Valence electron concentration- and N vacancy-induced elasticity in cubic early transition metal nitrides

Soheil Karimi Aghda\textsuperscript{a,\textstar}, Dimitri Bogdanovski\textsuperscript{a}, Lukas Löfler\textsuperscript{a}, Heng Han Sua\textsuperscript{a}, Lena Patterer\textsuperscript{a}, Damian M. Holzapfel\textsuperscript{b}, Arnaud le Febvrier\textsuperscript{b}, Marcus Hans\textsuperscript{a}, Daniel Primetzhofer\textsuperscript{c}, Jochen M. Schneider\textsuperscript{a}

\textsuperscript{a} Materials Chemistry, RWTH Aachen University, Kopernikusstr. 10, Aachen 52074, Germany
\textsuperscript{b} Thin Film Physics Division, Department of Chemistry and Biology (IFM), Linköping University, Linköping SE-58183, Sweden
\textsuperscript{c} Department of Physics and Astronomy, Uppsala University, Lägerhyddsvägen 1, Uppsala 75126, Sweden

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\textbf{ABSTRACT}

Motivated by frequently reported deviations from stoichiometry in cubic transition metal nitride (TMN\textsubscript{x}) thin films, the effect of N-vacancy concentration on the elastic properties of cubic TiN\textsubscript{x}, ZnN\textsubscript{x}, VN\textsubscript{x}, NbN\textsubscript{x}, and MoN\textsubscript{x} (0.72 \leq x \leq 1.00) is systematically studied by density functional theory (DFT) calculations. The predictions are validated experimentally for VN\textsubscript{x} (0.77 \leq x \leq 0.97). The DFT results indicate that the elastic behavior of the TMN\textsubscript{x} depends on both the N-vacancy concentration and the valence electron concentration (VEC) of the transition metal: While TiN\textsubscript{x} and ZnN\textsubscript{x} exhibit vacancy-induced reductions in elastic modulus, VN\textsubscript{x} and NbN\textsubscript{x} show an increase. These trends can be rationalized by considering vacancy-induced changes in elastic anisotropy and bonding. While introduction of N-vacancies in TiN\textsubscript{x} results in a significant reduction of elastic modulus along all directions and a lower average bond strength of Ti–N, the vacancy-induced reduction in [001] direction of VN\textsubscript{x} is overcompensated by the higher stiffness along [011] and [111] directions, resulting in a higher average bond strength of V–N. To validate the predicted vacancy-induced changes in elasticity experimentally, close-to-single-crystal VN\textsubscript{x} (0.77 \leq x \leq 0.97) are grown on MgO(001) substrates. As the N-content is reduced, the relaxed lattice parameter $a_0$, as probed by X-ray diffraction, decreases from 4.128 Å to 4.096 Å. This reduction in lattice parameter is accompanied by an anomalous 11% increase in elastic modulus, as determined by nanoindentation. As the experimental data agree with the predictions, the elasticity enhancement in VN\textsubscript{x} upon N-vacancy formation can be understood based on the concomitant changes in elastic anisotropy and bonding.

\textbf{1. Introduction}

When it comes to material systems suitable for hard protective coatings [1,2] and diffusion barrier layers [3,4], group IV, V, and VI transition metal nitrides, or TMNs, are often the materials of choice in industrial applications, due to their excellent thermal stability [1,5], corrosion resistance [6], and mechanical properties [7,8]. Additionally, the properties of binary TMN compounds can be enhanced by modifying the occupancy of metal and non-metal sublattices via alloying constituents. For example, metastable ternary (Ti,Al)N [9] shows age hardening at elevated temperatures before decomposing into its stable constituents [10], and metastable quaternary (Ti,Al)(O,N) exhibits significant thermal stability enhancement in comparison to the (Ti,Al)N counterpart [11].

TMNs usually crystallize in a cubic structure (space group Fm$\overline{3}$m, NaCl prototype) for group IV [12–14], V [15–17], and VI [18–20] elements. Most of these binary compounds exhibit a large single-phase field over a significant composition range, hence, the accommodation of point defects can be expected. Formation and stability of point defects such as vacancies [21–24], interstitials [22,25], and Frenkel defects [21,23,26] in TMNs and (TM,Al)Ns have recently been investigated. In general, point defects have been shown to exert great influence on the stability and mechanical properties of the nitride compounds. For instance, vacancies as the lowest-energy defects [22] stabilize the mechanically unstable cubic TaN [27], MoN [27,28], and WN [29], and enhance hardness in TiN [30,31], toughness in $V_{0.5}Mo_{0.5}N$ [32], and elastic modulus in NbN [16].

