Cation and anion vacancies in cubic molybdenum nitride

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Epitaxial MoN_x layers deposited on $\text{MgO}(001)$ by reactive magnetron sputtering in 20 mTorr N_2 at $T_s = 600\text{-}1000$ °C exhibit a cubic rock-salt type structure, a N-to-Mo ratio that decreases from $x = 1.25\text{-}0.69$ with increasing T_s , and a lattice constant that simultaneously decreases from 4.26-4.16 Å. A combination of composition, thickness, lattice-constant, and atomic area-density measurements indicate that the rock-salt structure contains both anion and cation vacancies, with the Mo site occupancy X_{Mo} decreasing from 0.89 ± 0.06 to 0.70 ± 0.04 while the N site occupancy X_{N} increases from 0.60 ± 0.04 to 0.88 ± 0.04 , as x increases from 0.69-1.25. Density functional calculations for over 200 cubic MoN_x configurations confirm the energetic stability of both cation and anion vacancies and predict X_{Mo} to decrease from 1.00 to 0.67 for $x = 0.54\text{-}1.50$, while X_{N} increases from 0.50 to 1.00 for $x = 0.50\text{-}1.36$. The simulations are in good agreement with experiments and indicate a preference for a 75% site occupancy on both sublattices for compositions near stoichiometry, with $X_{\text{Mo}} = 0.75$ for $x = 1.00\text{-}1.22$ and $X_{\text{N}} = 0.75$ for $x = 0.86\text{-}1.00$. Correspondingly, cubic stoichiometric MoN is most stable in the NbO structure.

Keywords: MoN; vacancies; transition metal nitrides; sputter deposition; reactive sputtering; thin films

1. Introduction

Transition metal nitrides have found wide use as hard and decorative coatings [1–3] due to their high hardness and high temperature stability [4,5]. Many transition metal nitrides crystallize in the cubic rock-salt structure including TiN [6], CrN [7], ScN [8], VN [9], NbN [10], TaN [11], ZrN [12], and HfN [13]. The layers often exhibit considerable deviations from stoichiometry [6,11] with the nitrogen to cation ratio x either below or above unity. This is typically attributed to nitrogen vacancies or interstitials [14–19], while anti-site substitutions have also been proposed [11]. In contrast, only a few studies have considered the possibility of a significant concentration of cation vacancies [6,14]. Nevertheless, the introduction of metal vacancies may occur for some transition metal nitrides due to kinetic barriers during growth or even due to thermodynamic driving forces [10], and are expected to strongly affect physical properties. This has recently been shown for the W-N system from both experimental and computational studies [20,21], suggesting considerable vacancy concentrations at both anion and cation sites [21,22]. Consequently, it is interesting to also quantify metal and nitrogen vacancy concentrations in MoN_x , which is isoelectric with WN_x .

The Mo-N system has been reported to crystallize in various phases, with the most common being (i) BCC Mo with a possible small amount of dissolved nitrogen, (ii) face-centered cubic $\gamma\text{-Mo}_2\text{N}_x$, (iii) body-centered tetragonal $\beta\text{-Mo}_2\text{N}_x$, and (iv) hexagonal $\delta\text{-MoN}$ [23–27]. Interestingly, the β and γ phases have nominally the same composition range, with some experiments reporting the γ and β phase forming below and above a critical temperature of 775 °C [28], in apparent contradiction to the reported Mo-N phase diagram which suggests γ to be the high-temperature phase and β the low-temperature phase [29]. The challenge to experimentally distinguish between these two phases which exhibit nearly identical x-ray

diffraction (XRD) peak positions has been overcome by asymmetric XRD analyses which, in particular, identify the tetragonal β phase [26]. It is frequently assumed in the cases of both the γ and the β phases that nitrogen vacancies or interstitials alone are sufficient to account for variations in composition, while cation vacancies are not typically taken into account [17]. Recent computational studies [21,30] propose also the cubic NbO structure, which can be described as a cubic NaCl structure for which a regular array of 25% of both cation and anion sites are vacant.

