The N-to-Mo ratio $x$ in epitaxial cubic molybdenum nitride $\gamma$-MoN$_x$(001) layers was varied from $x = 0.69$-1.25 by adjusting the substrate temperature $T_s = 1000$-$600$ °C during reactive magnetron sputter deposition. X-ray diffraction, reflection, and reciprocal space mapping measurements in combination with Rutherford backscattering spectroscopy indicate that the layers exhibit negligible strain and that increasing $x = 0.69$-1.25 leads to an increasing lattice constant $a = 4.16$-$4.26$ Å and a decreasing density $\rho = 8.7$-$6.8$ g/cm$^3$ which is primarily attributed to a decrease in the cation site occupation from 0.89 to 0.70. Time resolved pump-probe reflectivity measurements of the sound velocity parallel to the [001] growth direction indicate that increasing the nitrogen concentration leads to a velocity reduction, corresponding to a decrease in $C_{11}$ from 502±31 to 355±30 GPa for $x = 0.69$-1.25. Similarly, the transverse surface acoustic wave velocity measured by surface Brillouin scattering spectroscopy decreases from 4.00-3.52 km/s, providing values for $C_{44}$ from 100±7 to 73±3 GPa. The softening with increasing N concentration is primarily attributed to the decreasing Mo site occupancy, which causes a reduction in the valence electron concentration leading to a weakening of N-Mo bonds associated with hybridized N 2$p$ - Mo 4$d$ $e_g$ orbitals.

**Keywords:** molybdenum nitride; stiffness; elastic constant; Brillouin scattering; $C_{11}$; $C_{44}$;

1. Introduction

Transition metal nitrides are widely used as wear-resistant and self-lubricious hard and decorative coatings and as diffusion barriers and contacts in microelectronics [1-7]. The most widely studied transition metal nitride is TiN, which crystallizes in the cubic rock-salt structure and exhibits a high hardness and temperature stability [8, 9]. Similarly, the neighbors of Ti in the periodic table also form stoichiometric nitrides with a cubic structure, and their intrinsic physical properties including elastic constants and high hardness values have been determined from measurements on epitaxial layers, including ZrN(001) [10], ScN(001) [11], VN(001) [12], NbN(001) [13], TaN(001) [14], HfN(001) [15] and CrN(001) [16]. Cubic MoN promises interesting mechanical properties because it has three electrons per formula unit that occupy metal $d$ orbitals. This is expected to increase ductility in comparison to the above mentioned
nitrides and may therefore result in a high toughness [17-21]. However, the mechanical properties and particularly the elastic tensor of cubic MoN are not well established yet.

MoN crystallizes in various phases including face-centered cubic $\gamma$-Mo$_2$N$_x$, body-centered tetragonal $\beta$-Mo$_2$N$_x$, and hexagonal $\delta$-MoN [22-29]. All these MoN$_x$ phases have been synthesized with varying compositions $x = 0$-$1.4$ in thin film form using reactive DC sputtering [22-24, 30-38], RF sputtering [39-41] ion beam assisted deposition [42, 43], cathodic arc evaporation [26, 44-46], pulsed laser deposition (PLD) [25, 47, 48], molecular beam epitaxy [49], chemical vapor deposition [50, 51], chemical solution deposition [52], and nitridation by a microwave plasma [53]. The deviation from stoichiometry in MoN$_x$ is typically attributed to nitrogen vacancies or interstitials [54, 55], similar to what has been proposed for other transition metal nitrides [56] like TiN [9, 57], ScN [58], TaN [14], HfN [59], and CrN [60]. However, more recently, the presence of cation vacancies in transition metal nitrides has also been proposed [61, 62] and a cubic NbO phase which corresponds to a rock-salt phase with 25% of anion and cation vacancies is expected to be stable for the related WN [63-66]. We have recently reported the growth of epitaxial cubic MoN$_x$ on MgO(001) substrates and detected a considerable concentration (11-30%) of cation vacancies [67]. The epitaxial growth reported in this latter study builds the basis for this present paper which focuses on establishing the elastic properties of cubic $\gamma$-MoN$_x$ as a function of $x$.