\textsuperscript{*} Corresponding author.
\textit{E-mail address:} karimi@mch.rwth-aachen.de (S. Karimi Aghda).

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With respect to elasticity, vacancy-induced changes in the elastic modulus seem to follow a different trend for early TMN compounds. For TiN$_x$ (x = N/Ti) [31,33], an increase in N vacancy concentration, from TiN$_{1.00}$ to TiN$_{0.67}$, has been experimentally shown to continuously reduce the elastic modulus, from 428 to 325 GPa, respectively. The vacancy-induced reduction in elasticity of TiN$_x$ was attributed to a reduction in the bond density of the compound [31]. Similar behavior is also reported for HfN$_x$ [34], another compound from group IV TMNs. However, reports on group V NbN$_x$ indicated an anomalous increase in elastic modulus via both N and Nb vacancy incorporation, as observed both theoretically [16] and experimentally [35]. For TaN$_x$ thin films [36], a reduction in elastic modulus is measured as x is increased from stoichiometric x = 1.00 to overstoichiometric x = 1.35, which is the opposite of the behavior observed for NbN$_x$, another group V TMN [16]. Apart from the scattered literature on the vacancy-induced changes in mechanical properties of TMNs, there is no systematic study on the effect of vacancies in conjunction with the increase in valence electron concentration (VEC) on the elastic properties of group IV to V and VI TMNs.

Vivid morphological differences, which are typically not considered in the structural models used in ab initio simulations, make correlative experimental and theoretical studies challenging with respect to elastic properties. In order to deconvolute the intrinsic properties of the material systems from morphological effects such as grain boundaries, an effective approach is to carry out property measurements on epitaxial close-to-single-crystal layers, as previously done for Sn(001) [37], TiN (001) [4,38], HfN(001) [14], VN(001) [39], NbN(001) [16], and CrN (001) [18], to name a few.

Here, we systematically investigate the effect of N vacancy concentration on the elastic properties of binary cubic TiN$_x$, ZrN$_x$, VN$_x$, NbN$_x$, and MoN$_x$ (0.72 < x ≤ 1.00) by density functional theory (DFT) calculations. The predictions are validated experimentally for epitaxially grown VN$_{0.01}$ (0.77 ≤ x ≤ 0.97) thin films. The calculated bulk moduli, Poisson’s ratios, and elastic moduli of the binary compounds with varying N vacancy concentration exhibit dependency on the VEC in groups IV, V, and VI. It is demonstrated that while for TiN$_x$ an increase in N vacancy concentration results in a reduction in elastic modulus, a N vacancy-induced elasticity enhancement is observed in the VN$_x$. The results of crystal orbital Hamilton population (COHP) analyses and elastic anisotropy calculations reveal that the stiffness increase (decrease) upon vacancy introduction into VN$_x$ (TiN$_x$) is caused by direction-dependent bond-strengthening (bond-softening).

2. Computational details

Ab initio calculations were performed using density functional theory (DFT) [40,41] as implemented in the Vienna ab initio Simulation Package (VASP, version 5.4.4, University of Vienna) [42,44], employing projector-augmented waves (PAW) [45,46] with a cut-off energy of 500 eV for basis set representation. The electronic exchange-correlation energy was calculated with the well-established parametrization of the generalized gradient approximation (GGA) by Perdew, Burke, and Ernzerhof (PBE) [47]. A Γ-centered k-point mesh with dimensions of 9 × 9 × 9 constructed via the Monkhorst-Pack method [48] was used to sample the Brillouin zone, using the Methfessel-Paxton method for integration [49]. For all ab initio simulations, 2 × 2 × 2 supercells with cubic B1 symmetry containing 64 atoms were constructed for TiN, ZrN, VN, NbN, and MoN. Three (corresponding to 4.7%), six (9.4%), or nine (14.1%) vacancies on random positions of the N sublattice were then introduced, yielding a total of 20 different structures. The stiffness tensors of these systems were determined with the strain-stress method as implemented in Ref. [50] and projected onto the cubic symmetry as described in the literature [51]. From the stiffness tensor, the bulk, shear, and elastic moduli, as well as Poisson’s ratio, were calculated with Hill’s approximation [52]. Additionally, temperature-dependent equilibrium volume and elastic moduli were calculated by the Debye-Grüneisen model [53] as described elsewhere [54]. Furthermore, the directional elastic moduli were calculated with the help of Eq. (1), as derived by Nye [55].

$$\frac{1}{E_{\text{vol}}} = S_{11} - 2\left(S_{11} - S_{12} - 1\right)\left(\frac{h^2}{S_{11}} + \frac{k^2}{S_{12}} + \frac{l^2}{S_{13}}\right)$$

(1)

with $\mathbf{[R]}$ as the normalized vector along the direction [hkl] and $\mathbf{S}$ as elements from the compliance tensor ($\mathbf{S}$).