MoN_x layers have been deposited using a range of methods and processing parameters, leading to different compositions and phases. More specifically, reactive DC sputtering [23–25,28,31–39] yields MoN_x with $x = 1.08$ in the γ phase (with a small amount of possible δ phase) using 60 sccm of N₂ gas flow and 55 sccm of Ar gas flow as well as a -50 V substrate bias [31], $x = 0-0.54$ in the γ phase using 0-26% of N₂ process gas [33] and also from 0-0.35 in the γ phase with varying N₂/ (Ar + N₂) gas ratio [37]. RF sputtering [40–42] results in $x = 0.49-0.67$ in the γ phase [41], $x = 0.55-0.9$ in the γ phase and $x = 0.9-1.02$ in the δ phase [40], and $x = 0.9-1.8$ in the B1-MoN phase, which can be described as a cubic variant of the γ phase [42]. Other physical vapor deposition techniques such as ion beam assisted deposition (IBAD) [43,44], cathodic arc evaporation [27,45–47], pulsed laser deposition (PLD) [26,48,49], and molecular beam epitaxy [50] have also been employed to deposit MoN_x layers, yielding $x = 0.5-1.1$ by IBAD [43] to 0.86-1.03 for a slightly tetragonally distorted γ phase deposited by PLD [48], 0.43 for the β phase deposited by PLD [26], or 0.2-0.5 by PLD [49], to γ phase MoN_x with $x = 0.7-1.4$ by MBE [50], for which the $x = 0.7$ sample showed a slightly distorted cubic structure. In addition, chemical vapor deposition techniques [51,52] have been used to prepare γ phase MoN_x with $x = 0-0.5$ or a mixture of γ -MoN_x and δ -MoN with $x = 0.9-1.05$ [52], while polymer-assisted deposition using

ethylenediaminetetraacetic acid and polyethyleneimine and annealing in ammonia gas at up to 950 °C has been reported to yield epitaxial MoN layers on both cubic SrTiO₃ and c-plane hexagonal Al₂O₃ substrates [53], and nitridation of a Mo surface has been achieved in an expanding microwave plasma [54].

In this study, we report on the deposition of MoN_x/MgO(001) by reactive DC magnetron sputtering in 20 mTorr N₂. All layers show only a 002 γ -MoN_x XRD peak with lattice constants that vary with increasing growth temperature from 4.26-4.16 Å, while the nitrogen-to-molybdenum ratio decreases from $x = 1.25$ -0.69. The molybdenum area density of the layers is relatively constant while the density increases with increasing T_s , suggesting filling of Mo-vacancies. Correspondingly, Mo-site occupancies increase from 0.70-0.89 and N-site occupancies decrease from 0.88-0.60, indicating that nitrogen is lost from the layers with increasing T_s . Density functional theory (DFT) calculations of cubic γ -MoN_x quantitatively confirm the experimental results, in particular the simultaneous presence of both cation and anion vacancies and the decrease and increase of Mo and N site occupancies with increasing x , respectively.

2. Experimental and Computational Procedure

MoN_x layers were deposited on MgO(001) substrates in a load-locked ultra-high vacuum dc magnetron sputtering system with a base pressure of $<10^{-9}$ torr [10,55,56]. The substrates are one-side polished 10×10×0.5 mm³ wafers that were cleaned in successive rinses of trichloroethylene, acetone, isopropanol, and deionized water, blown dry with dry N₂, attached to a Mo block with silver paint, loaded into the system through a load-lock chamber, and thermally degassed at 900 °C for 1 hour. The substrate temperature T_s was measured by a thermocouple

below the sample stage that was cross-calibrated with a pyrometer focusing on the sample surface. The temperature was adjusted to the desired $T_s = 600\text{-}1000$ °C prior to deposition from a 99.95%-pure 51-mm-diameter Mo target which was sputter etched before deposition for 5 minutes with a shutter shielding the substrate. The target was facing the substrate at a 9 cm distance and from a 45° angle, with the substrate being continuously rotated at 60 rotations per minute to increase thickness uniformity. All depositions were done in 20 mTorr 99.999% pure N₂ and using a constant dc power of 300 W which was applied to the magnetron for a duration of 6.00 min, resulting a layer thickness ranging from 69-98 nm corresponding to a temperature-dependent deposition rate of 11.5-16.3 nm/min.