In this paper, we report on the measurement of the elastic constants $C_{11}$ and $C_{44}$ of epitaxial MoN$_x$(001) layers. The N-to-Mo ratio was varied from $x = 0.69$ to 1.25 by changing the deposition temperature from 1000-600 °C. This also affects the relaxed lattice constant, the layer density, and the Mo and N site occupancies, as quantified by X-ray diffraction methods and Rutherford back scattering spectroscopy. The bulk sound velocity and the transverse surface acoustic wave velocity are measured by time resolved pump-probe reflectivity measurements and Brillouin scattering spectroscopy, respectively, providing values for $C_{11}$ and $C_{44}$ as a function of $x = 0.69$-1.25. The results suggest a softening with increasing nitrogen concentration which is primarily attributed to a decreasing Mo site occupation.

2. Experimental 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 [68-71]. The substrates are one-side polished 10×10×0.5 mm$^3$ wafers that were cleaned in successive rinses of trichloroethylene, acetone, isopropanol, and deionized water, blown dry with dry N$_2$, 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 $T_s = 600$-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 N$_2$ and using a constant dc power of 300 W which was applied to the magnetron for a duration of 6 min, resulting in 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$_\alpha$ source. $\omega$-2$\theta$ scans were collected over a 2$\theta$ range from 5° - 80° using the Bragg-Brentano
geometry with a 1° divergent incident beam with $\lambda = 1.5418$ Å and a PixCEL solid-state line detector. The $2\theta$-values were calibrated using the substrate peak position, that is, $2\theta$ was set to the literature value of $42.909^\circ$ at the measured positions of the MgO 002 reflection measured using Cu K$_{\alpha 1}$ x-rays. Reciprocal space maps were collected around the 113 MoNx peaks using a hybrid mirror with a divergence of 0.0068° on the source side and parallel data collection with a PixCEL line detector, minimizing the exiting angle to reduce the beam width, as described in Ref. [72]. X-ray reflectivity (XRR) measurements were collected using a parabolic x-ray mirror with a divergence of 0.055° and a scintillator point detector. Rutherford backscattering spectroscopy (RBS) measurements were collected using a 2.0 MeV $^4$He$^+$ beam incident at an angle of 6° to the surface normal with the detector set at a scattering angle of 166°.

Time resolved reflectivity measurements were performed to determine the longitudinal acoustic velocity along the 001 direction of the MoNx(001) layers. An amplified Ti:sapphire laser was used as a light source, with a wavelength of 800 nm, a pulse width of 100 fs and a repetition rate of 1 kHz. The pump pulse was focused on the MoNx sample surface with a relatively large 100-μm-diameter spot size. Acoustic waves were excited through the absorption of the pump pulse and the following strain generation. A type-I beta barium borate crystal was used to create a probe pulse at the second harmonic frequency, that is, with a wavelength of 400 nm. The reflectivity change for the probe pulse induced by the generated acoustic wave was measured as a function of pump-probe delay time. The optical pump power was 3 mW, and the optical probe power was 5 μW.

Brillouin scattering (BS) spectra were obtained using a Verdi V2 DPSS green laser ($\lambda = 532.18$ nm) providing a 400 mW beam that was focused with an achromatic doublet lens (1 inch diameter, >90% central clear aperture) with a focal length of 76.2 mm and numerical aperture of 0.15 onto the sample surface from an average incident angle $\theta = 60\pm 1^\circ$ relative to the surface normal, while the scattered light was collected through the same optics using a six-pass high contrast Fabry–Perot interferometer (JSR Scientific Instruments) as described in reference [73]. The surface Rayleigh wave velocity $V_R$ was determined from the measured frequency shift $\Delta f$ using $V_R = \lambda \Delta f / (2 \sin \theta)$ [74]. The local strain associated with a surface wave is primarily a shear strain perpendicular to the direction of wave propagation. Therefore, the measured surface wave velocity is related to the transverse bulk wave velocity $V_t$ through $V_R = \beta V_t$ [54], where the factor $\beta$ is a value close to but smaller than unity, and is a function of the surface orientation and the wave propagation direction and is affected by the elastic anisotropy and the ratio of the effective shear modulus vs bulk modulus. For the analysis in this report we assume a constant $\beta = 0.94$, which is within the reported typical range of 0.90-0.97 [75] and corresponds to the value that has been reported for the analysis of sputter deposited Zr$_{1-x}$Ta$_x$N layers [75]. We note that an error in the assumed $\beta$ of, for example, 0.03 would introduce an error of 6% in our reported values for $G$.

