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Toughness Enhancement in Hard Single-Crystal Transition-Metal Nitrides:

V-Mo-N and V-W-N Alloys

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*A mis Padres y Hermano,
a la Abuela.*

ABSTRACT

Transition-metal nitrides are known for their high hardness, good wear resistance, high-temperature stability, and chemical inertness. Because of these properties, they are extensively used in many industrial applications, notably as protective wear, erosion, and scratch resistant coatings, which are often subjected to high thermo-mechanical stresses. While high hardness is essential, most applications also require high ductility, to avoid brittle failure due to cracking. However, transition-metal nitrides, as most ceramics, generally exhibit low ductility and hence poor toughness.

Improving toughness, the combination of hardness and ductility, of ceramic materials requires suppression of crack initiation and/or propagation, both of which depend on the microstructure, electronic structure, and bonding nature of the coating material. This, however, is an extremely challenging task that requires a fundamental understanding of the mechanical behavior of materials. Theoretical studies, for example, *ab initio* calculations and simulations are therefore useful in the design of “unbreakable” materials by providing information about the electronic origins of hardness and ductility. Recent density functional theory calculations predicted that alloying can increase toughness in a certain family of transition-metal nitrides such as V-Mo-N and V-W-N alloys. Toughness enhancement in these alloys arises from a near optimal filling of the metallic $d-t_{2g}$ states, due to their high valence electron concentrations, leading to an orbital overlap which favors ductility during shearing.

This thesis focuses on the growth and characterization of $V_{1-x}Mo_xN_y$ ($0 \leq x \leq 0.7$, $0.55 \leq y \leq 1.03$) and $V_{1-x}W_xN_y$ ($0 \leq x \leq 0.83$, $0.75 \leq y \leq 1.13$) cubic alloy thin films. I show that alloying VN with WN increases the alloy hardness and reduces the elastic modulus, an indication of enhanced toughness. I investigated the growth, nanostructure, and atomic ordering of as-deposited $V_{1-x}W_xN_y(001)/MgO(001)$ thin films. In addition, I studied the growth, structural and mechanical properties, and electronic structure of $V_{1-x}Mo_xN_y(001)/MgO(001)$ and $V_{0.5}Mo_{0.5}N_y(111)/Al_2O_3(0001)$ thin films. I demonstrate that these alloys exhibit not only higher hardness than the parent binary compound, VN, but also dramatically increased ductility. $V_{0.5}Mo_{0.5}N$ hardness is more than 25% higher than that of VN. Using nanoindentation I show that while VN and TiN reference samples undergo severe cracking typical of brittle ceramics, $V_{0.5}Mo_{0.5}N$ films do not crack. Instead, they exhibit material pile-up around nanoindents, characteristic of plastic flow in ductile materials. Furthermore, the wear resistance of $V_{0.5}Mo_{0.5}N$ is significantly higher than that of VN. I also show, for the first time, anion-vacancy-induced toughening of single-crystal $V_{0.5}Mo_{0.5}N_y/MgO(001)$ films. Nanoindentation hardness of these alloys increases with the introduction of N-vacancies, while the elastic modulus remains essentially constant. In addition, typical scanning electron micrographs of nanoindents show no cracks, which demonstrate that N-vacancies lead to toughness enhancement in these alloys. Valence band x-ray photoelectron spectroscopy analyses show that vacancy-induced toughening is due to a higher electron density of $d-t_{2g}(\text{Metal}) - d-t_{2g}(\text{Metal})$ orbitals with increasing N-vacancy concentration, and essentially equally dense $p(N) - d-e_g(\text{Metal})$ first neighbor bonds.

Overall, I demonstrate that it is possible to design and deposit hard and ductile transition-metal nitride coatings. My research results thus provide a pathway toward the development of new tough materials.

POPULÄRVETENSKAPLIG SAMMANFATTNING

En tunnfilm är ett tunt lager av material med tjocklek från delar av nanometer till flera mikrometer. På grund av dess dimension, kan egenskaperna skilja sig från ett normalt tjockare materials inre egenskaper och används därför, till exempel, som beläggning för att ändra ett materials ytegenskaper.

En typ av material som ofta används till beläggning är keramiska tunna filmer från nitrider av övergångsmetaller såsom t.ex. vanadinnitrid. Nitrider från övergångsmetaller är kända för deras höga hårdhet, goda nötningsegenskaper, höga temperaturstabilitet och att de är kemiskt inerta. På grund av dessa egenskaper, används de flitigt i industrin, speciellt som nötningsmaterial, mot erosion och i korrosionsmiljöer. Speciellt kan omnämnas, att dessa ytmaterial avsevärt kan förbättra ett verktygs skåregenskaper. Men, även om hårdheten är viktig, krävs också att materialet är segt för att undvika att materialet spricker p.g.a. termo-mekanisk påverkan. Nitrider från övergångsmetaller, liksom de flesta keramer, är inte särskilt sega utan mera spröda.

För att förbättra keramers seghet måste man därför dämpa materialets tendens till sprickbildning eller fortplantning, vilka är starkt förknippade med dess mikrostruktur, dess elektroniska struktur och den kemiska bindningen till beläggningsmaterialet. Teoretiska studier som använder ”*ab-initio* simuleringsteknik” är därför mycket användbar för att hjälpa till att utveckla ”obrytbara” material genom att ge information om dess fysiska och elektroniska egenskaper. Färska teoretiska beräkningar har förutsagt förhöjd seghet i speciella nitrider från övergångsmetaller såsom legeringar av V-Mo-N och V-W-N. Enligt dessa beräkningar, beror ökningen av segheten på en nästan optimal fyllning av de metalliska elektrontillstånden p.g.a. deras höga koncentration av valenselektroner, vilket gynnar materialets plastiska egenskaper.

Min avhandling inriktar sig på tillväxt och karaktärisering av kubiska legeringar av $V_{1-x}Mo_xN_y$ ($0 \leq x \leq 0.7$, $0.55 \leq y \leq 1.03$) och $V_{1-x}W_xN_y$ ($0 \leq x \leq 0.83$, $0.75 \leq y \leq 1.13$), vilka uppvisar ökad seghet. Jag visar att legeringar av VN med WN ökar materialets hårdhet och minskar dess elasticitetsmodul, vilket visar på ökad seghet. Vidare har jag studerat och diskuterat beläggningens tillväxt, dess nanostruktur samt hur atomerna är ordnade i tunna $V_{1-x}W_xN_y/MgO(001)$ -filmer. Jag har även studerat tillväxt, strukturella och mekaniska egenskaper, samt den elektroniska strukturen hos tunna filmer av $V_{1-x}Mo_xN_y$, och visat att dessa legeringar inte bara har förhöjd hårdhet i jämförelse med dess binära referensmaterial, VN, utan även uppvisar dramatiskt ökad plasticitet. Intrycksexperiment med djup inom nanometerområdet i referensmaterialen VN och TiN visar att de lider av allvarlig sprickbildning, typiskt hos spröda keramer, vilket inte förekommer hos mina $V_{0.5}Mo_{0.5}N$ -filmer. Istället, uppvisar de vallar runt kratrarna efter intrycket, vilket är karaktäristiskt för plastisk deformation i material. Dessutom, uppvisar $V_{0.5}Mo_{0.5}N$ avsevärt större nötningsmotstånd än VN. I avhandlingen visar jag också effekten av kväve-vakanser på de mekaniska egenskaperna, särskilt, segheten hos $V_{0.5}Mo_{0.5}N_y$ -filmer. Dessutom förklaras hur och varför segheten av dessa legeringar ökar vid införandet av N-vakanser. Med hjälp av röntgen-fotoelektron-spektroskopi av

valensbandet visar jag experimentellt att vakansinducerad seghet beror framför allt på att där blir flera metalliska elektronrörelser med minskad N-andel.

Generellt, demonstrerar jag i min avhandling att det är möjligt att tillverka hårda och samtidigt sega ytbeläggningar av nitrider från övergångsmetaller samt visar på en framtida väg för att framställa nya mycket starka ytbeläggningar.

PREFACE

This thesis compiles the most important results obtained during my doctoral studies in the Thin Film Physics Division at Linköping University.

The goal of my research has been to synthesize and characterize pseudobinary transition-metal nitride ceramics deposited as thin films. I have chosen VN as the parent compound and alloyed it with WN and MoN. This work includes results and discussions of the alloy thin film synthesis, characterization, and theoretical calculations.

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Hanna Kindlund
Linköping, June 2014

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1

INTRODUCTION

1.1. The quest for enhanced toughness in hard coatings

The combination of hardness and ductility is referred to as toughness, a measure of the resistance of a material to crack formation, i.e., the ability of a material to absorb energy before fracture [1]. The design and development of materials with high toughness, that is, materials with high hardness and high ductility, have always been a challenge, because an increase in hardness is usually accompanied by an increase in brittleness rather than ductility.

Over the past several decades, one of the major goals of materials scientists and hard coating industries has been the development of hard materials. Increase in hardness has been achieved, for example, by phase-stability tuning to restrict dislocation glide in transition-metal (TM) carbides [2] and polytype-mixtures in TM nitrides [3], the development of superlattices [4-6], nanolaminates and nanocomposites [7-11], and the introduction of vacancies [12-14]. While high hardness is indispensable, most applications also demand ductility in order to avoid brittle failure due to cracking in coatings exposed to high stresses. However, hard refractory ceramics such as TM carbides and nitrides are in general brittle.

The synthesis of hard and ductile (tough) ceramic coatings is not an easy task. To enhance toughness, both crack initiation and propagation have to be inhibited. In order for a crack to propagate, the stress at the crack tip has to be greater than the fracture stress of the material [15]. In polycrystalline materials, commonly used in most applications, grain

boundaries are the structurally weaker regions of the material and the cracks will spread along them. Therefore, one can hinder the propagation of cracks by strengthening the grain boundaries. As a result, the cracks will either branch out or bend in order to propagate, thus decelerating the crack motion. Moreover, since the crack size is generally proportional to the grain size, the propensity for crack propagation can also be attenuated by decreasing the size of grains or flaws to the nanoscale [15]. Such nanostructuring is known to enhance strength in thin films [16], and opened a new path to the development of hard-yet-tough ceramic coatings via the synthesis of nanoscale composites [15,17].

Nanoscale composites are solid materials with two or more different phases, where one of them has at least one dimension in the nanometer range, and they usually consist of a solid “bulk” matrix with solid nano-dimensional phase(s) as reinforcements [18]. Nanostructural toughening in composites has been achieved via the incorporation of ductile phases [19-23], introduction of small amount of compressive stresses [24], addition of carbon nanotubes [25-28], and phase transformations [29,30]. Other approaches to increase toughness involve composition or structure grading [15,17,31], grain boundary sliding [32], and multilayer structures [33-35]. Most of these toughening methods, which are based on techniques applied to bulk materials, when employed to toughen thin films, cause problems such as film delamination or hardness reduction [15,17]. Moreover, the above-mentioned toughening methods focus on hindering or decelerating crack propagation. Fundamental understanding of the origins of toughness, which would help inhibiting crack formation, is lacking and is probably the main reason for the slow progress in developing hard-yet-ductile ceramics. Progress in this area can only be achieved through atomic- and electronic-level understanding of the origins of brittleness *vs.* ductility. Such studies are, however, relatively few [36,37]. *Ab initio* theoretical studies, for example, density functional theory (DFT) calculations, and simulations, are extremely useful in the design of “unbreakable” materials by providing information concerning the relationship between electronic structure and mechanical properties.

This thesis aims to take advantage of existing DFT studies of toughness enhancement in TM nitrides to develop hard-yet-ductile TM nitrides deposited as thin films. The thesis presents results of the growth and characterization of cubic alloys of VN with WN and MoN.

1.2. Transition-metal nitrides

TM nitrides are refractory ceramics, which possess excellent properties such as high hardness, good wear resistance, high temperature stability, and good chemical inertness [38-40]. TM nitride coatings can withstand high temperatures and corrosive environments and therefore help avoid failure and guarantee a device’s performance. They are, hence, perfect candidates to be used as protective coatings against wear and erosion of cutting

tools and structural components in automobiles and aerospace vehicles. Furthermore, owing to the presence of metallic bonds in addition to ionic and covalent bonds [39,40], TM nitrides can, *in principle*, exhibit ductility. Among all TM nitrides, group IVb TM nitride alloys, particularly TiN and TiN-based alloys, have been extensively studied [12,41-43]. These TiN-based alloys include TiAlN [44-47], TiZrN [48,49], TiNbN [50,51], TiSiN [52] and similar ternary and quaternary alloys.