In addition to the elastic properties, the electronic structure and bonding characteristics were analyzed for two of the systems, VN$_x$ and TiN$_x$, with an ideal vacancy-free structure and the three N vacancy concentrations described above. The optimized structures used for the calculation of elastic properties were utilized as input structures. Single-point (static) DFT simulations using VASP were performed, employing a slightly reduced k-mesh of $5 \times 5 \times 5$ and the Blöchl tetrahedron method for Brillouin zone integration [56], with other key settings similar to the preceding simulation series described above. The valence electron configurations of the PAW potential files were $3p^64s^23d^4$ for V, $3s^23p^64s^23d^3$ for Ti and $2s^22p^6$ for N. The wavefunctions of the simulated systems were generated by VASP and post-processed with the LOBSTER package (version 4.0.0, Institute of Inorganic Chemistry, RWTH Aachen University) [57–60] in order to project the delocalized, plane-wave-based information onto local orbitals. This enables the calculation of a more precise, atom- and orbital-resolved density of states, as well as the (integrated) crystal orbital Hamilton population (COHP) [61] in order to estimate the bonding character and strength of individual interatomic bonds. It should be noted that, while the COHP is not a direct descriptor of the bond strength, it is strongly correlated with the latter property and is routinely used to assess it in various systems [62–65].

3. Experimental details

Vanadium nitride (VN$_x$) thin films from stoichiometric to under-stoichiometric were synthesized using reactive direct current magnetron sputtering (DCMS) in a load-locked ultra-high-vacuum chamber. The base pressure of the system was below 1 × 10$^{-5}$ Pa at respective deposition temperatures ($T_d$) of 230, 430, 600, and 700 °C. An elemental V target (~99.5% purity) with a diameter of 50 mm was powered in DC at a constant averaged-power of 100 W, which resulted in a power density of ~5 W/cm$^2$. Initial growth experiments performed in Ar/N$_2$ working gas mixture (not shown here) resulted in extremely N-deficient thin films, hence, near-stoichiometric cubic VN could not be achieved even at the lowest $T_d = 230$ °C employed here. This has also been reported by Mei et al. [39], where they systematically investigated the effect of N$_2$ partial pressure on the chemical composition of VN$_x$. In addition, high energetic Ar$^+$ irradiation-induced defects [23,66,67] could hinder the growth of high crystalline quality, epitaxial VN$_x$ thin films. Therefore, the working gas was pure N$_2$ (5.0 purity) with a deposition pressure of 2.6 Pa. Such a high discharge pressure was employed to thermalize sputtered atoms and neutralize the majority of ions [68].

MgO(001) substrates with a dimension of $10 \times 10 \times 0.5$ mm$^3$ were mounted at a defined target-to-substrate distance of 6 cm. Prior to the depositions, the unpolished backside of MgO(001) substrates were coated with TiN to optimize heat conduction and avoid localized heating effects. Moreover, in order to optimize the surface of MgO(001) substrates, wet-cleaning was conducted by using isopropanol and acetone in sonication [69], accompanied by a N$_2$ blow-drying procedure. Lastly, an annealing step was performed at 800 °C for one hour in the deposition chamber prior to the deposition of the desired thin films. The substrate holder was kept at floating potential for all depositions and the thin films were grown to a thickness of approximately 400 nm.

Time-of-flight elastic recoil detection analysis (ToF-ERDA) at the Tandem Laboratory of Uppsala University [70] was used for depth
profiling of the film composition. A primary ion beam of 36 MeV $^{127}$I$^+$ was employed and the detection telescope, including a solid-state detector, was located at 45° with respect to the primary ion beam. The incident and exit angle of the ions and detected recoils with respect to the specimen surface were both 22.5°. Depth profiles were obtained from time-energy coincidence spectra by using CONTES [71] and a TiN reference sample [72], which has been characterized by Rutherford backscattering spectrometry, was also probed. All resulting depth profiles were found homogeneous and the maximum oxygen impurity content was 1 at.%. The total maximum measurement uncertainties were 3% relative deviation of the deduced values for V and N.