X-ray diffraction was done in a Panalytical X'Pert PRO MPD system with a Cu K_α $\lambda = 1.5418$ Å source yielding a 1° divergent incident beam limited by an incident slit. θ - 2θ scans were collected over a 2θ range from 5° - 80° using the Bragg-Brentano geometry and a PixCEL solid-state line detector. The 2θ -values were calibrated using the substrate peak position, that is, 2θ was set to the literature value of 42.909° at the measured positions of the MgO 002 reflection measured using Cu K_{α1} x-rays. X-ray reflectivity (XRR) measurements were collected using a parabolic x-ray mirror with a divergence of 0.055° and a scintillator point detector. XRR data was analyzed by curve fitting using the recursive theory of Parrat based on the Fresnel reflectivity formalism, assuming a Gaussian distribution to model the surface and interface roughness.[57] Rutherford backscattering spectroscopy (RBS) measurements were collected using a 2.0 MeV ⁴He⁺ beam incident at an angle of 6° to the surface normal with the detector set at a scattering angle of 166°. The sample was continuously rotated to minimize the artifacts due to ion channeling. The RBS spectra were analyzed using the RUMP simulation software for curve fitting, in order to determine the area density of Mo atoms and the N-to-Mo ratio x .

First-principles DFT calculations are performed using the Vienna *ab initio* simulation package (VASP), employing periodic boundary conditions, a plane wave basis set, the Perdew-Burke-Ernzerhof generalized gradient approximation exchange correlation functional [58], and the projector-augmented wave method [59]. All computational parameters are chosen such that calculated total energy differences are converged to within 1 meV/atom. This includes a 500 eV cut-off energy for the plane-wave basis set expansion and Γ -centered k -point grids with, for example, $8 \times 8 \times 8$ k -points for 32-atom and 24-atom supercells or $10 \times 10 \times 10$ k -points for 16-atom supercells. Mo $4p$, $4d$, and $5s$ electrons are explicitly calculated, that is, they are not included in the core of the pseudo potential. Test calculations which explicitly calculate the Mo $4s$ electrons result in ~ 7 meV per Mo-atom higher formation energies for all tested nitride configurations, such that this error is not expected to affect the relative energies between different reported configurations.

MoN_x is simulated using supercells of stoichiometric rocksalt-structure MoN for which some Mo and/or N atoms are removed to form cation and/or anion vacancies, respectively. Various supercell sizes and geometries are used to sample diverse vacancy concentrations and ordering, while keeping the supercell size relatively small. Supercells include (i) the conventional 8-atom cell with basis vectors $[100]$, $[010]$, and $[001]$; (ii) a symmetric 16-atom cell with vectors $[110]$, $[101]$, and $[011]$; (iii) a 32-atom cell with $[\bar{1}11]$, $[1\bar{1}1]$, and $[11\bar{1}]$; (iv) a hexagonal-type 24-atom cell with $[111]$, $[1\bar{1}0]$, and $[10\bar{1}]$; as well as less conventional supercells like (v) a 14-atom cell with $[1\ \bar{5}\ .5]$, $[\ .5\ 1\ \bar{5}]$, and $[\bar{5}\ .5\ 1]$; or (vi) a 22-atom cell with $[2.5\ \bar{5}\ 0]$, $[120]$, and $[1.5\ 0\ .5]$; or (vii) a 30-atom cell with $[1.5\ .5\ 0]$, $[120]$, and $[\ .5\ 1\ 1.5]$; or (viii) a 20-atom cell with $[1\ 0\ 0]$, $[010]$, and $[\ .5\ 0\ 2.5]$. For each supercell type, the site occupancies X_{Mo} and X_{N} for Mo atoms on cation sites and N atoms on anion sites was varied from 0.5 to 1. For

example, simulated cells for calculations with the 32-atom-cell mentioned above include 8 to 16 Mo atoms on cation sites and 8 to 16 N atoms on anion sites of the NaCl-structure lattice. For a given number of Mo and N atoms, the lattice sites are populated such that the distance between any vacancies is maximized, as this was found to minimize the calculated total energy. Multiple calculations for the same supercell-size and the same number of Mo and N atoms are performed if it is not a priori evident which configuration results in the lowest energy. Only the lowest energy configuration is reported here.

For all simulated configurations, atomic positions and the supercell volume are iteratively relaxed, while the cell shape is kept fixed. All simulations use as starting point the NaCl structure lattice. Therefore, all configurations are for a cubic crystal structure even if the simulated cell (and therefore the vacancy lattice) have not a cubic symmetry.