TM nitride compounds form crystalline structures composed of closed-packed (or nearly closed-packed) arrangements of TM atoms with the N atoms placed in the interstitial sites [39]. TM nitrides of groups IVb (TiN, ZrN, HfN...) and Vb (VN, NbN, TaN...) generally crystallize in the B1 NaCl-structure [41,53-56], while group VIb TM nitrides, MoN and WN, crystallize in hexagonal structure [39]. The B1 structure of TM nitrides can be considered as a face-centered cubic lattice of metal atoms with non-metal atoms occupying the octahedral interstitial sites (see Fig. 1-1).

Figure 1-1: Schematic of the B1 (NaCl) crystal structure.

TM nitrides can usually be synthesized as single-crystalline films on selected substrates by depositing at high temperatures and by a careful control of parameters such as deposition flux and working gas pressure. TM nitrides have been synthesized by both chemical and physical vapor deposition (CVD and PVD) methods [41,57-59].

The bonding in NaCl-structure TM nitrides usually includes strong $p(\text{N}) - d-e_g(\text{Me})$ first-neighbor bonds and secondary metal-metal $d-t_{2g}(\text{Me}) - d-t_{2g}(\text{Me})$ interactions [60-62]. Metallic bonds, composed of free electrons are responsible for the malleability typical of metals. It seems therefore reasonable that increasing the density of the metallic interactions in TM nitrides would enhance the ductility of the material.

Previous studies have shown that by changing the valence electron concentration (VEC) one can tune the mechanical properties of TM nitrides. For example, Holleck [63] and Jhi *et al.* [64] have shown that the maximum hardness for TM nitrides is achieved at a VEC of ~ 8.4 electrons per formula unit, due to complete filling of the shear-resistive $p(\text{N}) - d-e_g(\text{Me})$ orbitals. At higher VEC, the shear-sensitive $d-t_{2g}$ states begin to be filled which reduces the shear resistance of the material [64]. More recently, Sangiovanni *et*

al. [65] using DFT calculations predicted enhanced toughness in pseudobinary B1-structure TM nitride alloys of VN with MoN or WN. In these alloys, the high VEC (10.5 valence electrons/formula unit for $V_{0.5}Mo_{0.5}N$ and $V_{0.5}W_{0.5}N$) leads, during shearing, to an electronic arrangement, which allows a selective response to tetragonal and trigonal deformations. The material will resist deformation upon application of compressive and tensile stresses, and will deform plastically if shear stresses are applied [65]. This specific mechanical behavior is attributed to a near optimal filling of the shear-sensitive $d-t_{2g}$ metallic states as a result of the high VEC of these alloys. In addition, other theoretical studies which employed the Cauchy pressures and shear-to-bulk moduli ratios as criteria to assess ductility, reported that addition of Mo and W to TiN or VN could increase the material's ductility [66,67].

While most experimental studies are on TiN and related alloys, substantially fewer reports are found on pseudobinary TM nitrides of groups Vb and VIb, such as alloys of VN and MoN or WN. Motivated by these theoretical predictions and the lack of literature on VN-based alloys, I focused on the synthesis and characterization of potentially tough, pseudobinary TM nitride coatings with VN as the parent compound.

Figure 1-2: Phase diagram of the V-N system (Ref. [68]). Adapted with permission of ASM international. All rights reserved. www.asminternational.org.

VN is of interest for applications requiring hard, low-friction, wear- and corrosion-resistant materials [69-71]. The binary V-N phase diagram shown in Fig. 1-2 (Ref. [68]) indicates that stoichiometric VN (δ -VN) crystallizes in the cubic B1 structure, while understoichiometric VN_{1-y} can form B1 or hexagonal β - V_2N structure depending on the N concentration. In comparison, the thermodynamically favorable crystal structure for stoichiometric binary nitrides of Mo and W is hexagonal, δ -MoN and δ -WN (see the W-N Ref. [72] and Mo-N Ref. [73] binary phase diagrams in Figs. 1-3(a) and 1-3(b), respectively). However, substoichiometric MoN_{1-y} and WN_{1-y} phases can also exhibit B1 structure [39,74,75]: metastable β - W_2N , in which half of the anion sublattice is vacant [39,72], and γ - Mo_2N at high temperatures [73]. Among the substoichiometric MoN_{1-y}

compounds, β - Mo_2N is a distorted cubic (tetragonal) phase, whose thermal stability is not well known. Existing literature is contradictory with one study reporting that β - Mo_2N is stable only at room temperature [73] while the other indicating that it is a high-temperature phase and γ - Mo_2N phase is stable at room temperature [39].

Figure 1-3: Binary phase diagrams of (a) N-W (Ref. [72]) and (b) Mo-N (Ref. [73]) systems. Adapted with permission of ASM international. All rights reserved. www.asminternational.org.

While there is little literature on the V-W-N or V-Mo-N systems, Figs. 1-2 and 1-3 indicate that it is possible to form nitrides of V, Mo, and W with B1 structure. Moreover, one of the advantages of choosing these alloy systems is that both Mo and W are completely miscible with V and form solid solutions over all compositions (see the V-W Ref. [76] and Mo-V Ref. [77] binary phase diagrams in Fig. 1-4). Therefore, I investigated the growth, structural evolution, as well as mechanical properties of $\text{V}_{1-x}\text{W}_x\text{N}_y$ and $\text{V}_{1-x}\text{Mo}_x\text{N}_y$ alloys, deposited as thin films.

Figure 1-4: Binary phase diagrams of (a) V-W (Ref. [76]) and (b) Mo-V (Ref. [77]) systems. Adapted with permission of ASM international. All rights reserved. www.asminternational.org.

All films are deposited by dual-target reactive magnetron sputtering on polished MgO(001) and Al₂O₃(0001) substrates. The film micro- and nano-structure is determined using x-ray diffraction (XRD) and transmission electron microscopy (TEM) techniques. Compositional analyses are carried out mostly utilizing Rutherford backscattering spectrometry (RBS). The density of states of the valence band is determined by x-ray photoelectron spectroscopy (XPS). And, the mechanical properties are measured by nanoindentation.

In the following sections, I introduce the deposition technique and the details of the V_{1-x}W_xN_y and V_{1-x}Mo_xN_y thin film growth conditions. The basic principles of the thin film characterization methods and the experimental procedures used for the analyses of V_{1-x}W_xN_y and V_{1-x}Mo_xN_y films are explained in chapter 3. Chapter 4 contains a summary of the results; the first part of chapter 4 focuses on V_{1-x}W_xN_y, the results of which are part of *Paper I* and *Paper II*. The second part of chapter 4 is a summary of the results of V_{1-x}Mo_xN_y alloys from *Papers III-VII*. A list of the papers included in this thesis is presented in chapter 5. Other papers related to but not included in this thesis are listed in chapter 6. My conclusions and contributions to the field are in chapter 7 and my suggestions for the future work in chapter 8. Appendix contains reprints of *Papers I-VII* and my contributions to each paper.

2

THIN FILM DEPOSITION

2.1. Magnetron sputter deposition

Sputtering is the process where atoms are ejected from a target after bombardment with energetic particles, usually ions. In magnetron sputtering, a high negative voltage is applied to the target (cathode), which is the material to be deposited. When a low pressure of Ar as the working gas is introduced into the vacuum chamber, the gas is ionized forming the plasma. The plasma is mainly formed of charged particles and electrons that help maintaining the discharge. The ions from the plasma are accelerated towards the target and, if their energy is high enough, the atoms from the target surface will be sputtered, being transported in vapor phase through the chamber, and deposited onto the substrate, such that a thin film starts to grow. Secondary electrons will also be emitted from the target.

In magnetron sputtering, a magnetic field is applied to avoid the loss of electrons in the plasma, by placing a magnet (magnetron) behind the target. The magnetic field generated, traps the electrons in the plasma, in a region between the target and the substrate, and helps producing more ions. This allows us to work at low gas pressures and with relatively low target voltages [78]. If a reactive gas (nitrogen here) is instead introduced in the chamber, it reacts with the sputtered material to form a compound on the substrate. This technique is called reactive magnetron sputtering [79].

One can power the magnetron in several ways: radio frequency (RF), direct current (DC), pulsed DC, and high-power impulse magnetron sputtering (HiPIMS). In this work all depositions are carried out using the DC mode of operation.

All $V_{1-x}W_xN_y$ and $V_{1-x}Mo_xN_y$ films presented in this thesis are grown by dual-target reactive magnetron sputtering in a stainless-steel ultra-high vacuum (UHV) system with a base pressure $\sim 2 \times 10^{-9}$ Torr. The targets, V (99.95 % purity), W (99.95 % purity), and Mo (99.95% purity) are separately sputter cleaned, with shutters protecting the substrate and the other target, before deposition. A -30 V bias is applied to the substrate during deposition of all layers. The target to substrate distance is approximately 15 cm. The gas pressure is controlled by a capacitance manometer and substrate temperatures are measured with a thermo-couple placed behind the substrate. The substrates are rotated at ~ 30 rpm during deposition to assure a uniform thickness along the whole film.

Single-crystal $MgO(001)$ and $Al_2O_3(0001)$ polished substrates are ultrasonically cleaned in acetone and 2-propanol for 5 min, and blown dry in N_2 . They are then degassed in UHV at 900 °C for 45 min before starting deposition at the selected growth temperature, which is known to result in a 1×1 surface reconstruction of both MgO and Al_2O_3 , which is desirable for promoting epitaxial film growth, as determined by high-energy electron diffraction patterns [80]. This process is also effective in removing water vapor from the substrate surface, where in particular MgO is hydrophilic.

2.2.1. Deposition of $V_{1-x}W_xN_y$ thin films

Two sets of $V_{1-x}W_xN_y$ samples are reported in this thesis. Both sets are grown in pure N_2 atmospheres at a constant pressure $P_{N_2} = 10$ mTorr. In order to obtain stoichiometric films, pure N_2 gas is chosen for these experiments, due to the low reactivity of W with N [74]. The targets are V and W discs with diameters 76 mm and 51 mm, respectively.

The first set covers a constant W/V ratio ≈ 1 , over a growth temperature range $600 \leq T_s \leq 900$ °C ($0.75 \leq y \leq 1.13$). These samples are mainly used for structure and atomic ordering analyses as a function of the growth temperature (*Paper I*). The powers used are 130 W for the vanadium target and 52 W for the tungsten target.

The second set of samples covers a range of $V_{1-x}W_xN$ film with different WN contents ($0 \leq x \leq 0.83$), at constant temperature $T_s = 700$ °C, to study the structural and mechanical properties as a function of the WN content (*Paper II*). Desired film compositions are obtained from target power *vs.* deposition rate calibrations using 30 to 350 W applied to the vanadium target and 10 to 124 W to the tungsten target.

2.2.2. Deposition of $V_{1-x}Mo_xN_y$ thin films

Four sets of $V_{1-x}Mo_xN_y$ ($0 \leq x \leq 0.70$, $0.55 \leq y \leq 1.03$) samples are reported in this work. All $V_{1-x}Mo_xN_y$ samples are grown in a mixture of N_2 and Ar atmospheres, at a total pressure of 5 mTorr.

The first set of films is deposited on MgO(001) substrates at constant temperature of 700 °C varying the molybdenum fraction x . Sputtering is carried out at a N_2 partial pressure of 3.2 mTorr from vanadium and molybdenum targets with diameters 76 mm and 51 mm, respectively (except for the film with $x = 0.7$ which is deposited using vanadium and molybdenum targets both of 76 mm). The film composition is obtained from target power vs. deposition rate calibrations, which are calculated by x-ray reflectivity (XRR) measurements performed on the reference binary compounds. The power to the vanadium target is varied between 180-430 W and 30-160 W for the molybdenum target. This set of samples is used for structural and mechanical analyses as a function of the MoN content.

The second set of samples is deposited on MgO(001) substrates at a constant temperature of 700 °C and a Mo/V ratio ~ 1 . The N_2 partial pressures are varied between 1 and 5 mTorr achieving nitrogen fractions y from 0.55 to 1.03. The targets used are vanadium and molybdenum discs with diameters of 76 mm. The power to the vanadium target is varied from 130 to 260 W and 50 to 150 W for the molybdenum target, to attain growth rates $R_{VMoN} \sim 70 \text{ \AA/min}$. This set of samples is used for structural and mechanical characterization as a function of the nitrogen vacancies (*Paper III* and *Paper IV*).

The third and fourth set of samples are deposited simultaneously on MgO(001) and $Al_2O_3(0001)$, respectively, where the Mo/V ratio is maintained constant at ~ 1 . The sputtering is carried out from vanadium and molybdenum targets with diameters of 76 mm, at a constant N_2 partial pressure of 3.2 mTorr, while the growth temperature is varied between 100 and 900 °C (*Paper V*, *Paper VI*).

3

THIN FILM CHARACTERIZATION

This chapter describes the characterization techniques used for the analyses of the synthesized thin films, as well as a brief description of the computational methods that are also relevant for this thesis. Film micro- and nano-structure are analyzed by x-ray diffraction and electron microscopy techniques. Alloy chemical composition is determined by Rutherford backscattering spectrometry. The mechanical characterization is performed utilizing nanoindentation. X-ray photoelectron spectroscopy is used to determine the chemical composition and electronic structure of the as-deposited films.