For the X-ray photoelectron spectroscopy (XPS) measurements, samples were inserted in an AXIS Supra instrument (Kratos Analytical Ltd.) equipped with a monochromatic Al-Kα X-ray source. The base pressure of the system during acquisition was $< 5.0 \times 10^{-6}$ Pa. High-resolution N 1s spectra were obtained using a pass energy of 10 eV and a step size of 0.04 eV (6 sweeps, dwell time 1000 ms). The measurement spot size was 700 $\times$ 300 µm$^2$. The binding energy (BE) scale of the spectrometer was calibrated using a sputter-cleaned Ag standard (Ag 3d$^{5/2}$ signal at 368.2 eV). No charging effect of the VN$\textsubscript{x}$ samples was observed.

Structural analysis of the thin films was performed with a Siemens D5000 X-ray diffraction (XRD) system (Munich, Germany) using a Cu Kα radiation source, operated at a voltage and current of 40 kV and 40 mA, respectively. The X-ray source and the detector were coupled in $\theta$-2$\theta$ scans (Bragg-Brentano geometry), scanning a $2\theta$ range from 41 to 46° to obtain the (200) diffractions from VN$\textsubscript{x}$ thin films and the MgO substrate. A step size of 0.05° and dwell time of 2 s per step were used for the measurements. $\theta$-rocking curves along (200) diffraction plane of VN$\textsubscript{x}$ were acquired with an incident parallel beam within the same diffractometer.

Reciprocal space maps (RSM) were acquired using a PANalytical Empyrean diffractometer with Cu Kα radiation for the phase structure and growth orientation analysis. Symmetric and asymmetric RSMs were recorded around MgO(002) and MgO(204), respectively using a four-axis goniometer and a primary optics consisting of a parabolic graded multilayer mirror, collimator, and a channel-cut 2-bounce Ge(220) monochromator. The in-plane coherence lengths ($\xi_\parallel$), corresponding to average mosaic domain sizes [73], are determined from the widths of (002) diffraction peaks parallel to the diffraction vector [74]:

$$\xi_\parallel = \frac{2\pi}{\Delta q_\parallel} = \frac{\lambda}{2I_\parallel \sin \theta}$$

where $I_\parallel$ is the full-width at half-maximum of the peak intensities of the VN$\textsubscript{x}$ (002) diffractions along the $\theta$ direction.

The surface topography and morphology of the thin films were characterized using scanning electron microscopy (SEM) at an acceleration voltage of 10 kV and a current of 50 pA within an FEI Helios Nanolab 660 dual-beam microscope (Hillsboro, OR, USA).

The elastic modulus $E$ was determined by nanoindentation using a Hysitron (Minneapolis, MN, USA) TI-900 Tribolindenter equipped with a Berkovich geometry diamond tip with 100 nm radius. At least 25 quasi-static indents with a maximum load of 0.8 mN were performed.
Indentation depths were less than 40 nm, which is 5% of the film thickness, to minimize the substrate effect [75]. The tip area function was determined with a fused silica reference before each measurement series and verified to remain unchanged thereafter. The reduced modulus was acquired from the unloading segment of load-displacement curves using the method of Oliver and Pharr [76]. The elastic moduli of the films were then obtained from the reduced moduli data using the concentration-dependent Poisson’s ratios calculated in this study and the isotropic approximation.

4. Results and discussion

The calculated bulk moduli, together with the Poisson’s ratios, and elastic moduli of the binary nitrides in the ground state, as a function of the N/TM ratio $x$ are depicted in Fig. 1 (a–c). The introduction of N vacancies in the cubic binary TMNx results in a reduction of the bulk modulus, independent of the TM element, see Fig. 1 (a). The decrease is 17% for group IV nitrides (TiNx and ZrNx), as $x$ changes from 1.00 to 0.72. A less significant vacancy-induced reduction in bulk modulus of 9% is calculated for the group V nitrides (VNx and NbNx). Moreover, for the group VI binary MoNx, the stoichiometric cubic structure is not mechanically stable, as already reported by Balasubramanian et al. [28]. However, it has been shown that the introduction of N vacancies results in the stabilization of the cubic understoichiometric MoNx. The influence of N vacancy concentration on the bulk modulus for MoNx is significantly lower than for the other nitrides, with a reduction of 2% from MoN0.91 to MoN0.72. These results indicate that increasing VEC in the cubic binary TMNx leads to a smaller N vacancy-induced variation in bulk modulus for the cubic binary compounds.