The cohesive energy E_c for the different structures is determined relative to BCC Mo and molecular nitrogen. That is, $E_c = E - N_{\text{Mo}}\mu_{\text{Mo}} - \frac{1}{2} N_{\text{N}}\mu_{\text{N}_2}$, where E is the calculated energy for a specific supercell containing N_{Mo} molybdenum and N_{N} nitrogen atoms, while μ_{Mo} and μ_{N_2} are the Mo and N_2 chemical potentials corresponding to the calculated energy of a one-atom BCC Mo unit cell and an isolated N_2 molecule, respectively. All calculations are for zero temperature. Considering finite temperatures would add correction terms, with the largest being associated with the entropy of the N_2 gas [10], driving the system at high temperature towards phase separation into N_2 gas and a reduction in x in the solid MoN_x phase. In order to directly compare formation energies E_f of different compositions, the calculated cohesive energies are presented in this paper as energy per atom, i.e. $E_f = E_c/(N_{\text{Mo}}+N_{\text{N}})$.

3. Results and Discussion

Figure 1 is a plot of the MoN_x lattice constant as a function of the growth temperature T_s = 600-1000 °C, as determined from X-ray diffraction measurements of $\text{MoN}_x/\text{MgO}(001)$ layers. A small section from a typical θ - 2θ scan is shown in the inset, in this case from a 68.9 ± 0.1 nm thick layer grown at 1000 °C. It exhibits a double peak feature at $2\theta = 42.909^\circ$ and 43.021° , which is associated with the MgO 002 substrate reflection of the Cu $K\alpha_1$ and $K\alpha_2$ lines, respectively, and a broader and 60 times weaker a peak at $2\theta = 43.46^\circ$ which is visible in the inset from the 30-times-magnified (red) curve and is labeled as MoN_x 002. No other peaks could be detected over the entire 2θ range from 5-80°, indicating a 002 texture and, in combination with asymmetric scans (not shown), confirming that the layer is epitaxial $\text{MoN}_x(001)$. The diffraction patterns from the other samples also show only a single MoN_x peak. However, its position shifts as a function of growth temperature from $2\theta = 42.43 \pm 0.01^\circ$ for $T_s = 600$ °C to $2\theta = 42.72 \pm 0.07^\circ$, $42.82 \pm 0.10^\circ$, and $43.42 \pm 0.25^\circ$ for $T_s = 700$, 800, and 900 °C. The peaks for $T_s = 700$ -900 °C partially overlap with the substrate peaks, causing a larger uncertainty in the determination of their position than for $T_s = 600$ and 1000 °C, as indicated with the error bars. The detected MoN_x peaks are close to the reported cubic $\gamma\text{-Mo}_3\text{N}_2$ 002 peak position at $2\theta = 43.418^\circ$ [JCPDS 01-089-3712] as well as the 200 and 400 reflections of the tetragonal $\beta\text{-Mo}_2\text{N}$ structure with a ratio of $a/(c/2) = 1.05$ and $2\theta = 43.038^\circ$ and 45.306° , respectively [JCPDS 01-075-1150]. However, our asymmetric XRD scans (not shown) are inconsistent with a tetragonal structure, such that we attribute the detected peaks to cubic MoN_x 002, and use their position to determine the lattice constant, as plotted in Fig. 1. More specifically, the plotted values are the out-of-plane lattice constants which decrease from $a_\perp = 4.258$ Å for $T_s = 600$ °C to $a_\perp = 4.230 \pm 0.007$, 4.220 ± 0.009 , 4.165 ± 0.023 , and 4.161 Å for $T_s = 700$, 800, 900 and 1000 °C. These values are within the range of previously reported lattice constants, with 4.215-4.303 Å for $x =$

0.49-0.67 [41], 4.161 Å for $x = 0.5$ [60], 4.20-4.27 Å for $x = 0.9-1.6$ [42], 4.07 Å for $x = 0.5$ [53], 4.235 Å for fcc MoN [25], 4.10-4.20 Å for $x = 0.10-0.35$ [37], 4.14-4.28 Å for $4-30 \times 10^{-5}$ torr N_2 partial pressure during sputter deposition [35], 4.18-4.28 Å for $N_2/(N_2+Ar_2) = 20-50\%$ (decreasing to 4.05 Å at $N_2/(N_2+Ar_2) = 80\%$) [38], and 4.19-4.29 Å for $N_2/(N_2+Ar_2) = 10-50\%$ [39].