3.1. X-ray diffraction

Elastic and coherent scattering (diffraction) of an electromagnetic radiation such as x-rays is widely used in materials science for structural characterization of materials. When diffraction occurs, the scattered waves cancel each other producing destructive interference in most directions. However, in specific directions, the waves interact constructively. Such constructive interference is determined by the Bragg's law, which is satisfied only if $\lambda \leq 2d$ [81]:

$$2d \sin \theta = n \lambda, \quad (3-1)$$

where d is the interplanar spacing, θ is the incidence angle, n is an integer, and λ is the wavelength of the radiation.

The interplanar distance d_{hkl} for cubic crystals is given by the following relationship:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}. \quad (3-2)$$

In eq. (3-2), a is the lattice parameter of the crystal, and h, k, l are the Miller indices of a set of crystallographic planes.

3.1.1. $\theta/2\theta$ and ω scans

The $\theta/2\theta$ diffractometer is the instrument most commonly used to determine Bragg reflections in thin films. In a typical experiment, the specimen is placed in the center of the diffractometer. The x-ray beam hits the sample surface at an incident angle ω and the beam scattered at an angle 2θ is collected by the detector. During the scan, both the incident and scattering angles are continuously varied, but both maintain the relationship $\omega = \frac{2\theta}{2}$, i.e., the incident and exiting beam angles are equal (see Fig. 3-1).

Figure 3-1: Schematic of the incident, exiting, and scattering angles in a $\theta/2\theta$ scan.

The results obtained from this type of scans are represented in the form of intensity I vs. scattering angle 2θ plots. In this configuration, the scattering vector is always perpendicular to the sample normal, which allows only those hkl planes that are oriented parallel to the surface to contribute to a Bragg reflection.

In this work, I have used XRD $\theta/2\theta$ scans to study the structure and crystallinity of the alloy films. Cu K_α radiation with average wavelength $\lambda_{avg.} = 1.541874 \text{ \AA}$ and 0.5° divergence and receiving slits are used to collect the data. Fig. 3-2 shows an example of XRD $\theta/2\theta$ scans obtained from $V_{1-x}Mo_xN/MgO(001)$ samples. The data shows that the $V_{1-x}Mo_xN$ layers grow epitaxially on $MgO(001)$.

Figure 3-2: XRD $\theta/2\theta$ scans of epitaxial $V_{1-x}Mo_xN/MgO(001)$ films as a function of Mo content.

This type of measurement provides us with data to determine the out-of-plane component of the lattice parameter of the epitaxial films. From the 002 reflection of the $\theta/2\theta$ scans shown above, and using equations (3-1) and (3-2), I determine the out-of-plane lattice parameters to increase with increasing Mo content, from $a \approx 4.15 \text{ \AA}$ ($x = 0.2$) to $a \approx 4.18 \text{ \AA}$ ($x = 0.7$). In the data, we observe two sets of peaks for both the substrate and the film, which are due to the $Cu K\alpha_1$ and $Cu K\alpha_2$ radiations. The fact that there is a clear separation between the $Cu K\alpha_1$ and $K\alpha_2$ contributions to the film peaks is indicative of the good crystallinity of these films. These types of scans are used in *Papers I-VI*.

The ω scans (or rocking curves) are useful to study the crystal quality of thin films, which is determined by measuring the full-width half maximum (FWHM) of the rocking curve. For a given Bragg reflection at an angle 2θ , the ω scans are acquired by fixing the detector at 2θ and tilting the ω angle around θ . In this way, the scattering angle 2θ and incident angle ω are independent of each other. The results obtained from this type of scans are shown in the form of I vs. ω plots.

3.1.2. Reciprocal space maps

In a $\theta/2\theta$ scan, only the planes that are parallel to the surface can contribute to a Bragg reflection, allowing only the out-of-plane component of the unit cell to be determined. Nevertheless, when performing an ω scan, the scattering vector will also have a non-zero in-plane component. A reciprocal space map (RSM) is a 2-dimensional measurement, where the selected Bragg reflection intensities are obtained as a function of both ω and 2θ [82]. RSMs are useful to determine in-plane and out-of-plane lattice parameters, strain, strain relaxation and mosaicity, and are represented as diffraction intensity contours plotted in the reciprocal space.

The ω and 2θ angles are connected to the scattering vectors $Q_{\parallel}$ and $Q_{\perp}$ in the reciprocal space [83] through the following relationship:

$$\begin{aligned} Q_{\parallel} &= 2r_E \sin \theta \sin(\theta - \omega), \\ Q_{\perp} &= 2r_E \sin \theta \cos(\theta - \omega), \end{aligned} \tag{3-3}$$

where $r_E = 1/\lambda$ is the radius of the Ewald sphere, and $\lambda = 1.5406 \text{ \AA}$ for the Cu $K_{\alpha 1}$ radiation used in these experiments. The in-plane $d_{\parallel}$ and out-of-plane $d_{\perp}$ interplanar spacings are given by $d_{\parallel} = 1/Q_{\parallel}$ and $d_{\perp} = 1/Q_{\perp}$.

All the RSMs shown in this thesis are acquired around the asymmetric 113 XRD reflection for 001-oriented films. Thus, the in plane and out-of-plane component of the lattice parameters are given by $a_{\parallel} = d_{\parallel}\sqrt{2}$ and $a_{\perp} = 3d_{\perp}$. For 111-oriented samples the RSMs are acquired around the 420 reflection. The in-plane and out-of plane lattice parameters are given in this case by $a_{\parallel} = d_{\parallel}\sqrt{8}$ and $a_{\perp} = d_{\perp}\sqrt{12}$. A schematic of the 420 diffracted vector of a NaCl-structure sample is shown in Fig. 3-3.

Figure 3-3: Schematic of the reciprocal lattice of a 111-oriented NaCl-structure sample viewed along the $[1-21]$ zone axis.

An example of a RSM obtained around the 113 reflection from a $V_{0.3}Mo_{0.7}N/MgO(001)$ sample is shown in Fig. 3-4. The diffracted intensity distributions are plotted as isointensity contours as a function of ω and 2θ angles in Fig. 3-4(a) and $Q_{\perp}$ and $Q_{\parallel}$ in Fig. 3-4(b). Both these plots are related by eq. (3-3).

Figure 3-4: XRD RSMs acquired around the 113 reflection of $V_{0.3}Mo_{0.7}N/MgO(001)$ with (a) ω and 2θ and (b) $Q_{\perp}$ and $Q_{\parallel}$ as reference frames.

The highest intensity contour located at the center of the map at $2\theta = 74.75^\circ$ and $\omega = 12.15^\circ$ ($Q_{\perp} = 0.713 \text{ \AA}^{-1}$ and $Q_{\parallel} = 0.336 \text{ \AA}^{-1}$) is due to the MgO 113 reflection. These coordinates correspond to a lattice parameter $a_{MgO} = 4.211 \text{ \AA}$, which is consistent with previous reports [84]. The $V_{0.3}Mo_{0.7}N$ 113 reflection appears at $2\theta = 75.29^\circ$ and $\omega =$

12.48° ($Q_{\perp} = 0.717 \text{ \AA}^{-1}$ and $Q_{\parallel} = 0.337 \text{ \AA}^{-1}$). Since the film has NaCl-structure, the out-of-plane and in-plane lattice parameters are given by $a_{\perp} = 3Q_{\perp} = 4.180 \text{ \AA}$ and $a_{\parallel} = Q_{\parallel}\sqrt{2} = 4.196 \text{ \AA}$, respectively.

All RSMs presented in this thesis are acquired in a 4-axis goniometer equipped with a hybrid mirror monochromator as primary optics and a scanning line detector. The x-ray generator is operated at 45 kV and 40 mA. Results obtained from this type of measurement are presented in *Papers I-VI*.

A term that is mentioned several times through *Papers I-VII* is *epitaxy*. This word is used to describe a growth phenomenon where the crystallographic orientations of the deposited single-crystalline film bear a simple relation with those of the single-crystalline substrate. The term heteroepitaxy refers to epitaxial growth of a material whose composition is different from that of the substrate [85].

In heteroepitaxial growth, crystallinity and microstructure of the film are, to some extent, determined by the lattice constants of the film and the substrate. If the lattice mismatch is negligible, then interfacial strain is minimal and the film will grow relatively defect-free on the substrate. In the presence of a small but non-negligible lattice mismatch, typically up to ~9% [85], the layers will tend to elastically adjust to the substrate lattice. In this case, we say that the film is strained. This situation, called pseudomorphic growth, occurs during the early stages of thin film growth and between materials with the same crystal structure. However, when the lattice mismatch between the film and the substrate is large and if lattice accommodation is not possible, then the film will relax by forming misfit dislocations along the film/substrate interface. In this case, we say that the film grows relaxed. Even in this latter case, pseudomorphic growth is present in the initial stages of thin film formation up to a certain thickness beyond which the film relaxes to its “bulk” structure.

The measurements of $a_{\parallel}$ and $a_{\perp}$ allow us to determine the film/substrate lattice mismatch, relaxed lattice parameter a_o , and the residual stresses in the film. The lattice mismatch Δ is defined as:

$$\Delta = \frac{a_{\parallel} - a_s}{a_s}, \quad (3-4)$$

where a_s is the substrate lattice parameter. The relaxed lattice parameter of the film, a_o is calculated using:

$$a_o = a_{\perp} \left(1 - \frac{2\nu(a_{\perp} - a_{\parallel})}{a_{\perp}(1 + \nu)} \right), \quad (3-5)$$

in which ν is the Poisson ratio of the film. For our alloy films, ν is calculated using DFT. Residual in-plane $\epsilon_{\parallel}$ strains and the degree of relaxation R are determined, respectively, from the following relationships:

$$\varepsilon_{\parallel} = \frac{a_{\parallel} - a_o}{a_o} \quad (3-6)$$

and

$$R = \frac{a_{\parallel} - a_s}{a_o - a_s}. \quad (3-7)$$

If $\varepsilon_{\parallel} < 0$, then the thin film lattice is considered to be in compression. In case $\varepsilon_{\parallel} > 0$, the film is said to be in tension.

In-plane stresses and the degree of relaxation have been studied for $V_{1-x}W_xN_y/MgO(001)$ alloys in *Paper I* and *Paper II*.

3.1.3. X-ray reflectivity

X-ray reflectivity (XRR) involves acquisition of symmetric $\theta/2\theta$ scans at low θ angles. It is based on constructive interference at surfaces and interfaces between layers with different indices of refraction. It is mainly used for measurements of film thickness and roughness, but one can also determine the density and refractive index of the material [82].

The thickness t of the layers is determined by utilizing the so-called *modified* Bragg's law, which accounts for the refractive index of the material, as follows:

$$n\lambda = 2t \sin \theta \sqrt{1 + \frac{\eta^2 - 1}{\sin^2 \theta}}. \quad (3-8)$$

In eq. (3-8), η is the refractive index of the film and n is an integer corresponding to constructive interference. By plotting $\sin^2 \theta$ vs. n^2 , one can extract the layer thickness from the slope of the curve as:

$$slope = \left(\frac{\lambda}{2t} \right)^2. \quad (3-9)$$

In this thesis, I have used XRR to determine thicknesses of the samples. Knowing the deposition time and the film thickness, I calculated the deposition rates of VN, WN, and MoN films. Using this information, I have calibrated sputter-target powers vs. deposition rates to obtain films of desired alloy composition and thickness, and the results are presented in *Papers I-VII*.

3.2. Electron microscopy

When a high energy electron beam is incident on a sample, the electrons interact with the atoms in the specimen generating secondary signals. These signals can be used for imaging and compositional studies of the material. Transmitted and scattered signals produced when the primary beam hits the sample are shown in Fig. 3-5.

Figure 3-5: Schematic of electron/sample interactions (adapted from Ref. [86]).

In a transmission electron microscope (TEM) transmitted and elastically scattered beams are used for imaging and for the determination of microstructure of the sample. In addition, inelastically scattered electrons and characteristic x-rays are used for compositional analyses in electron energy loss spectrometry (EELS) and energy dispersive x-ray spectroscopy (EDX), respectively. Secondary and backscattered electrons are used for imaging in scanning electron microscopes (SEM).

3.2.1. Transmission electron microscopy

The sample used for TEM analyses must be *electron transparent*, which is typically achieved with sample thicknesses below 100 nm [86]. The desired TEM imaging mode can be selected by inserting apertures and adjusting the lens currents. For example, for bright-field (BF) imaging, only the direct beam contributes to image formation and is

achieved by placing the objective aperture in the back focal plane of the objective lenses. The scattered beams that do not contribute to the image are blocked by the aperture. Dark field (DF) contrast, however, is obtained by selecting the scattered beams and blocking the primary beam. Thus, different information is obtained from these two imaging modes. BF imaging is used for microstructure and morphology analyses while DF imaging is used to study polycrystallinity, crystal distortions, and characterization of structural defects.