From the transverse bulk wave velocity and the mass density $\rho$ we determine an effective shear modulus $G = \rho V_t^2$ which refers to the shear perpendicular to the surface and perpendicular to the wave propagation [76]. The sample orientation for the BS in these experiments has been set such that the in-plane wave propagation direction is parallel to the substrate edge, corresponding to the MoN [100] direction for these MoN(001)/MgO(001) layers. Thus, the $G_{001}$ obtained from the measurement on MoN/MgO(001) corresponds to shear of the (100) plane along [001], and therefore $G_{001} = C_{44}$. In addition, we note that the layers deposited in this study have thicknesses between 69-98 nm, which is smaller than the estimated 300 nm wavelength of the surface acoustic wave [74, 75]. As shown in Refs. [77, 78], at low values of $kh$, $v_{SAW}$ can be significantly overestimated. For our calculated range of $kh = 1.4-2.0$, for which $k$ was calculated using the
equation in Ref. [78], we measure \( v_t = 3.7 - 4.3 \text{ km/s} \) [79]. Assuming \( v_{t:MgO} = 6.5 \text{ km/s} \), we note that the ratio \( v_t:MoN/v_t:MgO = 0.57 - 0.66 \). For TiC/diamond as seen in Ref. [77], \( v_t:TiC/v_t:diamond = 0.5 \), while for the TiC/SiC system, \( v_t:TiC/v_t:SiC = 0.9 \). Since the TiC/diamond system shows a much greater error in \( v_{SAW} \) estimation at low \( k_h \), we use this system to conservatively correct our \( C_{44} \) values, assuming the same trends with \( k_h \) as in the TiC/diamond system. This leads to a correction of our reported \( C_{44} \) values that increases from -21 GPa for \( d = 98 \text{ nm} \) to -56 GPa for \( d = 69 \text{ nm} \).

3. Results and Discussion

The composition of MoN\(_x\) layers is strongly dependent on the deposition temperature \( T_s \), as we have previously reported in detail in Ref. [67]. Here, we use a range of \( T_s = 600 - 1000 \text{ °C} \) to access various N-to-Mo ratios \( x = 0.69 - 1.25 \). More specifically, we present in this paper results from five MoN\(_x\) samples deposited at \( T_s = 600, 700, 800, 900, \) and 1000 °C. Rutherford back scattering spectroscopy indicates that their N concentration decreases with increasing \( T_s \), yielding \( x = 1.25 \pm 0.03, 1.15 \pm 0.03, 0.95 \pm 0.03, 0.75 \pm 0.02 \) and \( 0.69 \pm 0.02 \) for the five deposition temperatures. The 3% uncertainty in the composition is associated with the low back-scattering cross-section of light elements, and is achieved with relatively long data acquisition times and careful RBS spectra calibration. We attribute the decrease in the N-content with increasing growth temperature to the increasing importance of the entropy contribution to the free energy of the N\(_2\) gas during deposition [13, 80]. A similar decrease in \( x \) with increasing \( T_s \) has previously been reported for the epitaxial growth of various transition metal nitrides including NbN\(_x\) [13], CrN\(_x\) [16], HfN\(_x\) [59], WN\(_x\) [63], VN\(_x\) [81], and TaN\(_x\) [82].

Figure 1 is a plot of the measured lattice constant of the MoN\(_x\) layers as a function of composition \( x \), as determined from x-ray diffraction \( \theta-2\theta \) scans. The inset at the top left shows a small section of a typical pattern, in this case from the layer with \( x = 1.25 \). It exhibits a MoN 002 peak at \( 2\theta = 42.43^\circ \), which is to the left of a 100-times more intense substrate reflection that forms a double peak feature at \( 2\theta = 42.909^\circ \) and \( 43.021^\circ \), due to the Cu K\(_{\alpha 1}\) and K\(_{\alpha 2}\) lines, respectively, and is shown with the dotted line which represents the same data multiplied by a factor of 0.01. The minor feature at \( 42.1^\circ \) as well as the shoulder at \( 42.8^\circ \) are instrumental artifacts associated with the MgO 002 reflection caused by impurities in the Cu anode of the x-ray tube that lead to impurity lines with wavelengths of 1.513 and 1.537 Å. Both features are also detected for substrate scans without a MoN layer. The MoN 002 and MgO 002 reflections are the only detectable peaks in the entire measured \( 2\theta \) range from 5-80°. In fact, for all samples, the only detectable peaks are within a relatively narrow \( 2\theta \) range from 42.4-43.5°, as shown in the plot of the five scans provided as supplementary material. The absence of any other peaks from the MoN\(_x\) layers suggests a 002 texture and, in combination with reciprocal lattice map measurements, that the layers are epitaxial MoN\(_x\)(001).