Figure 2 is a plot of the thickness d of $MoN_x/MgO(001)$ layers vs deposition temperature, as measured by X-ray reflectivity (XRR). The inset is a typical XRR scan from a sample deposited at $T_s = 1000$ °C. It also shows the corresponding curve obtained from data fitting, which matches the measured data including the critical angle for total external reflection at 0.2° , the period of interference fringes as well as the intensity decay, and provides values for the layer thickness of 68.9 ± 0.1 nm and the rms surface roughness of 1.4 nm. The main plot in Fig. 2 shows that the thickness decreases with increasing growth temperature, from $d = 98.0 \pm 2.0$ nm for $T_s = 600$ °C to 96.5 ± 1.0 , 84.5 ± 1.0 , 78.8 ± 0.2 , and 68.9 ± 0.1 nm for $T_s = 700, 800, 900$, and 1000 °C, respectively. This monotonic decrease corresponds to a 30% reduction in the volume of the MoN_x as T_s is increased from 600 to 1000 °C, while keeping all other deposition parameters including deposition time, magnetron power, and processing gas pressure constant. As discussed in more detail below, the thickness reduction with increasing temperature is due to a decreasing N-content and a decreasing Mo vacancy concentration, while the Mo content per area remains constant. The error bars in the plot in Fig. 2 are obtained from the XRR fitting procedure and increase with decreasing T_s , which is due to a decreasing fringe intensity associated with the larger layer thickness and larger surface roughness for lower T_s . In particular, the rms surface roughness determined from XRR curve fitting decreases with increasing T_s from 2.8 to 2.5, 2.4, 2.0, and 1.4 nm for $T_s = 600-1000$ °C, which is attributed to reduced kinetic roughening at

elevated T_s , as previously reported for epitaxial nitrides like TiN(001) [61,62] and CrN(001) [63,64] .

Figure 3 shows the results obtained from Rutherford backscattering spectroscopy (RBS) analyses for MoN_x/MgO(001) layers deposited at $T_s = 600$ -1000 °C. The plot in Fig. 3(a) is the nitrogen-to-molybdenum ratio x , obtained from data fitting of the measured spectra, as illustrated in the inset for a layer deposited at 600 °C. The data points indicate the measured backscattered intensity while the solid line is the result from curve fitting for a simple simulated stack of a MoN_x layer on a semi-infinite MgO substrate, with the only fitting parameters being the area density Θ of Mo atoms and the compositional parameter x . Due to the relatively low intensity of backscattered He from the N-atoms, the N-peak intensity has been determined separate from the overall fitting procedure, yielding a reduced uncertainty in the N-content of $\pm 3\%$, which is also indicated by the error bars in the main plot of Fig. 3(a). The plot shows a relatively large nitrogen-to-molybdenum ratio $x = 1.25 \pm 0.03$ for $T_s = 600$ °C. As the deposition temperature increases, x decreases to 1.15 ± 0.03 for $T_s = 700$ °C, 0.95 ± 0.03 for $T_s = 800$ °C, 0.75 ± 0.02 for $T_s = 900$ °C, and $x = 0.69 \pm 0.02$ for $T_s = 1000$ °C. Thus, the MoN_x layers exhibit a range of compositions from overstoichiometric for $T_s = 600$ -700 °C, to nearly stoichiometric for $T_s = 800$ °C to understoichiometric for $T_s = 900$ -1000 °C. A similar decrease in the N-content with increasing growth temperature has previously been reported for various epitaxial transition metal nitrides including NbN_x above 900 °C [10], CrN_x above 730 °C [7], HfN_x above 650 °C [14], WN_x above 800 °C [20], and TaN_x above 400 °C [65], and has been attributed to nitrogen vacancies that form due to a higher rate of nitrogen recombination and desorption at higher temperature, and the increasing importance of the entropy contribution to the free energy of the

N₂ gas [10,66]. However, as discussed below, the deviation from stoichiometry in our MoN_x layers is not only due to N-vacancies but also Mo-vacancies.

Figure 3(b) is a plot of the area density Θ of Mo atoms in the MoN_x layers, as determined from the RBS spectra. It is nearly independent of T_s , with values ranging from 3.40 ± 0.13 - $3.58 \pm 0.12 \times 10^{17}$ atoms/cm². That is, within the experimental uncertainty, the amount of Mo deposited during the 6 min layer depositions is temperature-independent. This suggests, however, an increasing layer density since thickness d decreases with increasing T_s , as presented in Fig. 2. Correspondingly, Fig. 3(b) also shows a plot of the layer density ρ , as determined from the atomic mass of Mo and N and the measured values for Θ , d , and x . The density varies only slightly from $\rho = 6.9 \pm 0.3$ g/cm³ for $T_s = 600$ °C to 6.8 ± 0.3 g/cm³ at $T_s = 700$ °C, but increases to 7.5 ± 0.4 , 7.8 ± 0.4 , and 8.7 ± 0.5 g/cm³ for $T_s = 800$, 900 , and 1000 °C, respectively. That is, consistent with the approximately constant Mo content and the decreasing thickness, the density of MoN_x layers increases by 26% as T_s is increased from 600 to 1000 °C.