The calculated N vacancy-dependent Poisson’s ratios for the binary TMNx are shown in Fig. 1 (b). Here, the Poisson’s ratio values follow completely different trends with respect to the N vacancy concentration for each of the group IV, V, and VI nitrides. While for TiNx and ZrNx, the Poisson’s ratio increases with increasing N vacancy concentration, there is an opposite trend for VNx and NbNx and a nearly N vacancy-concentration-independent Poisson’s ratio is calculated for MoNx. As the elastic constant $E$ is linked to the bulk modulus $B$ and Poisson’s ratio $\nu$ via the relationship $E = 3 \times B \times (1 - 2\nu)$ within the isotropic approximation, the concomitant changes in both bulk modulus and Poisson’s ratio are consistent with the elastic modulus data in Fig. 1 (c).

For group IV nitrides, we observe a continuous reduction in $E$ with respect to N vacancy concentration. Contrary, VNx shows an anomalous increase in elastic modulus due to the presence of N vacancies, up to 10% from VN1.00 to VN0.72. For NbNx, which has the same VEC as VNx, there is also a slight, albeit much less pronounced, increase in elastic modulus as the N vacancy are introduced. This behavior is also present in the case of MoNx.

As the elastic modulus of binary TMN is known to be anisotropic [77], different directional elastic responses for TiNx and VNx, with and without vacancies, were analyzed. The results are depicted in Fig. 2 showing the elastic modulus in the three main planes, (001), (011), and (111). In both stoichiometric compounds the directional elastic modulus is the strongest along the [100] direction, see Fig. 2 (a) and (d), consistent with [77]. The introduction of N vacancies results in a significant reduction of the direction-dependent TMNx elastic modulus, see Fig. 2 (a), (b), and (c). In contrast, for VNx, the vacancy-induced reduction in elastic modulus along the [100] direction is smaller and overcompensated by concomitant changes along the [110] and [111] directions. Therefore, as vacancies are introduced in TiNx, marginal changes in directionality are accompanied by a reduced elastic modulus in all directions, while in VNx, N vacancies cause changes in the directional elastic moduli leading to an overall increase in stiffness.

To identify the cause for the different N vacancy-induced elastic modulus changes between group IV and V nitrides, total and partial densities of states (DOS) are calculated for TiNx and VNx, with the results shown in Fig. S 1 of the supplementary material. It is evident that there is a qualitative similarity regarding the general structure of the DOS between stoichiometric TiN and VN. However, in the proximity of the Fermi level ($E_F$), the VN DOS exhibits local maxima, which indicates localized states accounting for the electronic instability. Additionally,
introduction of a N vacancy in VN results in slightly fewer occupied states near \( E_F \), which indicates that N vacancies contribute to an electronic stabilization of the cubic structure of VN \([78]\). For both TiN\(_x\) and VN\(_x\), the emergence of peaks at \(-2\) eV is attributed to the vacancy-derived states, in good agreement with other reported electronic structures for the understoichiometric cubic TiN\(_x\) \([33]\) and VN\(_x\) \([78]\). Nonetheless, there is no other significant change in the DOS between the stoichiometric and understoichiometric compositions, which is why we will in the following focus on the differences in local electronic structure in the vicinity of a N vacancy and compare the DOS to that of the pristine non-vacancy-containing system. The results of total and partial differential density of states (dDOS) are illustrated in Fig. 3 (a) and (b) for TiN\(_x\) and VN\(_x\), respectively. The electronic structure of both TMN\(_x\) compounds is dominated by TM 3\(d\)-N 2\(p\) overlap, which indicates \(sp^3d^2\) hybridization. While the introduction of N vacancies in TiN\(_x\) resulted in reduced hybridization between Ti and N within the energy range \(-4\) eV to \(-9\) eV (Fig. 3 (a)), no significant changes between VN\(_{1.00}\) and VN\(_{0.81}\) can be observed in Fig. 3 (b) in this energy range. These results indicate that, unlike TiN\(_x\), the strong covalent bonding nature of VN\(_x\) remains unchanged as N vacancies are introduced. These local effects, however, are diluted in the total DOS and could not be resolved by considering the entire supercells.