High-resolution TEM (HRTEM) or lattice imaging is achieved by removing the objective aperture and allowing both the direct transmitted and the diffracted beams to pass through and form the image [85]. HRTEM is used for studying the crystal structure of the films at the atomic level and it also allows imaging of lattice defects, such as stacking faults.

One can also acquire selected-area electron diffraction (SAED) patterns, which are useful in the determination of crystal structure, grain orientation, and structural defects of the sample. Representative examples of a low-magnification bright-field TEM images, a HRTEM image, and a SAED pattern obtained from a $V_{0.45}Mo_{0.55}N_{0.6}$ film are shown in Fig. 3-6.

Figure 3-6: (a) Low-magnification cross-sectional TEM image and corresponding SAED pattern in the upper-right corner, and (b) high-resolution TEM image of a $V_{0.45}Mo_{0.55}N_{0.6}/MgO(001)$ sample deposited at 700 °C.

In the bright-field TEM image (Fig. 3-6 (a)), the lighter grey contrast visible toward the bottom of the image corresponds to the MgO(001) substrate, while the darker grey contrast in the rest of the image is due to the film. The contrast variations visible in the

film could arise due to small differences in grain orientations and thicknesses within the sample. The spot pattern seen in the insert in Fig. 3-6(a) indicates that the film is single-crystalline with 001-orientation. The HRTEM image in Fig. 3-6(b) is acquired from the region near the substrate-film interface. The highly periodic lattice and the lack of discontinuity at the interface is indicative of good epitaxial registry between the film and the substrate.

In *Paper I*, *Paper II*, *Paper III*, *Paper V*, and *Paper VI*, I have used HRTEM to study the micro- and nano-structure of as-deposited $V_{0.6}W_{0.4}N_y/MgO(001)$, $V_{1-x}W_xN_y/MgO(001)$, and $V_{0.5}Mo_{0.5}N_y(001)$ films. In *Paper IV*, HRTEM images are acquired to examine the film/substrate deformation after nanoindentation experiments on $V_{0.5}Mo_{0.5}N_y/MgO(001)$ films. In *Paper V* I used DF-TEM images for characterization of dislocations around nanoindents. Fig. 3-7 shows a DF-TEM image of an indent performed in a $V_{0.5}Mo_{0.5}N_{0.94}(001)$ sample. The image is acquired along the $[001]$ zone axis selecting the 0-20 diffracting vector $\mathbf{g}$. The Burgers vector $\mathbf{b}$ of the dislocations can be studied by applying the visibility criterion $\mathbf{g} \cdot \mathbf{b} \neq 0$.

Figure 3-7: DF-TEM image of an indented area in a $V_{0.5}Mo_{0.5}N_{0.94}(001)$ film.

In addition, one can acquire EDX maps in the TEM to determine the film composition. EDX technique is explained later in section 3.5 (compositional analyses) and are used in *Paper VI* to determine the local chemical composition in $V_{0.5}Mo_{0.5}N_y/Al_2O_3(0001)$.

3.2.2. Scanning electron microscopy

Scanning electron microscopy (SEM) is an outstanding technique for topographical imaging of surfaces, and therefore, I have used it to acquire images of nanoindents for ductility/toughness assessment. In the SEM, a focused electron beam is scanned across the surface of the sample. The incident electron-sample interactions may generate secondary electrons, photons and also result in backscattering of electrons. The emitted electrons are collected by a detector and each scanned point of the sample is mapped onto the screen. SEM images can be produced from: secondary electrons or backscattered electrons. Secondary electrons, which provide the best topographical resolution due to their small exit depth, are inelastically scattered electrons with energies typically below 50 eV [87]. Backscattered electrons (BSE) have higher energies and are those incident electrons that have been either elastically or inelastically scattered. Energies of BSE vary from 50 eV up to the energy of the primary beam. The SEM images presented in this thesis are acquired using a secondary electron detector.

Fig. 3-8(a) shows a SEM image of an indent created with a sharp indenter on a $V_{0.3}Mo_{0.7}N/MgO(001)$ thin film. The material pile-up around the impression together with the absence of cracks give a first qualitative indication of the enhanced ductility of this material compared to the parent binary compound, VN (see Fig. 3-8(b)).

Figure 3-8: Typical SEM images of nanoindentations performed with a cube-corner tip on (a) $V_{0.3}Mo_{0.7}N/MgO(001)$ and (b) $VN/MgO(001)$ samples.

3.2.3. Scanning transmission electron microscopy

In a scanning transmission electron microscope (STEM), similar to SEM, a focused electron beam is rastered across the sample and the *transmitted* electrons are used to form the image. In contrast with SEM, here, the sample must be *electron transparent*. One of the advantages of the STEM is that it allows simultaneous operation of two detectors to obtain more information from each scan [88]. A BF detector situated on the axis of the microscope collects information from the transmitted beam and an annular dark-field (ADF) detector intercepts the scattered electrons. High-angle ADF (HAADF) imaging, where the electrons scattered at angles > 50 mrad (around 3°) off-axis are used to form an image, is sensitive to atomic number (Z) [86]. This technique is more commonly referred to as “Z-contrast” imaging and is sensitive to variations in the film composition. Fig. 3-9 shows an example of a Z-contrast image obtained from a $V_{0.6}W_{0.4}N_{1.13}/MgO(001)$ layer studied in *Paper I* (Ref. [89]). The brighter contributions in the lattice image correspond to elements with higher atomic number. Tungsten, which is the heavier element in this alloy, appears brighter in the image. This microscopy technique enabled study of the atomic ordering of $V_{0.6}W_{0.4}N_y/MgO(001)$ thin films.

Figure 3-9: Z-contrast HR-STEM image and SAED pattern (shown in the lower-right panel), obtained along the $[110]$ zone axis, from an epitaxial $V_{0.6}W_{0.4}N_{1.13}/MgO(001)$ layer grown at $600^\circ C$. A higher magnification image is shown in the upper-right panel. (Adapted from *Paper I*, Ref. [89]).

3.3. Mechanical characterization

3.3.1. Nanoindentation

Nanoindentation is a non-destructive technique used to characterize mechanical properties of thin films. The data that is most commonly obtained from nanoindentation measurements are hardness, elastic modulus, creep, work-hardening, energy absorption, phase transformations, and fracture toughness [90]. A related technique, triboindentation is also used to measure, for example, friction and wear. In this thesis, I have used nanoindentation to determine the hardness, elastic modulus, and toughness of the alloy thin films. I have also performed wear tests, and measured the wear rates of the thin films. This section provides basic information on how to extract hardness and elastic modulus from load-displacement curves, obtained from nanoindentation measurements.

In nanoindentation, a diamond probe is brought in contact with the sample such that the loading direction is almost normal to the sample surface. During indentation, the sample will undergo elastic and plastic deformation depending on the maximum applied load. When the load exceeds the elastic limit, the indenter will leave a residual plastic impression, which is used to determine the hardness of the sample. In a typical experiment, displacements of the indenter, i.e. the indenter penetration (h) within the sample are measured as a function of applied load (P), i.e. the load-displacement data. Such data is most commonly analyzed using Oliver and Pharr method [91], from which three important parameters, the maximum applied load ($P_{\max}$), contact depth (h_c), and the elastic or contact stiffness (S), are extracted and used to determine the indentation hardness and the elastic modulus. Contact stiffness S is defined as the slope (dP/dh) of the upper portion of the unloading curve. During a nanoindentation experiment, the contact depth h_c is lower than the total indenter penetration h_t due to elastic deformation of the surface, and is given by [91]:

$$h_c = h_t - h_e \quad (3-10)$$

with

$$h_e = \varepsilon \frac{P_{\max}}{S} . \quad (3-11)$$

In eqs. (3-10) and (3-11), h_e is the elastic deflection at the surface and ε is a constant which depends on the indenter shape.

The hardness H is calculated from

$$H = \frac{P_{\max}}{A} , \quad (3-12)$$

where A is the projected contact area of the impression, which depends on the contact depth h_c . The nanoindentation modulus or reduced elastic modulus E_r takes into account the elastic displacements in both the specimen (with elastic modulus E and Poisson ratio ν) and the diamond indenter, and is obtained from the contact stiffness S using the following relationship [92]:

$$S = \frac{dP}{dh} = 2\beta \sqrt{\frac{A}{\pi}} E_r, \quad (3-13)$$

in which β is a correction factor accounting for the tip geometry. $\beta = 1.034$ for Berkovich and cube-corner indenters.

The elastic modulus E of the material can be calculated from E_r knowing the Poisson ratio by using the following relationship:

$$\frac{1}{E_r} = \frac{1-\nu^2}{E} + \frac{1-\nu_i^2}{E_i}, \quad (3-14)$$

where E_i and ν_i are the elastic modulus and Poisson ratio of the diamond indenter, respectively [92]. In order to determine the hardness and elastic modulus of a sample, one has to first calibrate the indenting probe by assigning to it a probe area function $A(h_c)$. The projected contact area A can be modeled by a polynomial function [92]:

$$A = \sum_{n=0}^m C_n (h_c)^{2-n} \quad (3-15)$$

$C_0 \dots C_m$ are constants that are determined from the curve fitting. The area function for a perfect indenter with conical or pyramidal shape is given by the first term alone, $C_0 h_c^2$, where C_0 is the geometry factor of the tip. For indenters with non-ideal shapes, constants $C_{m>0}$ are best-fit to the curve. To calibrate the tip-area function, a series of indents are performed on a reference sample, usually, fused silica with known elastic modulus $E_r = 69.6$ GPa [92]. To obtain reliable results and avoid substrate effects in the measurements, the indent penetration should not, in general, exceed 1/10th of the total film thickness.

Figure 3-10(a) shows a series of load-displacement curves obtained during nanoindentation experiments on a $V_{0.3}Mo_{0.7}N(001)$ film. Fig. 3-10(b) is a plot of hardness H vs. contact depth h_c obtained from the load-displacement data in Fig. 3-10(a). Using the data shown in Fig. 3-10(b), one can determine the film hardness H to be in the range 22.5 ± 0.5 GPa, which is the average of all data points, where the error is calculated as the standard deviation.

Figure 3-10: (a) Nanoindentation load-displacement curves obtained from a $V_{0.3}Mo_{0.7}N$ sample using a maximum load of 750 μN . (b) Hardness H data obtained from a $V_{0.3}Mo_{0.7}N_{0.7}(001)$ film plotted as a function of the contact depth h_c .

3.3.1.1. Nanoindentation probes

The probes used for nanoindentation measurements in this work are pyramidal indenters of the Berkovich or cube-corner type, depending on the experiment, and conical for friction measurements.

The contact radius a in a nanoindentation experiment is determined by [90]:

$$a = h_c \tan \theta, \quad (3-16)$$

where θ is the angle between one of the indenter surface facets and the indenter axis. θ is 65.3° and 35.3° for a Berkovich and a cube-corner indenter, respectively [90].

The Berkovich indenter, which has an ideal projected area

$$A = 3\sqrt{3}h_c^2 \tan^2 \theta = 3\sqrt{3}h_c^2 \tan^2 65.3 = 24.5 h_c^2, \quad (3-17)$$

is most commonly used for nanoindentation hardness and elastic modulus measurements.

With the Berkovich indenter, mainly compressive stresses are generated [90]. If one wishes to produce higher stresses during indentation, then sharper probes, such as cube-corner, are desirable. The cube-corner indenter is mainly used to induce cracks in the sample and from the measurements of the radial lengths of the cracks, fracture toughness of the sample can be determined. Due to its sharp face angles, the stresses generated underneath the cube-corner indenter are much higher than with a Berkovich indenter, and the plastic deformation is limited to a smaller volume. The cube-corner indenter has an ideal projected area

$$A = 3\sqrt{3}h_c^2 \tan^2 \theta = 3\sqrt{3}h_c^2 \tan^2 35.3 = 2.598 h_c^2. \quad (3-18)$$

In comparison, conical tip possesses axial symmetry, and its projected area is given by:

$$A = \pi h_c^2 \tan^2 \alpha, \quad (3-19)$$

where α is the effective cone angle equal to 60° in our case. This tip is used for friction measurements.

3.3.2. Friction and wear

The modern nanomechanical instruments offer, in addition to the typical nanoindentation tests, the possibility of measuring friction and wear.

Wear is the surface damage as a result of the mechanical interaction with another material. Wear in materials can be quantified in different ways. In this work, I have measured *abrasive wear*, which occurs when a hard material slides over the surface of a softer material.

