text{-Mo}_2\text{N}$ ; and  $B(hkl)$ , B1-type  $\text{MoN}$ .

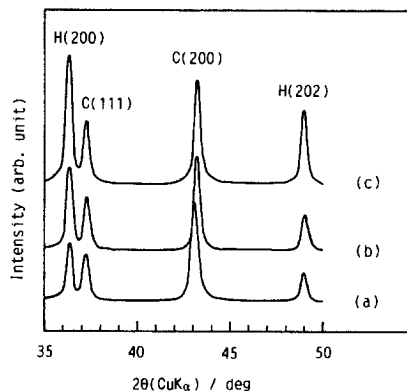


FIG. 2. XRD patterns of the  $\text{MoN}$  films annealed at 600°C for (a) 5 hr, (b) 24 hr, and (c) 100 hr.  $H(hkl)$ , for hexagonal  $\text{MoN}$ ; and  $C(hkl)$ ,  $\gamma\text{-Mo}_2\text{N}$ .

The change in the relative amount of transformation from the B1-type phase to the hexagonal phase at 600°C is shown as a function of annealing time in Fig. 2. Although the transformation to the hexagonal phase is not completed even after annealing for 100 hr, it is seen that the amount of hexagonal phase increased relatively with annealing time. This implies that the only hexagonal phase is a stable phase at 600°C under an ammonia atmosphere. The reflection peaks of the untransferred B1 phase, on the other hand, not only become relatively weaker, but also shift toward higher angles compared with those of the as-prepared samples. This indicates that the lattice parameter of the untransferred B1 phase has decreased, due to the release of some nitrogen during annealing.

### 2. Annealing of B1-Type $\text{Mo}_{1-x}\text{Nb}_x\text{N}$ Films

No change in crystal structure was observed for all solid solutions after annealing at 500°C similar to that for  $\text{MoN}$  ( $x = 0$ ). The hexagonal phase was not formed in the solid solutions after annealing at 600–800°C, but a decrease in the lattice parameter was observed for the Mo-rich samples.

Figure 3 shows the relation between lattice parameter and annealing time for the Mo-rich solid solutions ( $x \leq 0.38$ ) annealed at 600°C. Data for the untransferred B1-type MoN in the MoN films ( $x = 0$ ) are also shown in Fig. 3 as a reference. It is found that the lattice parameter of the samples decreases with increased annealing time, particularly for samples with smaller  $x$ , but the trend of the decrease changes in the vicinity of  $x = 0.1$ . The lattice parameter of the untransferred B1-type MoN and the solid solution with  $x = 0.06$  decreases appreciably and is close to that of  $\gamma$ -Mo<sub>2</sub>N ( $a = 4.163$  Å JCPDS card 25-1366), indicating that they can be classified with the  $\gamma$ -Mo<sub>2</sub>N-type phase rather than with the B1 phase. The annealed solid solutions with  $0.12 \leq x \leq 0.38$  can still be considered to belong to the B1 phase, although they have a certain nitrogen deficiency.

The relationship between the crystal phase of the solid solution and the annealing temperature is summarized in Fig. 4. The  $\gamma$ -Mo<sub>2</sub>N-type solid solution was formed in Mo-rich samples with  $x \leq 0.23$  by annealing the B1-type solid solution in ammonia gas, but the transition temperature from the B1 phase to the  $\gamma$ -Mo<sub>2</sub>N-type phase increased with an increase in  $x$ . At 900°C a new hexagonal solid solution with

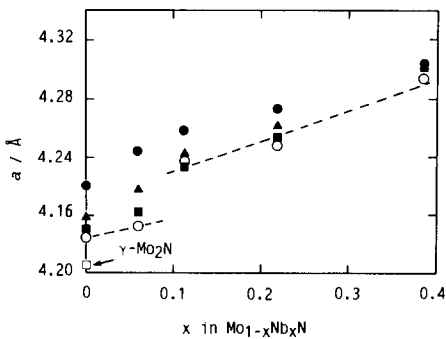


FIG. 3. Dependence of the lattice parameters on annealing time for the Mo-rich solid solution at 600°C. (●) Before annealing, (▲) for 5 hr, (■) 24 hr, and (○) 100 hr.

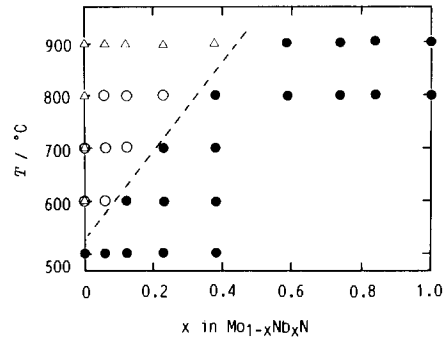


FIG. 4. Crystal phase in the Mo<sub>1-x</sub>Nb<sub>x</sub>N solid solution annealed at 500–900°C for 5–100 hr. (●) B1 phase, (Δ) hexagonal phase, and (○)  $\gamma$ -Mo<sub>2</sub>N-type phase.