To quantitatively evaluate the bond strength of the binary compounds with and without the presence of N vacancies, we will focus on the crystal orbital Hamilton population (COHP) analyses. The average bond energies for TM–N bonds in TiN\(_x\) and VN\(_x\) with respect to the N vacancy concentration are obtained from COHP calculations, where the integrated COHP (ICOHP) for these two binary nitrides is plotted in Fig. 1 (d). Interestingly, the trends of the ICOHP are completely different for TiN\(_x\) and VN\(_x\) with respect to N vacancy concentrations. While increasing N vacancy concentration in TiN\(_x\) results in a more positive ICOHP value, correlated with a weakening of the bond, a more negative ICOHP for VN\(_x\) with respect to increasing N vacancy concentration suggests that bond strengthening seems to be the primary reason behind the anomalous stiffness increase. These findings are consistent with the calculated data by Rueß \textit{et al.} \([54]\), who showed that V vacancy-induced bond strengthening is the origin of the stiffness increase in overstoichiometric VN\(_x\).

Another important aspect of the presence of N vacancies in cubic binary TMN\(_x\) is the local lattice relaxation. Therefore, we systematically analyze changes in the bonding character with respect to N vacancy concentration for both TiN\(_x\) and VN\(_x\) with the results summarized in Fig. 4. Fig. 4 (a) and (d) show the local lattice relaxations evident in the structural model, projected in the (100) plane, which are induced by the presence of a N vacancy in TiN\(_{0.81}\) and VN\(_{0.81}\), respectively. For TiN\(_{0.81}\) the distance between two Ti atoms along [100] is increased by ca. 2.6%
from 4.24 Å in pristine TiN to 4.35 Å near the vacancy site, which shows an outward displacement of the atoms. However, the local relaxation along the vacancy site of VN0.81 shows an inward displacement of V atoms from 4.13 Å to 3.86 Å by 6.5% towards the vacancy site. Fig. 4 (b), (c), (e), and (f) depict the effect of the local lattice relaxations upon bond length and bond strength (expressed via the ICOHP) distributions within TiN and VN as a function of the vacancy concentration. For both binary compounds, the introduction of a N vacancy leads to a distribution in the overall bond lengths and energies, in contrast to the stoichiometric systems. However, the vacancy-induced distribution is much larger in the case of VN0.81, as evident from the scattering from Fig. 4 (e). The bond strength histograms in Fig. 4 (c) and (f) illustrate the changes in the TM–N bond energy with respect to N vacancy concentration in TiN and VN0.81, respectively. It is evident that for TiN0.72, the average bond energy (ICOHP) becomes more positive as the N vacancy concentration is increased, going from −2.97 eV for TiN to −2.90 eV for TiN0.72. Thus, a
The presence of N vacancies has been further indicated by XPS measurements, with the N 1s spectrum shown for the VN$_{x}$ (0.86 ≤ x ≤ 0.97) thin films in Fig. 5 (b). The measured N 1s spectrum for the VN$_{0.97}$ thin film exhibits a main peak centered at 397.0 eV. Upon decreasing x from 0.97 to 0.86, the main N 1s binding energy (BE) continuously shifts towards higher values by approximately 0.5 eV, up to 397.5 eV. The appearance of an additional N 1s feature (BE 396 eV) in samples with lower x (≤ 0.86) is mainly correlated with the oxidized state [81]. The shift in BE with respect to x has also been observed for other transition metal nitrides and can be understood in terms of vacancy-induced changes in charge distributions [81–83].

XRD θ-2θ diffractograms over the 2θ range from 41 to 46°, across 002 Bragg diffraction peaks, obtained from VN$_{x}$/MgO(001) thin films with 0.86 ≤ x ≤ 0.97 together with a plain MgO(001) substrate are shown in Fig. 6 (a). The MgO(002) diffraction peak is positioned at 2θ = 43°. The (002) diffraction peak intensity of the deposited VN$_{x}$ thin films increases with higher T$_{s}$, accompanied by a N vacancy-induced monotonic shift from 43.4° at T$_{s}$ = 230° C and x = 0.97 to 44.2° at T$_{s}$ = 700° C and x = 0.77. This peak shift towards higher angles due to an increase in the lattice parameter accounts for a reduction in the mosaicity or enhancement in the crystalline quality of the grown thin films, as also reported by Mei et al. [80].

In an effort to experimentally validate the N vacancy-induced bond strengthening, VN$_{x}$ thin films were grown epitaxially on single crystal MgO(001) substrates as a function of T$_{s}$ in a pure N$_{2}$ atmosphere. The resulting thin film compositions, as obtained by ToF-ERDA, are plotted in Fig. 5 (a), showing the N/V ratio x with respect to T$_{s}$. A steep reduction in x is evident as a function of substrate temperature, where an increase from 230 to 700° C leads to a reduction in the x value from near-stoichiometric 0.97 ± 0.06 to understoichiometric 0.77 ± 0.04. The reduction in the N content of the layers at higher temperatures is evidently attributed to N$_{2}$ desorption due to the thermally-activated mechanisms on the surface of the growing film, as has been shown theoretically by Sangiovanni et al. [79]. It can be also learned from Fig. 5 (a), that near-stoichiometric VN(001) thin films can be synthesized at temperatures below 430° C under the here stated deposition conditions, as also reported by Mei et al. [80].