In a wear test, a diamond tip is first brought in contact with the surface of the sample. Then, a normal load is applied such that the tip penetrates the sample. The tip is then moved laterally across the sample while applying a constant load. This process is repeated several times and the resulting surface height profile is analyzed. The wear volume is determined via scanning probe microscopy (SPM) imaging by measuring the volume of material that was removed from within the scanned area. The wear rate is calculated as the difference in absolute values between the mean height outside and inside the scanned area.

Results obtained from wear tests depend on several factors. Some of the factors affecting the wear resistance of a material are determined by, for example, the hardness and microstructure of the material. However, the test parameters such as scan speed, tip shape, and tip quality can also influence the wear rate measurements and, hence, it is often difficult to obtain an absolute value of the wear rate.

One of the drawbacks of this type of measurement is that it damages the tip if the material to be tested is hard. Therefore, it is desirable to perform these measurements by scanning the tip over smaller areas while applying minimal loads that are high enough to induce wear in the film. The choice of the normal load used in these wear experiments will vary depending on the tip geometry, whether it is blunt or sharp. For example, a cube-corner tip will produce more wear at the same load than a blunter conical tip. Wear results shown in this thesis are performed with a maximum load of $100 \mu\text{N}$ when using cube-corner tips, and $1000 \mu\text{N}$ when using conical indenters. Wear measurements reported in *Paper III* are performed over a $2 \times 2 \mu\text{m}^2$ area at $100 \mu\text{N}$ for 5 cycles using a cube-corner tip, while wear data presented in *Paper V* and *Paper VI* are acquired by scanning along a $5\text{-}\mu\text{m}$ -long line at $1000 \mu\text{N}$ for 28 cycles.

Figures 3-11(a) and 3-11(b) are representative examples of wear measurements obtained from VN(001) and $V_{0.5}Mo_{0.5}N(001)$ samples, respectively, using a cube-corner probe. Wear results of $V_{0.5}Mo_{0.5}N_y(001)$ can be found in *Paper III*, *Paper V*, and *Paper VI*.

Figure 3-11: Topographic contour maps obtained from scanning probe microscopy (SPM) showing results of wear tests conducted on (a) VN and (b) $V_{0.5}Mo_{0.5}N$ layers. Data from *Paper III* (Ref. [93]).

In addition to measurement of surface wear resistance of a sample, similar tests can also be used to determine friction coefficient of a material. The coefficient of friction is a measure of the surface resistance of a material to lateral motion of an object on its surface. The friction coefficient is obtained as the ratio of the measured frictional force and the normal force applied by the indenter. When two materials in contact move relative to each other, common in any type of engines, cutting tools, and other devices, frictional forces resisting the motion can result in generation of heat and cause structural damage. Therefore, preparation of contact surfaces with minimal friction is highly desirable for such applications. The friction coefficient is affected by several factors such as surface roughness, adhesion forces, or applied normal force. Friction data of $V_{0.5}Mo_{0.5}N_y$ can be found in *Paper V* and *Paper VI*.

3.4. Thin film toughness assessment

Toughness is defined as the energy that a material can absorb before fracturing. In “bulk” materials, toughness is extracted from uniaxial compression or tensile tests by measuring the area under the curve of the stress-strain curve [1]. However, for coatings, the experimental procedure for the determination of toughness is not well established. This is

because, unlike bulk materials, measurements of uniaxial compression or tension vs. strain in thin films are not easy due to the presence of a substrate.

Thin film toughness is usually estimated in terms of fracture toughness, which is the resistance to crack propagation, that is, how easy or difficult it is to propagate an existing crack. Most of the fracture toughness measurement techniques were developed to study bulk materials and are not especially suited for thin films, mainly due to thickness limitations. Several alternate methods have been proposed to overcome this issue, for example, micro-tensile tests of freestanding thin films [94-97] or fracture toughness evaluation from indentation cracks [94,98-100].

Nanoindentation is a good technique for the study of mechanical properties of thin films deposited on substrates, and can provide a qualitative estimation of the film toughness by measuring the scratch-resistance of the coating or by analyzing the crack/pile-up formation around nanoindentations. In the latter approach, geometry of the cracks (radial or circumferential) formed around nanoindentations has been used to quantitatively determine the thin film toughness. A commonly employed method utilizes radial crack length data for the evaluation of fracture toughness (K_c) via [94]:

$$K_c = \alpha \left(\frac{E}{H} \right)^{1/2} \left(\frac{P}{c^{3/2}} \right), \quad (3-20)$$

where P is the maximum indentation load, c is the crack length, H and E are the hardness and elastic modulus of the film, respectively, and α is a geometric constant of the indenter. However, for accurate nanoindentation measurements the maximum penetration depth should be less than 10% of the total layer thickness. But, the load applied to achieve such depths is often too small to induce a radial crack in the sample [94].

In this work, I have used nanoindentation data, SEM and SPM images of radial cracks and material pile-up around the nanoindents to *qualitatively* assess thin film toughness and ductility. Nanoindentation tests are performed in displacement-control mode up to a constant penetration depth of 400 nm using a cube-corner tip. That is, the indenter penetrates the whole film (thickness ~300 nm), extending into the substrate ~100 nm.

3.5. Compositional analyses

3.5.1. Rutherford backscattering spectrometry

Rutherford backscattering spectrometry (RBS) is a surface sensitive technique used for quantitative determination of elemental composition of thin films. RBS uses elastic scattering of a high-energy (typically a few MeV) beam of protons or $^4\text{He}^+$ to determine

the mass of the target elements. The incident beam with mass M_0 , atomic number Z_0 , and energy E_0 hits the sample at an incidence angle α (see Fig. 3-12).

Figure 3-12: Sketch of the RBS process in coatings.

The energy E_0' of the backscattered beam is given by $E_0' = k E_0$, where k is the so-called kinematic factor, which depends on the mass M_1 of the target atoms, M_0 , and the scattering angle θ [101]:

$$k = \left[\frac{\sqrt{M_1^2 - M_0^2 \sin^2 \theta} + M_0 \cos \theta}{M_0 + M_1} \right]^2, M_0 < M_1 \quad (3-21)$$

$$E_1 = E_0 - \Delta E_{in}, \quad (3-22)$$

and

$$E_1' = (E_0 - \Delta E_{in}) \cdot k - \Delta E_{out}, \quad (3-23)$$

in which ΔE_{in} and ΔE_{out} depend on the stopping power of the material.

The backscattered signal is plotted as number of counts per energy channel, as shown in Fig. 3-13. I have used the SIMNRA simulation program [102] to quantify the RBS data. Fig. 3-13 shows the RBS spectrum obtained from a $V_{0.47}Mo_{0.53}N_{0.94}/MgO(001)$ sample using a 2 MeV $^4He^+$ beam incident at 11° and a backscattering angle of 172° . In the spectrum, one can see contributions from Mo, V, Mg, O and N atoms. The signals from heavy elements are easily resolved. RBS is good to detect heavy elements deposited on light substrates, such as V, W and Mo on MgO. However, it is less sensitive to light elements on heavier substrates, for example, resolving N on MgO, due to overlap of the spectral signals, which makes the analysis more difficult.

Figure 3-13: RBS spectra obtained from a $V_{0.47}Mo_{0.53}N_{0.94}/MgO(001)$ thin film.

RBS is used in *Papers I-VI* to determine the chemical composition of the alloy films. All RBS measurements are performed using a 2.0 MeV $^4He^+$ beam incident at 7° - 11° relative to the surface normal with a 172° backscattering angle.

3.5.2. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a surface-characterization technique used for the determination of the surface elemental composition and chemical as well as electronic state of a material.

An XPS spectrum is obtained by irradiating the sample with a monochromatic x-ray beam and analyzing the kinetic energy E_K and number of electrons emitted from, approximately, the first 10 nm of the sample surface [103]. (XPS data presented in this thesis are obtained with a monochromatic Al $K\alpha$ radiation of energy $h\nu = 1486.6$ eV). The binding energy E_B of the photoelectrons emitted from the core levels is specific to the element and is determined as [103]:

$$E_K = h\nu - E_B - \varphi, \quad (3-24)$$

where $h\nu$ is the energy of the x-ray radiation and φ is the work function of the spectrometer.

XPS can also be used to determine the density of states (DOS) of the valence band. Valence electrons are those electrons far away from the nucleus, which are involved in the bonding. Thus, their binding energy is much lower than that of core electrons and their energies in the photoemission spectra are located much closer to the Fermi level.

In TM nitrides with the NaCl-structure, the bonding stems mainly from the interaction of the $2p$ orbitals of nitrogen, with the metal d -orbitals. The valence band structure of TM nitrides is mainly composed of the $2s(N)$ states localized at lower binding energies and those resulting from the interactions between $p(N) - d-e_g(Me)$ orbitals and the metallic $d-t_{2g}(Me) - d-t_{2g}(Me)$ orbitals situated at higher binding energies [40,65,104-106]. Figure 3-14 shows the valence band spectrum obtained from XPS measurements of a $V_{0.5}Mo_{0.5}N_{1.03}$ sample. The peak at ~ 18 eV is attributed to the $s(N) - s(Me)$ orbital interactions in accordance with the DFT calculated DOS of $V_{0.5}Mo_{0.5}N_y$ [107]. The spectral contributions at ~ 6.5 eV and ~ 2 eV are due to the $p(N) - d-e_g(Me)$ and $d-t_{2g}(Me) - d-t_{2g}(Me)$ interactions, respectively.

Figure 3-14: XPS valence band spectrum of a $V_{0.5}Mo_{0.5}N_{1.03}(001)$ thin film.

In this thesis, I have used XPS to explain the ductility enhancement in $V_{0.5}Mo_{0.5}N_y$ by comparing intensities of spectral peaks corresponding to metallic $d-t_{2g}$ states as a function of N concentration, y .

3.5.3. Energy dispersive x-ray spectroscopy

Energy dispersive x-ray spectroscopy (EDX) is an analytical technique used for the determination of elemental composition of a material. EDX can detect, in principle, elements from Be to U in the periodic table, although elements with $Z < 10$ are more

difficult to detect and the accuracy of the data obtained for light elements is lower than for heavier elements. EDX utilizes the characteristic x-rays emitted from the sample when it is irradiated by a high-energy electron beam to determine the composition of the sample. When EDX is performed in the TEM, it gives localized chemical information since the probe used for scanning is of the order of a few nm in diameter (typically less than 5 nm [86]), which provides a good spatial resolution. A quantitative elemental analysis is performed by comparing the peak intensities of emitted x-ray spectra with those of a standard calibration sample of known composition. EDX compositional maps are two-dimensional intensity maps of the desired x-ray spectral lines of the elements. They are obtained by scanning the electron beam across the region of interest and are used to determine compositional variations in the sample [87].

EDX maps are used in this thesis to determine if there are spatial variations in Mo and V composition in the $V_{0.5}Mo_{0.5}N_{0.75}/Al_2O_3(0001)$ films.

3.6. Density functional theory

Density functional theory (DFT) is a quantum mechanical method applied in materials science to predict properties of atoms, molecules, or solids. In DFT, the many-body Schrödinger equation is reduced to a single-particle problem, where the energy is a function of the electronic charge density [108]. DFT calculations are usually performed at 0 K on simulation supercells that are relatively small with a maximum size of some hundred atoms. The simulation supercell is repeated in space by applying periodic boundary conditions in order to account for the large number of atoms contained in real materials, allowing us to calculate the physical and mechanical properties of the films.

The density of states (DOS) is probably the most important electronic structure information of materials. DOS represents the number of electronic states per energy interval, and can be obtained directly from DFT calculations. The DOS function in solids is a continuous distribution, usually plotted with the Fermi level (separating populated and non-populated electronic-states) as the zero energy value.

The DOS function indicates which atomic-orbitals/electronic-states primarily contribute to the formation of chemical bonds, but does not provide direct information about their bonding or anti-bonding characters, and is therefore not sufficient for a detailed analysis of the mechanical properties. To identify the bonding and anti-bonding characters of the electronic-states, the crystal orbital overlap population (COOP) [109] function is commonly used. This technique relies on projection of the DOS into bonding (positive COOP values) and anti-bonding (negative COOP values) states. From the integration of COOP (ICOOP) over all occupied states, one obtains indications of the bond strength. The COOP analysis, however, provides information only regarding the covalent character of the chemical bonds.

To probe the ionic contribution to chemical bonds one can calculate the charge transfer maps. These are obtained in DFT calculations by subtracting the atomic electron densities from the crystal electron density.

Paper II, *Paper III*, and *Paper IV* contain DFT calculations on lattice parameters and elastic constants of $V_{1-x}W_xN_y$ and $V_{0.5}Mo_{0.5}N_y$ alloys. The elastic constants values, more specifically the differences between C_{12} - C_{44} , (called Cauchy pressure) are used as a ductility indicator (see section 3.6.1). *Paper III* shows, in addition to DFT elastic constants and lattice parameters, $V_{0.5}Mo_{0.5}N$ charge density maps and results from COOP calculations, which were also carried out in *Paper IV*. The charge transfer maps and COOP results are used to study the changes in the chemical bonding in $V_{0.5}Mo_{0.5}N_y$.