Figure 4 is a plot of the Mo and N site occupancies X_{Mo} and X_{N} vs deposition temperature $T_s = 600$ - 1000 °C for MoN_x layers. The values are obtained by dividing the measured number density of Mo and N atoms by the anion and cation lattice site density corresponding to a rock-salt structure, where the atomic number density is determined by dividing the area density measured by RBS by the thickness measured by XRR, and the rock-salt structure has a lattice constant measured by XRD. That is, the plot in Fig. 4 is a direct result from data presented in Figs. 1-3. The plotted nitrogen site occupancy is 0.88 ± 0.04 for $T_s = 600$ °C. However, as the growth temperature increases, X_{N} decreases to 0.80 ± 0.05 for $T_s = 700$ °C and to 0.74 ± 0.05 for $T_s = 800$ °C, and then to $X_{\text{N}} = 0.60 \pm 0.04$ and 0.61 ± 0.05 for $T_s = 900$ and 1000 °C. That is, at low T_s , the nitrogen site occupancy is relatively high, corresponding to a low N vacancy concentration of

12% for the layer deposited at 600 °C. Subsequently, X_N drops within the 600-900 °C temperature range to an approximately constant value for $T_s \geq 900$ °C. This suggests that temperature activated nitrogen loss during reactive sputter deposition of MoN_x is only partial for $T_s \leq 900$ °C, while a considerable nitrogen fraction corresponding to a site occupancy of 0.60 ± 0.04 - 0.61 ± 0.05 is retained up to at least 1000 °C. This is in contrast to the reported complete nitrogen loss and the transition to metallic layers for MoN_x above 800 °C [42] and WN_x above 820 °C [67]. The disagreement with Ref. [42] may be related to different temperature calibrations of the deposition systems. Nevertheless, we expect X_N to further decrease at some temperature > 1000 °C.

In contrast, the molybdenum site occupancy plotted in Fig. 4 increases with increasing temperature, from $X_{\text{Mo}} = 0.70 \pm 0.04$ for $T_s = 600$ -700 °C to 0.78 ± 0.05 , 0.80 ± 0.05 , and 0.89 ± 0.06 for $T_s = 800$, 900 and 1000 °C. This corresponds to a Mo vacancy concentration that decreases by nearly a factor of three, from 30 to 11%, which may be attributed to temperature activated Mo mobility or may be related to the lower nitrogen content which favors a higher Mo occupancy. This is consistent with the density functional calculation results presented below, which suggest an anti-correlation between Mo and N site occupancies.

Fig. 5 summarizes the results from first-principles calculations which are done to explore thermodynamic (total energy) driving forces which explain the experimentally measured formation of both cation and anion vacancies. The plot in Fig. 5(a) shows the calculated formation energy per atom E_f as a function of the N-to-Mo ratio x in MoN_x . Each data point corresponds to the energy of one of the over 200 calculated configurations which are obtained by removing some Mo and/or N atoms within a super cell of cubic NaCl structure MoN, as described in more detail in Section 3. That is, all simulated configurations exhibit a cubic