WC-structure was formed in the films with  $x \leq 0.38$ , and the lattice parameters of both  $a$ - and  $c$ -axes increased linearly with an increase in Nb, which has a larger atomic radius than Mo, as shown in Fig. 5. The phase transition from the B1 to the hexagonal structure did not take place until 900°C in the solid solution with  $x \geq 0.59$ .

## Discussion

### 1. Phase Transition in MoN Films

The B1 phase in the MoN film prepared by sputtering remained after annealing in ammonia below 500°C, which is consistent

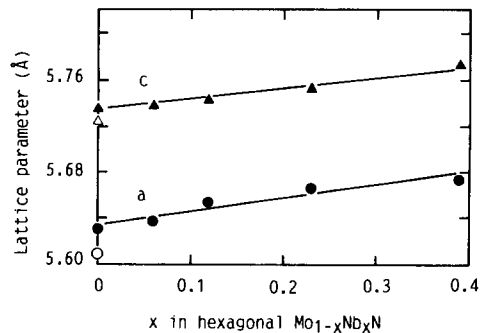


FIG. 5. Change of the lattice parameters of the hexagonal Mo<sub>1-x</sub>Nb<sub>x</sub>N solid solution as a function of Nb content; (a)  $a$ -axis, (c)  $c$ -axis, and (Δ, ○) reported values for hexagonal MoN from JCPDS card 25-1367.

with the results of annealing of the B1-type MoN in nitrogen gas (12). However, a hexagonal phase was formed by annealing B1-type MoN in ammonia gas at 600°C, while annealing in nitrogen gas above 600°C was said to transfer the B1-type MoN to  $\gamma\text{-Mo}_2\text{N}$  (12). These results suggest that annealing in ammonia gas, which is more active than nitrogen gas, can restrain the release of nitrogen from the samples and the formation of  $\gamma\text{-Mo}_2\text{N}$ , but cannot stabilize B1-type MoN above 600°C. The phase transition from the B1 phase to the hexagonal phase took place very slowly at 600–700°C, and or complete transition to the hexagonal phase could not be obtained even after annealing for 100 hr at 600°C (see Fig. 2). This is comparable with the fact that the nitridation of molybdenum in ammonia is very slow at low temperatures; e.g., the formation of about 70% hexagonal phase takes 2 weeks even at 700°C (15). The dependence of the rate of the phase transition in the MoN samples on the annealing temperature may be related to the diffusion rate of nitrogen ( $D_N$ ) in the samples. Below 500°C,  $D_N$  is so small that the phase transition cannot take place. Phase transition occurs at 600°C and becomes fast above 800°C because  $D_N$  increases with an increase in temperature. With this in mind, we will discuss phase formation in the Mo–N system observed in sputtering and high-pressure processes.

Linker *et al.* (7) reported that stoichiometric B1-type MoN was formed by reactive sputtering at substrate temperatures ( $T_s$ ) around 500°C, and the lattice parameter of the MoN films decreased rapidly with increases in  $T_s$  above 600°C. The same result was also found by Yamamoto *et al.* (9), who investigated the relation between the lattice parameter of sputtered  $\text{MoN}_y$  films and  $T_s$  in detail. Their results are compatible with the present result that B1-type MoN is unstable above 600°C. In the case of sputtering, the activity of nitrogen used

as a sputtering gas can be increased as nitrogen molecules are raised to the excited state in the plasma. However, it is considered that the activity of nitrogen is still low because of the lower pressure of the sputtering gas (generally 1–10 Pa). Consequently above 600°C  $\gamma\text{-Mo}_2\text{N}$  can be formed more easily than B1-type MoN; that is to say, B1-type MoN will release nitrogen to convert to  $\gamma\text{-Mo}_2\text{N}$  above 600°C, even if B1-type MoN was probably formed in the sputtering process.

It has been suggested that B1-type MoN could be stabilized by high pressure because of its larger coefficient of compactness  $q = 0.66$  than that of hexagonal MoN ( $q = 0.63$ ) (3). Thus, several high-pressure experiments, up to 2 G Pa for nitrogen pressure and 7 G Pa for mechanical pressure, have been carried out at temperatures of 1100–1700°C for preparation of stoichiometric B1-type MoN, but no stoichiometric B1-type MoN was obtained and only hexagonal MoN with stoichiometric composition was formed (13, 16–18). In light of the present experiment, there could be at least two reasons why B1-type MoN was not obtained, i.e., insufficient pressure and relatively high temperature. High pressure might enhance the activity of nitrogen because hexagonal MoN was formed which is stable at high temperatures up to 1700°C under high pressure (17). While attempts to stabilize hexagonal MoN in ammonia gas above 1000°C have been unsuccessful and hexagonal MoN transferred to  $\gamma\text{-Mo}_2\text{N}$  at 1000°C in the present experiment, it seems possible to prepare ideal B1-type MoN by a process combining high pressure and low temperature which would be suitable for preventing the dissociation of nitrogen and stabilizing the metastable phase.