A typical reciprocal lattice map from the MoN\(_x\) layer with \( x = 0.69 \) is shown as inset at the right bottom of Fig. 1. The plot shows iso-intensity contours in \( k\)-space corresponding to a logarithmic intensity scale where successive colors represent an intensity change by a factor of 2. Here, \( k_\perp = 2\sin \theta \cos (\omega-\theta)/\lambda \) and \( k_\parallel = 2\sin \theta \sin (\omega-\theta)/\lambda \) [83] correspond to directions perpendicular and parallel to the substrate surface [84]. The map shows a MgO 113 peak and a considerably weaker and broader MoN 113 peak that is displaced from the substrate peak approximately along the \( \omega-2\theta \) scanning direction, indicating negligible strain within the deposited layer. In fact, using the relative peak position in the reciprocal map, we determine the in-plane and out-of-plane lattice constants for this MoN\(_{0.69}\) layer of \( a_\perp = 4.170 \pm 0.009 \text{ Å} \) and \( a_\parallel = 4.179 \pm 0.011 \text{ Å} \), and a
relaxed lattice constant $a_0 = (a_\perp - a_\perp \nu + 2 a_\perp |\nu|)/(1 + \nu) = 4.173\pm0.010$ Å, assuming a Poisson’s ratio of $\nu = 0.25$ as typical for many transition metal nitrides [15, 73, 85]. These values suggest a negligible in-plane strain $\epsilon_\parallel = (a_\parallel - a_\parallel \nu)/a_\parallel = 0.1\pm0.3\%$. That is, within the experimental uncertainty of $0.3\%$, the MoN$_x$ layer is completely relaxed. Similar maps are measured for all layers and the MoN 113 peak is detected for all but the sample with the lowest growth temperature ($x = 1.25$), which is attributed to a reduced MoN 113 peak intensity associated with a lower crystalline quality. In summary, these maps demonstrate that the MoN layers have a nearly identical in-plane and out-of-plane lattice constant, indicating that they have a cubic $\gamma$-phase, rather than the tetragonal $\beta$-phase that is discussed in the introduction. In addition, the maps indicate a negligible strain for all layers and confirm the epitaxial cube-on-cube relationship between the MgO(001) substrate and the MoN$_x$(001) layers.

The main part of Fig. 1 is a plot of the MoN$_x$ lattice constant $a$ vs $x$. It is directly determined from the MoN 002 peak positions in the XRD $\theta$-2$\theta$ scans, using the fact that the layers exhibit a relaxed cubic structure as determined from the reciprocal maps. The lattice constant increases from 4.161$\pm$0.006 Å for $x = 0.69$ to $a = 4.165\pm0.023$ Å for $x = 0.75$, $a = 4.220\pm0.009$ Å for $x = 0.95$, $a = 4.230\pm0.007$ Å for $x = 1.15$, and $a = 4.258\pm0.005$ Å for $x = 1.25$. We note here that the uncertainty in the lattice constant is largest for the intermediate compositions. This is because the MoN 002 peak most strongly overlaps with the MgO 002 substrate reflection for $x = 0.75$-1.0, while it is to the left and the right of the substrate peak for large and small $x$, respectively. The increasing lattice constant is primarily attributed to a decreasing density and an increasing cation site occupancy, as previously reported [67] and also discussed in the following. The measured lattice constants (4.161-4.258 Å) for our epitaxial layers is within the range of previously reported values for cubic polycrystalline MoN$_x$, which is $4.1$-4.3 Å for $x = 0.16$-1.6 [24, 36-38, 40, 41, 52, 86].