structure, which was chosen in this study in order to be directly comparable with the experimental results presented above. Each configuration is primarily characterized by the cation and anion site occupancy X_{Mo} and X_{N} , which determine the composition $x = X_{\text{N}}/X_{\text{Mo}}$. To illustrate this, some of the data points are highlighted with hollow colored symbols that are also connected with lines, where each set of connected points corresponds to configurations with the same supercell size and same X_{Mo} but varying X_{N} . For example, the curve labeled $X_{\text{Mo}} = 0.94$ is obtained using a 32-atom supercell size, where 15 of the 16 cation sites are occupied ($X_{\text{Mo}} = 15/16 = 0.9375$) while X_{N} varies from 0.5 to 1, corresponding to 8-16 anion sites being occupied, yielding compositions from $x = 8/15 = 0.53$ to $x = 16/15 = 1.07$. The calculated formation energy of this curve decreases from $E_f = -0.226$ eV at $x = 0.53$ to a minimum of -0.372 eV at $x = 0.67$ and increases again to -0.128 eV at $x = 1.07$. All these energies are negative, indicating that these configurations are stable against complete phase separation into metallic Mo and molecular N_2 . However, within this constant X_{Mo} curve, the energy is lowered by nitrogen removal or uptake to achieve $X_{\text{N}} = 0.63$ (corresponding to $x = 0.67$) where E_f is at a minimum. We note that the position of this minimum moves to smaller x values if accounting for entropic terms (particularly of the N_2 gas) at finite temperatures, and moves to larger x values in the presence of energetic particles or atomic nitrogen, as common during reactive sputter deposition. The other highlighted data point curves in Fig. 5(a) are for other cation site occupancies and super cell sizes, more specifically, 11 Mo atoms in a 24-site cell, 14 and 13 Mo atoms in a 32-site cell, 6 Mo atoms in a 16-site cell, 11 Mo atoms in a 30-site cell, 5 Mo atoms in a 14-site cell, and 8 Mo atoms in a 24-site cell. Each of these curves exhibits a minimum which indicates the energetically most favorable nitrogen site occupancy for the given X_{Mo} . The position of the minimum increases from $x = 0.67$ for $X_{\text{Mo}} = 0.94$ to $x = 0.73, 0.79, 0.92, 1.0, 1.36$, and 1.40 for $X_{\text{Mo}} = 0.92, 0.88, 0.81,$

0.75, 0.73, and 0.71, indicating that a decreasing Mo site occupancy results in an increasing N content. Stated differently, an increasing N-to-Mo ratio x results in a decreasing Mo site occupancy. In order to quantify this trend, we consider the configuration with the lowest energy [plotted in Fig. 5(a)] for a given x as most stable, and plot the corresponding X_{Mo} and X_{N} vs x in Fig. 5(b).

Figure 5(b) is a plot of the calculated Mo and N site occupancies of cubic MoN_x as a function x . At $x = 0.5$, the Mo and N site occupancies are $X_{\text{Mo}} = 1$ and $X_{\text{N}} = 0.5$, as expected for a $\text{MoN}_{0.5}$ compound. X_{N} increases approximately linearly with x to reach a plateau of $X_{\text{N}} \approx 0.75$ at $x = 0.87$ -1.00, followed by a continued increase to reach $X_{\text{N}} = 1.00$ at $x = 1.36$. In contrast, the Mo site occupancy decreases from $X_{\text{Mo}} = 1.00$ for $x \leq 0.54$ to a plateau of $X_{\text{Mo}} = 0.75$ at $x = 1.00$ -1.22, followed by a gradual decrease to 0.73, 0.71, and 0.67 for $x = 1.36$, 1.4, and 1.5. The corresponding experimental values are also plotted as open symbols in Fig. 5(b). These measured site occupancies are the same as those plotted in Fig. 4, however, they are plotted here as a function of the measured compositional parameter x . There is relatively good agreement between the first-principles predictions and the measurements, with a tendency for slightly lower measured X_{Mo} and X_{N} values at all compositions. This deviation can be attributed to the experimental uncertainty but could also indicate a small systematic error in the compositional or thickness measurements.

The good agreement between experiment and simulation confirms that cubic MoN_x simultaneously contains both, cation and anion vacancies. In addition, it clearly shows the anti-correlation between cation and anion site occupancies: As X_{N} increases, X_{Mo} decreases, leaving the total cation+anion site occupancy $(X_{\text{Mo}}+X_{\text{N}})/2$ nearly constant between 0.75 and 0.85. For stoichiometric MoN ($x = 1$), the most stable cubic phase exhibits the NbO structure, which can