## 2. Phase Transition in $\text{Mo}_{1-x}\text{Nb}_x\text{N}$ Solid Solution

The annealed NbN ( $x = 1.0$ ) films showed no phase transition until 900°C, and

only a small decrease in lattice parameter was observed above 800°C. The present result is consistent with that reported by Talvacchio *et al.* (19) who annealed NbN single crystal with B1 structure under a high vacuum ( $<10^{-8}$  Pa) at 800–1100°C. They reported that no phase transition was observed and only nitrogen loss was found after annealing, particularly at the high temperature of 1100°C. That no hexagonal phase, which is reported to be the stable phase below 1230°C, was formed during annealing may be due to the nitrogen deficiency in B1-type NbN.

In the solid solution, the temperature below which the B1 phase remained increased from 500°C to 900°C as  $x$  increased from 0.06 to 0.59, as shown in Fig. 4. It is obvious that the stability of the B1 phase in the solid solution increases with the increment of the content of NbN, whose valence electrons are one less than those of MoN. This can be explained by the fact that the contribution of antibonding orbitals to the chemical bond decreases with a decrease in  $N_{VE}$  in the solid solution. In the Mo-rich solid solution with  $x \leq 0.23$ , the formation of a hexagonal phase was restrained until 900°C by the addition of Nb, although hexagonal phase was formed in MoN above 600°C. This is thought to be due to the difference in the crystal structure between hexagonal MoN, WC type, and hexagonal NbN, TiP type or anti-NiAs type (5).

The packing of molybdenum atoms and the occupied sites of nitrogen atoms are the same for both  $\gamma$ -Mo<sub>2</sub>N and B1-type MoN. The only difference between them is that in the former one-half of the nitrogen sites are unoccupied. In hexagonal MoN, both molybdenum and nitrogen atoms assume a simple hexagonal arrangement which is different from that of B1-type MoN, although both have the same chemical composition. It is therefore considered that B1-type MoN may be obtained from  $\gamma$ -Mo<sub>2</sub>N by a topotaxial reaction in which nitrogen can

probably be added to  $\gamma$ -Mo<sub>2</sub>N at relatively low temperatures without reconstruction of the crystal lattice of  $\gamma$ -Mo<sub>2</sub>N. The temperature at which the migration of nitrogen occurred obviously was over 600°C, as mentioned above. However, hexagonal MoN is easily formed in active nitrogen such as ammonia gas at temperatures up to 600°C, and the transition to B1-type MoN is more difficult once hexagonal MoN has been formed. The formation of the hexagonal phase must be depressed in order to prepare B1-type MoN at temperatures above 600°C. The present results on the solid solution Mo<sub>1-x</sub>Nb<sub>x</sub>N indicate that the  $\gamma$ -Mo<sub>2</sub>N-type phase rather than the hexagonal phase is formed for the Mo-rich samples at 600–800°C. Therefore, it may be possible to obtain B1-type Mo-rich solid solution with stoichiometric composition in a much more highly active nitrogen atmosphere, e.g., nitrogen plasma, or high-pressure processes within the temperature range of 600–800°C.

## Conclusions

The influence of chemical composition and temperature on the stability of the B1 structure and phase transitions in B1-type solid solution Mo<sub>1-x</sub>Nb<sub>x</sub>N sputtered films has been studied by annealing under flowing ammonia in the temperature range between 500 and 900°C for 5–100 hr. No phase transition was observed at 500°C in all annealed solid solution films. Hexagonal MoN and  $\gamma$ -Mo<sub>2</sub>N-type solid solution were formed in MoN ( $x = 0$ ) and in the Mo-rich solid solution films ( $x \leq 0.23$ ) above 600°C, respectively. For the solid solution, the transition temperature from the B1 phase to the  $\gamma$ -Mo<sub>2</sub>N-type phase increased from 600 to 800°C with increases in  $x$  from 0.06 to 0.23. This indicates that the stability of the B1 phase increases with increased content of NbN, viz., the decrease of  $N_{VE}$  in the solid solution. A new hexagonal solid solution (WC-structure) was formed in the an-

nealed Mo-rich films with  $x \leq 0.38$  at  $900^\circ\text{C}$ , while no phase transition took place in the Nb-rich films with  $x \geq 0.59$  below  $900^\circ\text{C}$ . The present results suggest that a low-temperature process using active nitrogen or high-pressure nitrogen with the addition of a small quantity of other stable B1-type nitrides to MoN may be suitable to prepare stoichiometric B1-type Mo-rich solid solutions.

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