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structures within the (002) matrix of the VN$_{0.97}$ deposited at low $T_s$ ($230^\circ$C) can be correlated with limited adatom surface mobility [84]. On the other hand, very smooth featureless surfaces have been obtained as $T_s$ is increased to above 600$^\circ$C, see Fig. 6 (e) and (f).

The results of high-resolution XRD reciprocal space maps (HR-RSM) of the thin films grown at $T_s$ = 430, 600, and 700$^\circ$C with $x$ = 0.93, 0.86, and 0.77, respectively, acquired over symmetric 002 and asymmetric 204 reflections are shown in Fig. 7. Moreover, the in-plane coherence length ($\xi_\parallel$), in-plane strain ($\epsilon_\parallel$), and relaxed lattice parameter ($a_0$) were determined as a function of $T_s$ from the HR-RSM results and are listed in Table 1.

At $T_s$ = 430$^\circ$C, a significant broadening is observed for the in-plane direction ($q_\parallel$) along the $\theta$-2$\theta$ direction is observed, see Fig. 7 (a), which accounts for a large mosaicity in this sample. The mosaicity is significantly reduced at higher deposition temperatures, as denoted by a smaller in-plane diffraction broadening, Fig. 7 (b) and (c). In-plane coherence length $\xi_\parallel$ increases from 17 to 93 nm as $T_s$ is increased from 230 to 600$^\circ$C, respectively. The here reported $\xi_\parallel$ = 93 nm for under-stoichiometric VN$_{0.86}$ is among the largest in-plane coherence lengths obtained for the epitaxially grown binary transition-metal nitrides reported so far [13,18,34-39], which reflects the high crystalline quality of this thin film. Further increase in $T_s$ to 700$^\circ$C for the growth of VN$_{0.77}$ resulted in a reduction of $\xi_\parallel$ to 62 nm, which can be correlated to...
a higher concentration of N vacancies in this highly understoichiometric film [39].

Furthermore, from the asymmetric maps, a fully-relaxed thin film on the single crystal substrate has the 204 diffraction peaks centered on the dashed line extending from the origin along the 204 diffraction peaks of the substrate. Here, the lateral displacement of the 204 diffraction peaks of the film deposited at \( T_s = 430 \)°C to the right side of the line indicates the presence of compressive strain with an in-plane biaxial strain \( \varepsilon_{\|} \) of \(-1.46\%\) in this layer. A slightly higher \( \varepsilon_{\|} \approx -2.01\% \) has been measured for the VN\(_{0.97}\) film deposited at 230°C. However, almost fully-relaxed thin films are obtained at \( T_s = 600 \) and 700°C with \( \varepsilon_{\|} \approx -0.51 \) and \(-0.18\), respectively.

Relaxed lattice parameters \( a_0(x) \) obtained from the HR-RSMSs are summarized in Table 1. The \( a_0(x) \) decreases from 4.128 Å for VN\(_{0.97}\) to 4.096 Å for VN\(_{0.77}\), following a nearly linear trend. This negative slope with respect to \( x \) is also observed in other works for VN\(_x\) [39] and TiN\(_x\) [31]. The relaxed lattice parameters from the thin films are plotted in Fig. 8 (a) together with the lattice parameters obtained from the DFT calculations by considering N vacancies as the origin of understoichiometry in VN\(_x\). The maximum deviations between the calculated and measured values are below 1.0%, signifying good agreement. In general, the calculated lattice parameters are found to be smaller than the experimentally measured values, however, showing a similar negative trend with respect to \( x \). The good agreement between the experimental data and the predictions in turn suggests that the formation of understoichiometric VN\(_x\) is governed by N vacancies.