Figure 2(a) is a plot of the density $\rho$ of MoN$_x$/MgO(001) layers vs composition $x$. It is obtained from a combination of RBS and XRR data. More specifically, the total number of Mo and N atoms per thin film area is determined by RBS, multiplied by their respective atomic masses, added up and divided by the film thickness that is measured by XRR. This procedure is done recursively because the XRR fitting requires the density as an input parameter, as described in more detail in Ref. [67]. The plotted density decreases from 8.7$\pm$0.5 g/cm$^3$ for $x = 0.69$ to 7.8$\pm$0.4 and 7.5$\pm$0.4 g/cm$^3$ for $x = 0.75$ and 0.95, and then further to $\rho = 6.8\pm0.3$ and 6.9$\pm$0.3 g/cm$^3$ for $x = 1.15$ and 1.25. That is, the MoN$_x$(001) density decreases by 21% as the N-to-Mo ratio is increased from 0.69 to 1.25. We note here that calculating the density of perfect stoichiometric NaCl-structure MoN with a lattice constant of 4.22 Å yields 9.7 g/cm$^3$, which is 10-40% larger than all of the measured values. This indicates a considerable concentration of vacancies in the cubic MoN. In order to quantify this effect, we determine the Mo site occupancy by dividing the measured area density of Mo atoms by the cation site density which is calculated from the measured lattice constant and thickness. Correspondingly, we determine the N site occupancy with the same procedure. Fig. 2(b) shows the results of this analysis. The plotted Mo site occupancy decreases with increasing $x$, from 0.89$\pm$0.06 for $x = 0.69$ to 0.70$\pm$0.04 for $x = 1.25$. Conversely, the N site occupancy increases from 0.61$\pm$0.05 to 0.88$\pm$0.04 for $x = 0.69$-1.25. That is, the layers simultaneously contain both cation and anion vacancies, where the change in relative concentrations of cation and anion vacancies as a function of $x$ account for the changing composition. We note that the total site occupancy remains nearly unaffected by $x$. It is 0.75$\pm$0.04, which corresponds exactly to the expected site occupancy of the NbO structure, which has been predicted to be the most stable cubic stoichiometric structure for MoN [67, 87].
Figure 3(a) is the time resolved reflectivity from the MoN₁.25 layer with \( x = 1.25 \). The plot shows the change in reflectivity \( \Delta R \) as a function of time \( t \) after the primary pump laser pulse at \( t = 0 \). \( \Delta R \) exhibits an initial reflectivity spike with a time delay of \( t = 2 \) ps, which corresponds to the time for the mechanical strain to be generated. The two oscillations near \( t = 10 \) and 18 ps correspond to Brillouin oscillations due to the interference between the probe beam that is partially reflected at the MoN₁.25 layer surface and the moving strain pulse in the MoN₁.25 layer [88]. The well-developed peaks labeled 1\(^{st}\) and 2\(^{nd}\) echo at \( t = 27.1 \) and 54.4 ps are the 1\(^{st}\) and 2\(^{nd}\) echoes of the induced strain pulse, and correspond to the time required for a longitudinal wave to travel twice and four times through the layer, respectively. The second echo occurs at almost perfectly twice the time delay (0.4\% deviation) of the first echo, suggesting a negligible time delay associated with phonon generation. Nevertheless, we use the time delay between first and second echo to determine the sound velocity, which cancels any possible time delay associated with the photothermal phonon generation mechanism that is associated with the local heating and resultant thermal stress at the surface [89, 90]. This yields for the MoN₁.25 layer with a thickness \( d = 98 \pm 2 \) nm a velocity of \( v_{001} = 7.2 \pm 0.1 \) km/s for the wave travelling perpendicular to the layer surface, which is along the [001] crystallographic direction for an epitaxial MoN₄(001) layer.