3.6.1. Elastic constants C_{11} , C_{12} , and C_{44} as a theoretical tool to assess ductility

The most general Hooke's law relates the strain tensor ϵ and the stress tensor σ through the elastic constants C as:

$$\sigma_{ij} = C_{ijkl} \epsilon_{kl}. \quad (3-25)$$

In Eq. (3-25), C_{ijkl} is a matrix with 81 components, which reduces to only 36 due to symmetry of the stress and the strain tensors, i.e. $\sigma_{ij} = \sigma_{ji}$ and $\epsilon_{kl} = \epsilon_{lk}$ [1]. The elastic constants C_{ijkl} are often represented in a contracted notation, C_{uw} , where u and w are integers defined as: 1=xx, 2=yy, 3=zz, 4=yz, 5=zx, and 6=xy [81]. Therefore, eq. (3-25) can be presented as follows:

$$\begin{pmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \sigma_{zz} \\ \sigma_{yz} \\ \sigma_{zx} \\ \sigma_{xy} \end{pmatrix} = \begin{pmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ C_{21} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ C_{31} & C_{32} & C_{33} & C_{34} & C_{35} & C_{36} \\ C_{41} & C_{42} & C_{43} & C_{44} & C_{45} & C_{46} \\ C_{51} & C_{52} & C_{53} & C_{54} & C_{55} & C_{56} \\ C_{61} & C_{62} & C_{63} & C_{64} & C_{65} & C_{66} \end{pmatrix} \begin{pmatrix} \epsilon_{xx} \\ \epsilon_{yy} \\ \epsilon_{zz} \\ \epsilon_{yz} \\ \epsilon_{zx} \\ \epsilon_{xy} \end{pmatrix}. \quad (3-26)$$

For solids with cubic symmetry, there are only three independent elastic constants C_{11} , C_{12} , and C_{44} , which are given by

$$C_{11} = \frac{\sigma_{xx}}{\epsilon_{xx}}, \quad (3-27)$$

$$C_{12} = \frac{\sigma_{xx}}{\epsilon_{yy}}, \quad (3-28)$$

and

$$C_{44} = \frac{\sigma_{xy}}{\epsilon_{xy}}. \quad (3-29)$$

For an isotropic material, C_{11} is related to the Young modulus E , and C_{44} to the shear modulus G [1].

Pettifor [110] proposed that Cauchy pressure, defined as $(C_{12}-C_{44})$, can be used as an indicator to classify a material as brittle or ductile. The changes in $C_{12}-C_{44}$ are connected with the nature of the atomic bonding. If the bonding is more metallic, $C_{12}-C_{44} > 0$, while for more brittle materials with directional bonding, $C_{12}-C_{44} < 0$.

4

SCIENTIFIC RESULTS

4.1. Atomic ordering in $V_{0.6}W_{0.4}N_y/MgO(001)$

Atomic ordering in alloys can result in properties that are different from a compositionally homogenous solid. Tian *et al.* [111] showed that sputter deposited TiWN alloys exhibit ordering in the cation metal sublattice leading to the formation of the Cu-Pt structure. Sangiovanni *et al.* [65] calculated mechanical properties of ordered VWN alloys with Cu-Pt structure. That is, their simulation supercell consisted in an ordered NaCl-structure cell with alternating V-rich and W-rich $\{111\}$ metal planes. In such an ordered VWN, DFT calculations predict enhanced toughness due to a layered electronic arrangement leading to a selective mechanical response under applied stress.

To probe whether this ordering exists in VWN, I have grown $V_{0.6}W_{0.4}N_y/MgO(001)$ alloys at different growth temperatures T_s , ranging from 600 to 900 °C, and investigated the micro- and nanostructure as a function of T_s . The idea is to vary the atomic diffusion by changing the growth temperature.

First, I show that the alloys grow epitaxially with the NaCl-structure on MgO(001) substrates. The alloy films are slightly overstoichiometric at $T_s = 600$ °C, essentially stoichiometric at $T_s = 700$ °C, and understoichiometric at $T_s = 800$ -900 °C, due to the increased N desorption occurring at higher temperatures related with the low reactivity of tungsten with nitrogen [74]. Relaxed lattice parameters a_0 obtained from RSM decrease from $a_0 = 4.185$ Å for films grown at 700 °C to $a_0 = 4.174$ Å at 800 °C to $a_0 = 4.134$ Å at 900 °C, which is consistent with the N loss at higher T_s . In addition, the in-plane and out-

of-plane lattice parameters show that the films deposited at 700 °C are in compression, while the films grown at higher temperatures are in tension.

The observed stresses in the as-deposited film can be due to extrinsic thermal stresses and intrinsic stresses, which originate from crystallographic defects arising during deposition [112]. The thermal stresses arise during cooling from T_s to room temperature due to the differences in thermal expansion coefficients α between the film and the substrate. Thermal stresses are given by the following relationship [112]:

$$\sigma_{th} = E_f (\alpha_f - \alpha_s) (T_s - T), \quad (4-1)$$

in which E_f is the Young modulus of the film, α_f and α_s are the coefficients of thermal expansion of film and substrate, respectively; T_s is the deposition temperature and T is the temperature during measurement. $\sigma_{th} > 0$ corresponds to tensile thermal stresses and $\sigma_{th} < 0$ to compressive thermal stresses.

The coefficient of thermal expansion of VWN, α_{VWN} , is not reported in the literature. However, α_{VN} is $\sim 9.7 \times 10^{-6} \text{ K}^{-1}$ [113] and α of pure V and W are $7.8 \times 10^{-6} \text{ K}^{-1}$ and $4.5 \times 10^{-6} \text{ K}^{-1}$, respectively [114]. The coefficient of thermal expansion of alloys usually varies monotonically depending on α of the two alloying elements. Consequently, since $\alpha_W < \alpha_V$, it is expected that $\alpha_{VWN} < \alpha_{VN}$. α_{MgO} is $14 \times 10^{-6} \text{ K}^{-1}$ [114]. Thus, from eq. (4-1), compressive thermal stresses will be expected in the films. Assuming that $\alpha_{VWN} = \alpha_{VN}$, the compressive strain in the film deposited at 700 °C develops because of differential thermal contraction during cooling. The film is essentially fully relaxed at the growth temperature due to the formation of misfit dislocations during deposition. The films deposited at 800 and 900 °C are, however, in tension. Accounting for differential thermal contraction, the layers remain highly strained with $R = 20\%$ at 800 °C and 55% at 900 °C.

To study if any ordering exists along $\{111\}$ planes, HR-XTEM images and SAED patterns are acquired along the $[110]$ zone axis of $V_{0.6}W_{0.4}N_y(001)$. The SAED patterns from the alloys grown at 600 and 700 °C show 111 diffraction streaks in addition to the fundamental Bragg reflections, which is seen as evidence of stacking faults or lattice defects. In addition, the contrast variations observed in the high-resolution STEM Z-contrast lattice images show alternating brighter/darker contrast along $\{111\}$ planes which demonstrates the onset of W-rich planes on adjacent (neighboring) 111 planes of the cation sublattice. On the contrary, the SAED patterns of $V_{0.6}W_{0.4}N_y(001)$ films deposited at 800 and 900 °C consist of only sharp symmetric reflections with no diffraction streaks, which is characteristic of homogeneous solid solutions, consistent with the HR-TEM images showing uniform contrast. It is likely that the larger N-vacancy concentration observed in the high-temperature samples is favorable to place the larger W atoms into a homogeneous solid solution.

Overall, I demonstrate that cubic NaCl-structure $V_{0.6}W_{0.4}N_y(001)$ films can be grown epitaxially on MgO(001) substrates at temperatures between 600 and 900 °C and that the onset of W-ordering is achieved at $T_s = 600$ and 700 °C. These results are part of *Paper I* (Ref. [89]).

4.2. Structure and mechanical properties of $V_{1-x}W_xN/MgO(001)$

Paper II (Ref. [115]) reports the structure and mechanical properties of epitaxial NaCl-structure $V_{1-x}W_xN/MgO(001)$ thin films with $0 \leq x \leq 0.60$ deposited at 700 °C.

The Gibbs free energy of mixing, calculated using DFT is negative over this compositional range, i.e. these alloys are stable against spinodal decomposition and separation into the equilibrium binary phases cubic-VN and hexagonal-WN.

The in-plane and out-of-plane lattice parameters obtained from RSM measurements reveal that all layers are slightly in compression with residual in-plane strains $\epsilon_{||}$ varying between $\epsilon_{||} = -0.14\%$ with $x = 0$ to $\epsilon_{||} = -0.57\%$ with $x = 0.31$. That is, the film strain increases with the addition of WN into the VN lattice.

I have also grown $V_{1-x}W_xN$ with $x = 0.83$, which, according to the $\theta/2\theta$ XRD scans, is a two-phase mixture of VWN and pure bcc-W. I have not observed any other peaks corresponding to other nitride phases such as cubic- W_2N or hexagonal-WN.

Alloying VN with WN leads to a monotonic increase in relaxed lattice parameters, from $a_0 = 4.12 \text{ \AA}$ (VN) to $a_0 = 4.20 \text{ \AA}$ ($V_{0.4}W_{0.6}N$). The hardness of the alloys increases continuously with the addition of WN, from $16 \pm 1 \text{ GPa}$ in the case of VN to $25 \pm 2 \text{ GPa}$ for $V_{0.4}W_{0.6}N$, while the elastic modulus decreases first from $404 \pm 20 \text{ GPa}$ from VN to $335 \pm 30 \text{ GPa}$ for $V_{0.86}W_{0.14}N$ and then increases continuously up to $376 \pm 40 \text{ GPa}$ for $V_{0.40}W_{0.60}N$. The increase in alloy hardness with decrease in elastic modulus is a first indication of enhanced toughness [116] due to WN alloying.

Cauchy pressures (C_{12} - C_{44}) and shear/bulk moduli ratios (G/B), commonly used as ductility criteria [110,117] for cubic systems, are calculated using DFT. C_{12} - C_{44} are more positive, while G/B is reduced by alloying VN with WN. That is, the $V_{1-x}W_xN$ alloys, irrespective of the WN content in the films, are more ductile (tougher) than the parent binary compound, VN. For example, calculated G/B for VN is 0.60, while it is 0.33 for $V_{0.5}W_{0.5}N$. Cauchy pressures increase from 1 GPa for VN [65] to 140 GPa for $V_{0.5}W_{0.5}N$ [115].

In summary, I show that NaCl-structure $V_{1-x}W_xN$ alloys with $0 \leq x \leq 0.60$, can be grown epitaxially by reactive magnetron sputtering on $MgO(001)$ substrates at 700 °C. The increase in alloy hardness and reduced elastic modulus of $V_{1-x}W_xN(001)$ compared to $VN(001)$, in addition to the more positive Cauchy pressures and lower G/B ratios of the alloy provide an indication of the enhanced ductility/toughness of $V_{1-x}W_xN$ compared to the parent binary compound VN.

4.3. Structure and mechanical properties of $V_{0.5}Mo_{0.5}N_y/MgO(001)$

The enhanced toughness of VMoN alloys was first predicted for a B1-structure VMoN crystal with a specific cation ordering (Cu-Pt) which is composed of alternating $\{111\}$ Mo-rich and V-rich planes. According to DFT calculations [65], this ordered structure produces upon shear stresses, a charge distribution consisting on alternating high and low charge density orthogonal to the applied stress, which allows the material to respond selectively against compressive/tensile and shear stresses [65].

Paper III (Ref. [93]) demonstrates that such ordered structure is not crucial to achieve a high ductility in $V_{0.5}Mo_{0.5}N$ alloys, i.e. the high hardness and increased toughness in $V_{0.5}Mo_{0.5}N$ compared to the binary VN is independent of the atomic ordering.

HR-XTEM micrographs acquired along the $[100]$ and $[110]$ zone axes show that the $V_{0.5}Mo_{0.5}N$ films deposited at $700^\circ C$ are B1 NaCl-structure and exhibit no ordering, i.e. $V_{0.5}Mo_{0.5}N$ films form homogeneous solid solutions. $\theta/2\theta$ XRD scans show single film peaks with no superstructure reflections, and the SAED patterns and HRTEM images indicate that the $V_{0.5}Mo_{0.5}N$ film grows epitaxial on MgO(001): $(001)_{VMoN}|| (001)_{MgO}$ and $[100]_{VMoN}|| [100]_{MgO}$.