By considering the high crystalline quality of the synthesized thin films, and therefore neglecting the morphological differences, the chemical composition-induced changes in elastic modulus of VN\(_x\) (0.77 ≤ \( x \) ≤ 0.97) are evaluated using nanoindentation experiments and the results are depicted in Fig. 8 (b). Additionally, the calculated elastic moduli of VN\(_{0.72}\) (0.72 ≤ \( x \) ≤ 1.00) are included, together with the measured and calculated elastic modulus of the stoichiometric VN\(_{1.00}\) from literature. For the near-stoichiometric VN\(_{0.97}\) thin film, the measured elastic modulus is 400 ± 25 GPa, which is in good agreement with other reported values for bulk [86], thin film [15], and calculated VN\(_{1.00}\) [85]. As \( x \) is reduced from 0.97 to 0.77, the elastic modulus increases continuously to 444 ± 24 GPa. This anomalous 11% increase in the stiffness of VN\(_x\) due to the N vacancy concentration is consistent with the predicted elasticities, as evident in Fig. 8 (b). As shown in Figs. 1 and 4, this anomalous elastic increase can be rationalized by the N vacancy-induced elastic anisotropy and bond strengthening, as a characteristic of the group IV binary cubic VN\(_x\) compound. Based on the above presented theoretical predictions on the effect of VEC and N-vacancies on the elastic properties of group IV (TiN\(_x\)) and V (VN\(_x\)) cubic transition metal nitrides the different trends in the mechanical properties reported in literature can readily be rationalized: On one hand, experimental reports on N vacancy-induced reduction in elasticity of TiN\(_x\) by Jhi et al. [33] and Shin et al. [31] are consistent with the here presented predictions. On the other hand, also the reported elasticity of the group V NbN\(_x\) thin films exhibited an anomalous behavior with respect to N vacancy concentration [16].

5. Conclusions

By employing ab initio calculations, we have systematically investigated the effect of N vacancy concentration on the elastic properties of cubic early transition metal nitrides, TiN\(_x\), ZrN\(_x\), VN\(_x\), NbN\(_x\), and MoN\(_x\) (0.72 ≤ \( x \) ≤ 1.00). A different elastic response due to the presence of N vacancies is exhibited between the group IV, V, and VI nitrides and hence between different transition metal valence electron concentrations. In group IV TiN\(_x\) and ZrN\(_x\), N vacancies reduce the elastic modulus, while an opposite trend is observed for group V VN\(_x\) and NbN\(_x\), where an anomalous enhancement in elastic modulus is evident due to the presence of N vacancies. To understand the origin of N vacancy-induced elastic response for different transition metal valence electron concentrations in these systems, the directional elastic modulus and bond characteristics within TiN\(_x\) and VN\(_x\) are compared. In TiN\(_x\), N vacancy incorporation results in a significant reduction of elasticity along the [001], [011], and [111] directions. However, the vacancy-induced softening in elastic modulus for VN\(_x\) along [001] is overcompensated by strengthening along [011] and [111] resulting in an increased elastic modulus. In addition, individual bond strengths and their averages are obtained from crystal orbital Hamilton population (COHP) analyses. By considering the integrated COHP values, directly correlated with the bond strength, N vacancies seem to weaken the Ti–N bond overall, with ICOHP values from −2.97 eV for TiN to −2.90 eV for TiN\(_{0.72}\). In contrast, V–N bonds are strengthened, with ICOHP values from −2.62 eV for VN to −2.70 eV for VN\(_{0.72}\) due to structural relaxation in the presence of N vacancies. To validate the anomalous elasticity enhancement with respect to N vacancy concentration experimentally, close-to-single-crystal VN\(_x\) thin films (0.77 ≤ \( x \) ≤ 0.97) were grown on single crystal MgO(001) substrates. Reduction of N content in VN\(_x\)/MgO(001) from \( x = 0.97 ± 0.06 \) to 0.77 ± 0.04 leads to a decrease in the relaxed lattice parameter \( a_0(x) \) from 4.128 Å to 4.096 Å, respectively, as determined by X-ray diffraction. The understoichiometric thin films show high in-plane coherence length \( \xi \) of up to 92 nm. Nanoindentation results reveal that the reduction in lattice parameter of VN\(_x\), with increasing N vacancy concentration goes in hand with an anomalous 11% increase in elastic modulus and in very good agreement with DFT predictions. Based on the theoretical and experimental data presented here, it is evident that the elastic behavior of early transition metal nitrides is defined by the N vacancy concentration and the transition metal valence electron concentration. COHP analyses and elastic anisotropy calculations reveal that this behavior can be rationalized by considering the direction-dependent bond-strengthening (bond-softening) upon vacancy introduction into VN\(_x\) (TiN\(_x\)). This study offers a strategy to design nitride thin films with defined elastic properties by controlling the valence electron- and vacancy-concentration and is expected to be relevant for other isostructural binary and ternary nitrides as well.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

References