Figure 3(b) is a plot of the bulk sound velocity \( v_{001} \) vs \( x \), determined from the time delay between the 1\(^{st}\) and 2\(^{nd}\) echoes of the \( \Delta R \) vs \( t \) curves, using the layer thickness measured for each sample by XRR. The plotted \( v_{001} \) corresponds to the velocity along the 001 growth direction, that is, the direction perpendicular to the MoN₄(001) layer surfaces. It is only weakly dependent on \( x \), increasing gradually from 7.6±0.1 km/s for \( x = 0.69 \) to \( v_{001} = 7.9 \pm 0.1 \) km/s for \( x = 1.15 \), followed by a decrease to 7.2±0.1 km/s for \( x = 1.25 \). That is, all measured velocities are within 4\% of 7.7 km/s. This nearly constant \( v_{001} \), in combination with the density increase plotted in Fig. 2(a), suggests that the stiffness \( C_{11} \) along [001] is approximately proportional to the density \( \rho \), since \( v_{001}^2 = C_{11}/\rho \). Correspondingly, we use the measured \( v_{001} \) and \( \rho \) to determine \( C_{11} \) as a function of \( x \), as plotted in Fig. 3(c). It decreases from \( C_{11} = 502 \pm 31 \) GPa for \( x = 0.69 \) to a plateau with \( C_{11} = 449 \pm 29, 461 \pm 34, \) and \( 426 \pm 28 \) GPa for \( x = 0.75, 0.95, \) and 1.15, followed by a second drop to \( 355 \pm 30 \) GPa for \( x = 1.25 \). We attribute the general trend of a decreasing \( C_{11} \) with increasing \( x \) to a combination of the increasing lattice constant (see Fig. 1) and the decreasing Mo site occupancy [Fig. 2(b)]. However, this trend is partially compensated by an increasing N site occupancy, which increases the stiffness through hybridized N2p-Mo4d-\( e_g \) orbitals along \langle001\rangle directions and may cause the nearly constant \( C_{11} \) for \( x = 0.75-1.15 \). Our \( C_{11} \) values are comparable to those reported for other transition metal nitrides including TiNₓ with \( C_{11} = 439-626 \) GPa as \( x \) varies from 0.67-1 [91] or VN with \( C_{11} = 585 \pm 30 \) GPa [12]. They are also within the reported range of values predicted using density functional theory calculations for cubic stoichiometric MoN, with \( C_{11} = 340 \) GPa for zincblende structure MoN, \( C_{11} = 544 \) GPa for rocksalt MoN, and \( C_{11} = 517-812 \) GPa for the NbO-structure MoN [87, 92].

Figure 4(a) shows a typical Brillouin spectrum collected from the MoN₁.15 layer. The spectrum shows a strong central peak near \( \Delta f = 0 \) GHz from the elastically scattered direct laser beam, and peaks at both a positive and negative \( \Delta f \) corresponding to scattering from surface acoustic waves. The peaks are at -11.55±0.02 and 11.36±0.02 GHz, corresponding to an average frequency shift of \( \Delta f = 11.45 \pm 0.04 \) GHz. In addition, the spectrum also shows lower intensity features between \( \Delta f = \pm 17-25 \) GHz which are likely associated to higher order Sezawa modes [93] that are not used in the analysis below, and a discontinuity at \( \Delta f = \pm 6.9 \) GHz which corresponds to the edge of the mechanical shutter that blocks the elastic backscattering peak to prevent damage of the photomultiplier tube in the Fabry–Perot interferometer. All MoNₓ samples exhibit
comparable spectra as the one shown in Fig. 4(a), however, with frequency shifts that decrease
with increasing $x$, corresponding to a decreasing wave velocity and a corresponding softening, as
discussed in the following.

Figure 4(b) shows the Rayleigh surface acoustic wave velocity $V_R$ vs N-to-Mo ratio $x$, as
determined from the measured average frequency shifts. The plot also includes the shear elastic
constant $C_{44}$ vs $x$, indicated using the right y-axis. The wave velocity continuously decreases
with increasing nitrogen concentration, from $V_R = 4.00 \pm 0.02$ km/s for $x = 0.69$ to $V_R = 3.52 \pm 0.01$
km/s for $x = 1.25$. Similarly, $C_{44}$ decreases from 100$\pm$7 GPa for $x = 0.69$ to $C_{44} = 86 \pm 5$, 80$\pm$5,
and 73$\pm$4 GPa for $x = 0.75, 0.95, and 1.15, and remains approximately constant to reach $C_{44} = 73 \pm 3$ GPa for $x = 1.25$. That is, $C_{44}$ decreases by 27% over the composition range $x = 0.69$-1.15,
but remains approximately constant between $x = 1.15$ and 1.25. This composition dependence
closely matches the Mo site occupancy, plotted in Fig. 2(b), which decreases by 22% from
0.89$\pm$0.06 for $x = 0.69$ to 0.69$\pm$0.04 for $x = 1.15, and remains approximately constant to reach 0.70$\pm$0.04 for $x = 1.25$. Correspondingly, we attribute the decrease in $C_{44}$ to a reduction in the density of valence electrons which, in turn,
considerably reduce the density of occupied hybridized N 2p - Mo 4$d$ eg orbitals. These orbitals
form bonds along orthogonal <100> directions, and are therefore expected to provide (if occupied by valence electrons) a restoring force to shear deformation.