The nanoindentation hardness H of $V_{0.5}Mo_{0.5}N(001)$ is more than 25% higher than that of $VN(001)$ ($H_{VN} = 16 \pm 1$ GPa), and exhibit considerable improved wear resistance. In addition, SEM micrographs and SPM images of nanoindenters in $V_{0.5}Mo_{0.5}N(001)$ show, despite the severe penetration, that the material flows without cracking and exhibit material pile-up around the indent edges indicative of plastic flow, which is typically observed in ductile materials. This is to be compared to epitaxial $VN(001)$ and $TiN(001)$ tested reference samples, in which severe cracking is observed starting from the corner of the indent edges, characteristic of brittle ceramics. For these nitrides, cracking is along $\langle 110 \rangle$ directions.

DFT calculations performed on *disordered* $V_{0.5}Mo_{0.5}N$ indicate that the ductility enhancement in these alloys is inherent to cubic $V_{0.5}Mo_{0.5}N$ and arises due to their high VEC, which leads, upon shearing, to the formation of stronger metal-metal bonds along the slip direction and weaker metal-N and metal-metal bonds across the slip plane, favoring dislocation mobility.

To deeper analyze the structure and the mechanical response of $V_{0.5}Mo_{0.5}N$ alloys under different growth conditions, I have deposited $V_{0.5}Mo_{0.5}N_y/MgO(001)$ films at $T_s = 700^\circ C$ under different nitrogen partial pressures PN_2 , ranging from 1 to 5 mTorr. Results from such study are collected in *Paper IV* (Ref. [107]).

Paper IV shows the results on growth, structure and mechanical properties of $V_{0.5}Mo_{0.5}N_y(001)$ films with $0.55 \leq y \leq 1.03$. All the as-deposited films are single-crystals and grow epitaxially on MgO(001), which indicates that $V_{0.5}Mo_{0.5}N_y$ alloys grow cubic with the NaCl-structure over a wide range of N concentrations. In-plane and out-of-plane lattice parameters obtained from RSM indicate that all films grow essentially fully relaxed. Relaxed lattice parameter are found to increase with increasing y , varying from

$a_0 = 4.124 \pm 0.005$ Å with $y = 0.55$, $a_0 = 4.140 \pm 0.005$ Å with $y = 0.72$, $a_0 = 4.175 \pm 0.005$ Å for $y = 0.94$, to $a_0 = 4.195 \pm 0.005$ Å with $y = 1.03$.

The nanoindentation hardness increases with increasing N-vacancy concentration, from 17 ± 1 GPa ($y = 1.03$), to 20 ± 1 GPa ($y = 0.94$), to 22 ± 1 GPa ($y = 0.72$), to 26 ± 1 GPa ($y = 0.55$). This is consistent with the vacancy hardening effect observed for other transition-metal nitrides such as TiN_y [12], where vacancy hardening is attributed to dislocation pinning at the vacancy sites. However, there is no appreciable change in the elastic modulus of the understoichiometric samples, remaining almost constant at ~ 370 GPa, and decreasing to 265 ± 10 GPa for the overstoichiometric alloy. The H/E ratio increases with y for the understoichiometric alloys.

Film ductility is evaluated via nanoindentation experiments. Typical SEM images of nanoindents show ductile plastic flow resulting in material pile-up instead of cracks as commonly observed in brittle TM nitrides. Of all the 40 indents made in four samples, only two of them (one indent in each of the hardest samples, $y = 0.55$ and $y = 0.72$) present a very small crack of length less than 200 nm. These results, compared to severe cracking observed in $\text{VN}(001)$ and $\text{TiN}(001)$, i.e. several cracks with considerable length along $\langle 110 \rangle$ directions around all nanoindented regions, demonstrate that $\text{V}_{0.5}\text{Mo}_{0.5}\text{N}_y$ alloys are significantly tougher than the parent binary compound $\text{VN}(001)$ and $\text{TiN}(001)$ reference samples. $\text{VN}(001)$ is softer than $\text{V}_{0.5}\text{Mo}_{0.5}\text{N}_y$ (compare $H_{\text{VN}} = 16 \pm 1$ GPa with $H_{\text{VMoN}0.94} = 20 \pm 1$ GPa or $H_{\text{VMoN}0.55} = 26 \pm 1$ GPa) and $\text{TiN}(001)$ has a relatively similar hardness ($H_{\text{TiN}} = 23 \pm 2$ GPa). Despite their high hardness, $\text{V}_{0.5}\text{Mo}_{0.5}\text{N}_y$ alloys are more ductile than VN and TiN, as observed in the SEM and SPM images of nanoindented regions. Nanoindentation results are presented in Fig. 4-1 for $\text{V}_{0.5}\text{Mo}_{0.5}\text{N}_{0.94}(001)$, and the reference samples $\text{VN}_{0.89}(001)$ and $\text{TiN}_{0.96}(001)$. Results for $\text{V}_{0.5}\text{Mo}_{0.5}\text{N}_y$ with $y = 0.55$, 0.72 , and 1.03 are essentially similar than for the sample with $y = 0.94$, with the amount of material pile-up decreasing with the N content y .

DFT calculated $\text{V}_{0.5}\text{Mo}_{0.5}\text{N}_y$ Cauchy pressures are much greater than that of VN (compare the C_{12} - C_{44} for $\text{V}_{0.5}\text{Mo}_{0.5}\text{N}_y$ being in the range 76-89 GPa with the 1 GPa for VN), and the G/B ratios are low, of the order of 0.404-0.444, compared to the 0.597 of VN [65]. These results provide a further indication that $\text{V}_{0.5}\text{Mo}_{0.5}\text{N}_y$ alloys, independently of y , are ductile. With the help of additional DFT COOP calculations, the toughness enhancement in $\text{V}_{0.5}\text{Mo}_{0.5}\text{N}_y$ is explained by the presence of stronger covalent metal-N bonds as the N-vacancy concentration increases, which maintains hardness, and at the same time, strong metal-metal bonds which contribute to ductility.

Figure 4-1: (a) SEM image of nanoindentations in 300 nm-thick $V_{0.5}Mo_{0.5}N/MgO(001)$. (b) SPM images of nanoindentations in $V_{0.5}Mo_{0.5}N/MgO(001)$. (c) SEM image of a nanoindentation in 300 nm-thick $VN/MgO(001)$, and (d) SEM image of a nanoindentation in 300 nm-thick $TiN/MgO(001)$. Indentation depths are 400 nm. Image from Ref. [93] (*Paper III*).

In *Paper V*, the structure and mechanical properties of $V_{0.5}Mo_{0.5}N_y/MgO(001)$ layers are investigated as a function of the deposition temperature ($100 \leq T_s \leq 900$ °C). It is found that the nitrogen content y decreases with increasing T_s and varies from $y = 0.64 \pm 0.05$ ($T_s = 900$ °C) up to $y = 1.02 \pm 0.05$ ($T_s = 100$ -500 °C). XRD $\theta/2\theta$ scans and TEM and SAED studies show that films deposited at $T_s \geq 700$ °C are epitaxial single-crystal, while at lower T_s they are highly 002-textured. a_o varies from 4.121 ± 0.005 Å with $y = 0.64$ to 4.212 ± 0.005 Å with $y = 1.02$.

The alloy hardness increases with increasing T_s , as expected due to the higher vacancy concentration in the films deposited at high temperatures. H values are 17 ± 3 GPa for the alloys grown at 100 °C, are essentially constant with $H \approx 20$ GPa for the films deposited at 300-700 °C, and increase to 26 ± 1 GPa for the 900 °C sample. The reduced modulus varies from 274 ± 31 GPa ($T_s = 100$ °C) to 303 ± 10 GPa ($T_s = 900$ °C).

Cracks are never observed in the sample deposited at 900 °C, similar to the samples grown at 700 °C. Only the highly 002-textured film deposited at 500 °C shows cracks. All the other textured layers obtained at lower T_s do not crack. SPM images show material pile-up around the indents in all the samples, irrespective of T_s .

$V_{0.5}Mo_{0.5}N_y$ samples deposited at higher T_s (e.g., 700 and 900 °C) exhibit better wear resistance than those synthesized at lower T_s (300 °C). The coefficients of friction for these films, measured at normal loads of 1 mN, are found to be of the order of 0.09.

XPS analyses of the density of states in the valence band region of single-crystal $V_{0.5}Mo_{0.5}N_y$ deposited as a function of PN_2 and T_s (Fig. 4-2) show an increase intensity of the $d-t_{2g}$ photoelectron peaks with increasing N vacancies, which indicates denser $d-t_{2g} - d-t_{2g}$ metallic orbitals. In contrast, the changes between the $p - d-e_g$ peaks are much smaller. For comparison, the XPS valence band spectrum of VN was also measured, and shows much lower intensity in both first neighbor $p - d-e_g$ and second neighbor $d-t_{2g} - d-t_{2g}$ photoelectron peaks.

The vacancy-induced toughening is explained, by combining experimental hardness and XPS results, as follows: the increase in hardness is most likely due to a combination of strong first neighbor $p - d-e_g$ bonds, as evidenced in the XPS spectra of $V_{0.5}Mo_{0.5}N_y$, and dislocation pinning at the vacancy sites, which is known to increase hardness of the substoichiometric alloys [12,14]. The directional $p - d-e_g$ bonds are called *shear resistant*, while the metallic $d-t_{2g}$ states are referred to as *shear sensitive* orbitals. The increased density of the latter as the N concentration decreases is responsible for enhancing the ductility of these alloys, which combined with the increased hardness demonstrates that the $V_{0.5}Mo_{0.5}N_y$ alloys are:

- (a) tougher than the binary compound VN, and
- (b) tougher as the N content decreases from 1.03 to 0.55.

Figure 4-2: XPS valence band spectra of (a) VN, $V_{0.5}Mo_{0.5}N_{0.94}$, and $V_{0.5}Mo_{0.5}N_{0.64}$; (b) $V_{0.5}Mo_{0.5}N_{1.03}$, $V_{0.5}Mo_{0.5}N_{0.72}$, and $V_{0.5}Mo_{0.5}N_{0.55}$.

In summary:

1) Hardness of the alloys increases with the introduction of N vacancies. This is due to the combination of dislocation pinning at the defect sites and strong $p(N) - d-e_g(Me)$ bonds in $V_{0.5}Mo_{0.5}N_y$ ($0.55 \leq y \leq 1.03$), as evidenced in the XPS photoelectron spectra shown in Fig. 4-2.

2) Typical SEM images of nanoindentations performed in single-crystal $V_{0.5}Mo_{0.5}N_y$ show essentially no cracks. Instead the films present material pile-up around nanoindents indicative of plastic flow.

3) Ductility in $V_{0.5}Mo_{0.5}N_y$ is explained by valence band x-ray photoelectron spectroscopy analyses, which show an enhanced volume density of the shear sensitive $d-t_{2g} - d-t_{2g}$ metallic states in $V_{0.5}Mo_{0.5}N_y$ compared to VN, and the density of these orbitals increases with increasing deposition temperature, i.e., the metallic states become more populated with the introduction of N vacancies.

Additional XPS data of the core levels of $V_{0.5}Mo_{0.5}N_y$ show that the N(1s) photoelectron peaks shift to lower binding energies with increasing N content: from 397.6 eV ($y = 0.64$) to 397.5 eV ($y = 0.94$) to 397.4 eV ($y = 1.02$); while the metal atom peaks shift to higher binding energies by 0.2-0.4 eV [118-120] (see Mo(3p_{3/2}) and N(1s) photoelectron peaks in Fig. 4-3). These results demonstrate that negative charge transfer occurs from metal atoms to N atoms with increasing N content indicating that $V_{0.5}Mo_{0.5}N_y$ becomes less ionic with increasing N-vacancy concentration. These results are presented in *Paper VII* (Ref. [118]) and Refs. [119,120].

Figure 4-3: Mo(3p_{3/2}) and N(1s) XPS photoelectron peaks of $V_{0.5}Mo_{0.5}N_y$ as a function y . Data from Refs. [118] (*Paper VII*), [119] and [120].

4.4. Structure and mechanical properties of $V_{0.5}Mo_{0.5}N_y/Al_2O_3(0001)$

$V_{0.5}Mo_{0.5}N_y$ films are deposited on $Al_2O_3(0001)$ substrates in order to study their structure and mechanical properties as a function of the growth orientation and substrate temperature with $100 \leq T_s \leq 900$ °C.

It is found that the N content in the $V_{0.5}Mo_{0.5}N_y(111)/Al_2O_3(0001)$ films varies from $y = 0.43$ at $T_s = 900$ °C to $y = 0.96$ at $T_s = 100$ °C. The nitrogen content in these films is lower than that in the 001-oriented layers deposited at the same T_s on $MgO(001)$ substrates. This result can be explained as follows. 111-oriented B1-structured crystals are polar with each 111-plane composed of all metal or all N atoms. During film growth, the growth surface is likely to be N-terminated because of high N_2 partial pressures used during sputter deposition. And, since binding energies for N to metal atoms arranged in 111-planes are lower compared to N atoms in (001) planes, they are more likely to desorb from a 111-surface than from a 001-surface.