be described as a NaCl structure with $X_{\text{Mo}} = X_{\text{N}} = 0.75$ [30]. The layer deposited at $T_s = 800$ °C nearly perfectly matches these expected site occupancies of 0.75, with the measured $X_{\text{N}} = 0.74 \pm 0.05$ and $X_{\text{Mo}} = 0.78 \pm 0.05$. In fact, the plot in Fig. 5(b) suggests that an occupancy of 0.75 is preferred for both cation and anion sites, based on the plateaus of X_{Mo} and X_{N} at $x = 0.87$ -1.00 and at $x = 1.00$ -1.22, respectively. That is, a reduction in the N-to-Mo ratio for moderately understoichiometric compositions $0.87 < x < 1.00$ is accounted for by an increase in X_{Mo} while X_{N} remains constant at 0.75. Conversely, increasing x above 1.0 results in an increase in X_{N} but a constant $X_{\text{Mo}} = 0.75$ for $1 < x < 1.22$. This means that deviations from stoichiometric MoN in the NbO structure (exhibiting 25% vacancies) is achieved by filling cation or anion vacancies with Mo or N, respectively, yielding under- or over-stoichiometric MoN_x , respectively, similar to what has been proposed for deviations from stoichiometry in WN_x [20]. However, as shown in Fig. 5(b), further deviations from stoichiometry including $x < 0.87$ and $x > 1.22$, cause both X_{Mo} and X_{N} to diverge from their “favorite” 0.75. We note, though, that while X_{N} decreases considerably below 0.75 and ultimately reaches 0.5 at $x = 0.5$, the decrease in X_{Mo} with increasing $x > 1$ is very moderate, suggesting that a NaCl-structure MoN with more than 25% cation vacancies becomes increasingly unstable, as also evident from the steeply increasing E_f for $x > 1.4$ in Fig. 5(a). Nevertheless, the composition that forms during MoN_x layer growth is not purely defined by the E_f vs x plotted in Fig. 5(a). This is because, as discussed above, the nitrogen chemical potential is a function of the temperature, N_2 partial pressure, as well as the partial pressure and flux of atomic nitrogen and energetic particles including N_2^+ -ions which are common during reactive sputter deposition. In addition, kinetic barriers for adatom diffusion, for N_2 dissociation, recombination, and desorption as well as for cation and anion vacancy diffusion

are expected to play a critical role in the development of the atomic arrangement as well as the composition of a growing MoN_x thin film.

5. Conclusions

$\text{MoN}_x/\text{MgO}(001)$ layers deposited at $T_s = 600\text{-}1000\text{ }^\circ\text{C}$ exhibit a cubic rock-salt type structure, an 001 orientation, and a N-to-Mo ratio that decreases with increasing T_s from $x = 1.25\text{-}0.69$. A combination of composition, thickness, lattice-constant, and atomic area-density measurements indicate that the layers have a rock-salt structure that simultaneously contains both anion and cation vacancies, in good agreement with first-principles calculations that indicate that cubic MoN_x with $0.54 < x < 1.3$ is most stable if containing both anion and cation vacancies. A quantitative analysis of the Mo and N site occupancies vs composition x shows good agreement between the measured values and the DFT predictions, and indicates that an occupancy of 0.75 is most preferred for both cation and anion sites, such that stoichiometric cubic MoN is most stable in the NbO structure and moderate deviations from stoichiometry are realized by filling cation or anion vacancies which increases X_{Mo} or X_{N} , respectively.

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Figure Captions

Figure 1: The out-of-plane lattice constant $a_{\perp}$ vs growth temperature $T_s = 600\text{-}1000$ °C, as determined from XRD θ - 2θ scans from $\text{MoN}_x/\text{MgO}(001)$ layers. The inset is a section of a typical XRD pattern, showing the MoN_x layer peak using a 30-fold magnified (red) curve, from a layer grown at $T_s = 1000$ °C.

Figure 2: The layer thickness d vs growth temperature T_s of epitaxial $\text{MoN}_x/\text{MgO}(001)$ layers, obtained from XRR analyses. The inset shows a typical XRR spectrum and corresponding curve from data fitting, from a 69-nm-thick $\text{MoN}_x(001)$ layer deposited at $T_s = 1000$ °C.

Figure 3: (a) The N-to-Mo ratio x and (b) the area density Θ and volume density ρ , of $\text{MoN}_x/\text{MgO}(001)$ layers vs deposition temperature T_s , measured by RBS. The inset shows a typical RBS spectrum including the simulated fitting curve for the layer deposited at $T_s = 600$ °C.

Figure 4: Mo and N site occupancies X_{Mo} and X_{N} vs deposition temperature T_s , for $\text{MoN}_x(001)$ layers where a complete occupancy $X_{\text{Mo}} = X_{\text{N}} = 1$ corresponds to MoN in the rock-salt structure.

Figure 5: First principles predictions of (a) the formation energy per atom E_f and (b) the Mo and N site occupancies X_{Mo} and X_{N} vs concentration x in MoN_x . The lines and open symbols in (a) indicate energies calculated for specific Mo site occupancies, as labeled. The open symbols in (b) are the experimental data points.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5