Our measured $C_{44}$ values for MoN$_x$ can be compared to those of other transition metal
nitrides. The reported $C_{44}$ for TiN$_x$ increases from 92-156 GPa as $x$ increases from 0.67-1 [91],
while the reported value for VN is $C_{44} = 126 \pm 3$ GPa [12]. Thus, our $C_{44}$ range from 73-100 GPa
is comparable but slightly smaller than $C_{44}$ for these other nitrides, which may be attributed to
the higher valence electron concentration which is expected to lower the shear modulus [17] but
could also be attributed to a systematic error in our correction for the finite layer thickness,
which accounts for 21-56 GPa, as discussed in the Section 2. We note that $C_{44}$ increases with $x$ in
TiN$_x$, while we observe the opposite trend for MoN$_x$. This difference can be accounted for by the
difference of the vacancies in these two materials: TiN exhibits a negligible cation vacancy
concentration, such that the variation in $x$ is all accounted for by changes in the anion vacancy
concentration. In contrast, as discussed above, MoN$_x$ has a considerable cation vacancy
concentration and $C_{44}$ exhibits the same concentration dependency as the Mo site occupancy,
further supporting the above statement that $C_{44}$ is primarily related to the Mo site occupancy.

Conclusions

Epitaxial cubic MoN$_x$/MgO(001) layers have a lattice constant that increases from 4.16-
4.26 Å with increasing $x = 0.69$-1.25. The change in composition is accounted for by an
increasing N site occupancy from 0.61- 0.88 and a decreasing Mo site occupancy from 0.89-0.70
for $x = 0.69$-1.25, which results in a decreasing density of 8.7-6.9 g/cm$^3$. Time-resolved
reflectivity pump probe measurements and surface Brillouin scattering spectroscopy show that
these composition changes affect the stiffness constants $C_{11}$ and $C_{44}$. More specifically, $C_{11}$
decreases from 502-355 GPa and $C_{44}$ decreases from 100-73 GPa as $x$ increases from 0.69-1.25.
This softening is primarily attributed to the decreasing Mo site occupancy, as the decreasing
density of valence electrons weakens the N-Mo bond strength associated with hybridized N 2p -
Mo 4$d$ eg orbitals.

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Figures

Figure 1: Lattice constant $a$ of epitaxial MoN$_x$(001) layers as a function of N-to-Mo ratio $x$. Top left inset: portion of a typical XRD $\omega$-$2\theta$ scan from a MoN$_{1.25}$(001) layer. The dotted line is the same data with 100× reduced intensity to show the substrate reflection. Right bottom inset: typical XRD reciprocal space map near the asymmetric MgO 113 and MoN 113 reflections, from a MoN$_{0.69}$(001) layer.
Figure 2: (a) Density $\rho$ and (b) Mo and N site occupancies of epitaxial MoN$_x$/MgO(001) layers vs $x$. 
Figure 3: (a) Reflectivity change $\Delta R$ vs time delay $t$ from a time-resolved reflectivity measurement on a MoN$_{1.25}$/MgO(001) layer. (b) The longitudinal sound velocity $v$ and (c) $C_{11}$ of MoN$_x$(001) layers vs $x$. 
Figure 4: (a) Typical Brillouin spectrum collected for a MoN$_{1.15}$/MgO(001) layer. (b) Rayleigh wave velocity $V_R$ and $C_{44}$ of MoN$_x$ vs $x$. 
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