Electronic structures of B1 MoN, fcc Mo₂N, and hexagonal MoN

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The electronic structures of B1 MoN, fcc Mo₂N, and hexagonal MoN were observed by photoelectron spectroscopic measurement. The B1-MoN phase has been predicted to be a high- T_c superconductor because of a large density of states at Fermi level. The observed electronic structure of the stoichiometric B1-MoN phase is different from that of the real B1-MoN type. The nitrogen excess B1-MoN_x ($x \ge 1.3$) phase, however, shows the B1-type electronic structure. This is explained by the occurrence of a nitrogen vacancy in the apparent stoichiometric B1 phase and the occupation of the nitrogen vacancy in the nitrogen-excess B1 phase. This property is related to the previously reported low T_c of the B1-MoN crystals.

MoN with the B1-type structure has been predicted to have a higher superconducting transition temperature (T_c) than NbN. On the basis of electronic-band calculation a theoretical prediction gives 29.3 K of T_c ,¹ and an empirical prediction gives 20–25 K.² The B1-MoN phase, however, does not appear in the equilibrium-phase diagram of Mo-N system.³ Therefore, it is very difficult to synthesize the substance. Some attempts have been made to prepare it by nonequilibrium or other techniques.⁴⁻¹⁰

Recently, Saur, Schlechinger, and Rinderer,⁹ and Linker, Smithey, and Meyer¹⁰ have reported the existence of the B1 phase. The lattice parameter obtained by Saur *et al.*, however, is 4.16 Å, which corresponds to that of fcc Mo₂N.³ Linker *et al.* have prepared B1-MoN_x films with large lattice constants of 4.20–4.26 Å and high nitrogen concentrations (x = 0.9-1.8), but T_c of the films has been below 5 K.

In this Rapid Communication we show the electronic structures of B1 MoN, fcc Mo₂N, and hexagonal MoN observed by x-ray photoelectron spectroscopic (XPS) measurement. This is the first observation of the electronic structure of a Mo-N system. From these results it is explained why the T_c of a B1-MoN phase at the present stage is so low.

The MoN films were prepared by a reactive dc sputtering from a Mo target in N₂ gas atmosphere. The N₂ gas pressure was varied from 50 to 140 Pa. The substrate temperature was changed from 400 to 800 °C. The base pressure in preparation chamber was 2×10^{-5} Pa. The preparation method will be described in detail elsewhere. The XPS analysis chamber was connected with the sputtering chamber in order to do *in situ* XPS observation after sample preparation without breaking the vacuum. The XPS spectrometer is a Hewlett-Packard 5950A electron spectroscopy for chemical analysis (ESCA) system equipped with an Al- $K\alpha$ monochromater source with a resolution of 0.8 eV. The pressure in the analyzing chamber was below 1×10^{-6} Pa.

The T_c of fcc Mo₂N films was 6–7 K with a wide transition width of 1–2 K. The T_{co} (the onset of T_c) of single B1-MoN_x phase films decreased from 12.5 to below 4.2 K with increasing x from 1.1 to 1.8. This T_c behavior is nearly similar to that of Linker *et al.* A hexagonal MoN film had T_c of 13.2 K with a transition width of 0.4 K. A B1 and hexagonal mixed-phase MoN film had T_c of 12.9 K with a transition width of 1.4 K. The lattice parameter of the fcc Mo₂N film was 4.16-4.19Å. The lattice parameter of B1-MoN_x films increased generally from 4.20 to 4.27 Å with the increase of x from 1.0 to 1.8. This tendency is consistent with the result of Linker *et al.* The lattice parameters of the hexagonal MoN film were a = 5.72 Å and c = 5.60 Å.

The nitrogen concentration was determined from the core level XPS spectra in reference to the high T_c hexagonal MoN film as a stoichiometric composition. This estimation method is consistent with the method of using the Scofield cross section¹¹ of N 1s and Mo $3d_{5/2}$ levels within an experimental error of 10%.

The XPS spectra of the valence band of Mo-N films and a pure Mo metal are shown in Fig. 1. The valence-band spectra change continuously from Mo to B1 MoN_{1.8} with increasing nitrogen concentration. The intensity of peak A decreases with nitrogen concentration. On the contrary peak B and the N 2s peak increase. The valence-band spectra of B1-MoN_x film at $x \ge 1.3$, especially x = 1.5 have a strong resemblance to the theoretical density of state (DOS)¹ as shown in Fig. 2. The direct comparison between XPS valence-band spectra and theoretical DOS is possible in the case of transition metal carbide and nitride com-



FIG. 1. X-ray photoelectron spectra of the valence band of MoN_x (x = 0-1.8).

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FIG. 2. Comparison between the x-ray photoelectron spectra of $B1 \text{ MoN}_{1.5}$ and hexagonal MoN and a theoretical DOS after Pickett *et al.* (Ref. 1).

pounds.¹² The valence-band spectra of a stoichiometric B1-MoN_{1.0} phase is not similar to the theoretical DOS. Therefore, the present B1-MoN_{1.0} film is not a perfect B1-type crystal. The composition is thought to be apparently stoichiometric. A part of the nitrogen atoms contained in the film might be located in such irregular sites as interstitial sites and grain boundaries. Then in the apparent stoichiometric B1-MoN film, the vacancies of nitrogen would exist in no small quantities. The vacancy sites would be occupied with excess nitrogen atoms in the $MoN_{x>1.3}$ films.

Since T_c of the B1 transition-metal nitrides is very sensitive to the nitrogen/metal ratio,¹³ the T_c of B1-MoN films would decrease because of the vacancies and interstitial defects. This is why the T_c of B1-MoN films reported is lower than the predicted values. Then it will be possible to attain a higher T_c , if we succeed in the preparation of a more perfect B1-MoN crystal.

The intensity of the valence-band spectrum at the Fermi edge is larger in B1 MoN_{1.5} than in hexagonal MoN as shown in Fig. 2. This fact suggests a larger DOS at Fermi level $[N(E_F)]$ and then a higher T_c in the perfect B1 MoN than in the hexagonal MoN. This presumption is based on the predominantly large contribution of the Mo 4d state and the small contribution of the N 2p state to the valence-band spectrum consisting of both A and B peaks. This is supported by the ratio of photoemission cross section of Mo 4d:N $2p = 1:0.02.^{11}$

In summary, the valence-band spectra of fcc MoN_x crystals vary continuously from the pure Mo metal through fcc Mo_2N to $B1 MoN_{1.8}$ with the increase of x. The B1-MoN crystal with apparently stoichiometric composition does not have the electronic structure of the B1-type, but the nitrogen-excess B1-MoN_{x>1.3} crystal has the electronic structure of the real B1 type. The vacancies and interstitial defects are thought to deteriorate the superconductivity of the B1-MoN crystals. The comparison of the valence-band spectra indicates that the $N(E_F)$ of the real B1 MoN is larger than that of the hexagonal MoN. This implies that a perfect B1-MoN crystal has a higher T_c than hexagonal MoN.

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