Figure 4-4: XRD $\theta/2\theta$ scans of $V_{0.5}Mo_{0.5}N_y/Al_2O_3(0001)$ thin films as a function of T_s . The arrows indicate the position of the additional film reflection and * indicates the $V_{0.5}Mo_{0.5}N_y$ 111 peak.

The data in Fig. 4-4 shows, in addition to the Al_2O_3 substrate 0006 reflection at $\sim 41.7^\circ$, two film reflections at each T_s between 100 and 700 °C, which suggest the existence of two phases. One of the peaks is identified as the 111 $V_{0.5}Mo_{0.5}N_y$ reflection. The XRD film peaks for these samples appear at 2θ angles of 37.77° and 37.46° for the film grown at $T_s = 700$ °C, 37.50° and 36.97° at $T_s = 500$ °C, and 37.22° and $\sim 36.01^\circ$ at

$T_s = 300\text{ }^\circ\text{C}$. At $100\text{ }^\circ\text{C}$, the $\theta/2\theta$ scans show an XRD peak at 36.83° and diffuse intensity around $\sim 35^\circ$. At $T_s = 900\text{ }^\circ\text{C}$, only a single film peak is detected, which corresponds to the 111 $\text{V}_{0.5}\text{Mo}_{0.5}\text{N}_{0.43}$ reflection.

Additional RSM are acquired around the 420 film reflection in order to investigate the crystal structure of the second film reflection. A typical example of an RSM of the 111 and 420 reflections of $\text{V}_{0.5}\text{Mo}_{0.5}\text{N}_y/\text{Al}_2\text{O}_3(0001)$ film deposited at $700\text{ }^\circ\text{C}$ are shown in Fig. 4-5(a) and 4-5(b). The RSM in Fig. 4-5(a) shows the 111 reflection of a $\text{V}_{0.5}\text{Mo}_{0.5}\text{N}_{0.54}/\text{Al}_2\text{O}_3(0001)$ layer, which corresponds to an out-of-plane component of the lattice parameter of $a_\perp = 4.130 \pm 0.005\text{ \AA}$. This is consistent with the lattice parameter obtained from the 111 reflection observed in the $\theta/2\theta$ scans at $2\theta = 37.77^\circ$. In addition to the 111 film reflection, diffracted intensity is observed at lower $Q_\perp$ coordinates, which most likely corresponds to the extra reflection detected in the $\theta/2\theta$ scan at $\sim 37.46^\circ$ for the film deposited at $700\text{ }^\circ\text{C}$. If the XRD peak at 37.46° is a 111 reflection of a NaCl-structure crystal, it would correspond to a lattice parameter of $a_\perp = \sim 4.16\text{ \AA}$, which translates in the reciprocal space, presented in Fig. 4-5(b), in $Q_\perp = \sqrt{12}/a_\perp \approx 0.833$. The intensity distribution in Fig. 4-5(b) extends its shape into this area. It is therefore reasonable to consider this extra peak as a reflection which corresponds to grains with the same crystal structure as that of the main matrix/crystal $\text{V}_{0.5}\text{Mo}_{0.5}\text{N}_y$. However, it still needs to be determined if the additional reflections are due to differences in composition, for example, MoN-rich regions or if it is stress related.

Figure 4-5: RSM of $\text{V}_{0.5}\text{Mo}_{0.5}\text{N}_{0.54}(111)/\text{Al}_2\text{O}_3(0001)$ grown at $700\text{ }^\circ\text{C}$. The maps are acquired around the (a) 111 symmetric reflection and (b) 420 asymmetric reflection.

XTEM micrographs of $\text{V}_{0.5}\text{Mo}_{0.5}\text{N}_y(111)/\text{Al}_2\text{O}_3(0001)$ deposited at $300\text{ }^\circ\text{C}$ show that the film exhibits a columnar structure, with approximately 10-nm-wide columns, characteristic of low-temperature growth where surface diffusion is limited. In addition, the SAED patterns show diffraction arcs with an angular dispersion of $\pm 16^\circ$, typical of a 111-textured film. XTEM micrographs of $\text{V}_{0.5}\text{Mo}_{0.5}\text{N}_y(111)/\text{Al}_2\text{O}_3(0001)$ deposited at $700\text{ }^\circ\text{C}$ also show columnar structure in the film but with 30-40 nm wide columns. The

SAED pattern shows single film reflections. No additional reflections that could correspond to the above mentioned extra XRD peak are observed in the SAED patterns.

Results from STEM investigations of $V_{0.5}Mo_{0.5}N_{0.75}/Al_2O_3(0001)$ deposited at 300 °C are presented in Fig. 4-6. The high-angle annular dark field (HAADF), or Z-contrast, image shows brighter regions along the nano-columns and darker regions between columns (most likely voids). Within the columns, contrast changes are also observable. In order to determine the origin of this contrast, whether it is due to variations in composition or thickness, EDX data are acquired from the sample. EDX maps from a region within the STEM images in Fig. 4-6 are shown in Fig. 4-7. The images are color coded for clarity with each of the colors corresponding to the elements Mo, V, and N. The constant/uniform intensities in each of the images indicate that, within the experimental resolution, there are no spatial variations in Mo, V, and N compositions. That is, the data is inconclusive regarding Mo(N) or V(N) segregation in the film.

Figure 4-6: Z-contrast STEM images of a $V_{0.5}Mo_{0.5}N_{0.75}/Al_2O_3(0001)$ thin film deposited at 300 °C. The left and right images show the film microstructure at lower and higher magnifications, respectively.

Figure 4-7: EDX maps of $V_{0.5}Mo_{0.5}N_{0.75}$ showing contributions from Mo, N, and V.

EDX line scans showing spatial variations in Mo and V composition in the $V_{0.5}Mo_{0.5}N_{0.75}(111)$ sample deposited at 300 °C are presented in Fig. 4-8. This data, obtained along the white line in the STEM image (see Fig. 4-8), indicates that the alloy composition is homogeneous, i.e. Mo and V are uniformly distributed across the sample, in agreement with the EDX maps shown in Fig. 4-7. Thus, the second film reflection observed in the XRD spectra is less likely due to compositional changes in the sample. The origins of this second peak are not clear at this time and require further investigation.

Figure 4-8: STEM image of a $V_{0.5}Mo_{0.5}N_{0.75}$ sample with EDX line scan acquired along the white arrow shown as an insert in the upper right corner.

The alloy hardness is found to increase from 15 ± 1 GPa at $T_s = 100$ °C, to 23 ± 2 GPa at $T_s = 900$ °C. In general, hardnesses of the layers deposited on $MgO(001)$ are a few GPa higher than those of the films grown on $Al_2O_3(0001)$, see Fig. 4-9. That is, the 100-oriented films exhibit slightly higher hardness than the 111-oriented, despite the higher N-vacancy concentration observed in the latter ones. Measured E_r values for $V_{0.5}Mo_{0.5}N_y/Al_2O_3(0001)$ layers vary between 220 ± 5 GPa and 318 ± 13 GPa.

Figure 4-9: $V_{0.5}Mo_{0.5}N_y$ hardness and elastic modulus as a function of (a) the N content y and (b) the deposition temperature T_s .

SEM and SPM imaging of nanoindents is used to evaluate the ductility of the $V_{0.5}Mo_{0.5}N_y/Al_2O_3(0001)$ films. $V_{0.5}Mo_{0.5}N_y(111)$ deposited at 900 °C do not present cracks around or near the indented area. SEM images of nanoindents performed in $V_{0.5}Mo_{0.5}N_y(111)$ deposited at 500 and 700 °C do not show cracks as a result of nanoindentation experiments, but surface cracks are instead observed, most likely due to high internal stresses, while at even lower deposition temperatures, 300 and 100 °C, cracks are never observed. Analysis of the SPM files reveal in these cases as well, material pile-up around the indents, typical of ductile materials. The material pile-up decreases with decreasing T_s .

In addition to hardness and indentation modulus, friction and wear tests are also performed in $V_{0.5}Mo_{0.5}N_y(111)$ layers. Wear resistance is found to increase with increasing deposition temperature, which is consistent with the enhanced hardness observed at higher T_s . Friction coefficients measured at normal loads of 1000 μ N are found to be of the order of ~ 0.09 , and ~ 0.16 at loads of 100 μ N.

All these results are part of *Paper VI*.

4.5. Structure and mechanical properties of $V_{1-x}Mo_xN/MgO(001)$

$V_{1-x}Mo_xN_y/MgO(001)$ alloys with $0.2 \leq x \leq 0.7$ deposited at 700 °C are cubic B1 NaCl-structure single crystals as determined by the combination of XRD and TEM analyses. In addition to the 002 MgO reflection at 42.92° , the 002 $V_{1-x}Mo_xN_y$ reflections are observed at angles 43.71° , 43.58° , 43.52° , 43.51° , and 43.38° for $x = 0.2, 0.3, 0.4, 0.55$, and 0.7 , respectively. In-plane $a_{\parallel}$ and out-of-plane $a_{\perp}$ lattice parameters obtained from RSMs increase with increasing MoN content, from $a_{\parallel} = 4.16$ Å and $a_{\perp} = 4.15$ Å with $x = 0.2$ to $a_{\parallel} = 4.20$ Å and $a_{\perp} = 4.18$ Å with $x = 0.7$, as shown in Fig. 4-10. RSM of $V_{1-x}Mo_xN$ films show that the films are relaxed for $x \leq 0.3$ and strained at higher Mo contents with $x > 0.4$.

Figure 4-10: In-plane $a_{\parallel}$ and out-of-plane $a_{\perp}$ lattice parameters of $V_{1-x}Mo_xN_y/MgO(001)$ as a function of x .

$V_{1-x}Mo_xN_y(001)$ alloy hardness is found to increase from $\sim 17.5 \pm 2$ GPa with $x = 0.2$ to 21 ± 3 GPa with $x = 0.3$. The hardness decreases slightly thereafter to 18 ± 3 GPa with $x = 0.4$ and then increases to $\sim 22.5 \pm 3$ GPa with $x = 0.7$ (see Fig. 4-11). The reduced elastic modulus of the alloy films increases first from 314 ± 22 GPa ($x = 0.2$) to 333 ± 20 GPa with $x = 0.3$. Then E_r decreases to 289 ± 25 GPa and increases thereafter to 332 ± 30 GPa with $x = 0.7$.

Figure 4-11: Hardness and reduced elastic modulus of $V_{1-x}Mo_xN_y(001)$ as a function of x .

Fig. 4-12 shows typical SEM images of nanoindentations carried out in $V_{1-x}Mo_xN_y(001)$ alloys. Of all the indents performed in these samples, only 1/9 of the indents present a crack along the edge of the indentation in the samples with $x = 0.2$ and $x = 0.7$. The sample with $x = 0.4$ shows one crack along the edge of 2/9 indentations. This is to be compared with results from $TiN(001)$ and $VN(001)$ reference samples, for which several cracks are observed around the edges of all nanoindents [93].

These results indicate that alloying VN with MoN leads to an increase in hardness (from 16 ± 1 GPa with $x = 0$, to 17.5 ± 2 GPa with $x = 0.2$, and to 22.5 ± 3 GPa with $x = 0.7$), and enhanced ductility, as evidenced in the SEM micrographs of nanoindents, which show significantly improved mechanical response compared to the parent binary compound VN.

Overall, I show that $V_{1-x}Mo_xN_y$ alloys with $0.2 \leq x \leq 0.7$ exhibit enhanced ductility and hardness with respect to the reference binary compound VN.

Figure 4-12: SEM micrographs of indents performed on $V_{1-x}Mo_xN_y(001)$ with (a) $x = 0.2$, (b) $x = 0.3$, (c) $x = 0.4$, and (d) $x = 0.7$. The indenter penetration is 400 nm and the film thickness ~ 400 nm.

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LIST OF INCLUDED PAPERS

Paper I:

Epitaxial $V_{0.6}W_{0.4}N/MgO(001)$: evidence for ordering on the cation sublattice

H. Kindlund, J. Lu, J. Jensen, I. Petrov, J. E. Greene, and L. Hultman

Journal of Vacuum Science and Technology A 2013, **31**:040602

Paper II:

Effect of WN content on toughness enhancement in $V_{1-x}W_xN/MgO(001)$ thin films

H. Kindlund, D. G. Sangiovanni, J. Lu, J. Jensen, V. Chirita, I. Petrov, J. E. Greene, and L. Hultman

Journal of Vacuum Science and Technology A 2014, **32**:030603

Paper III:

Toughness enhancement in hard ceramic thin films by alloy design

H. Kindlund, D.G. Sangiovanni, L. Martínez-de-Olcoz, J. Lu, J. Jensen, J. Birch, I. Petrov, J. E. Greene, V. Chirita, and L. Hultman

APL Materials 2013, **1**:042104

Paper IV:

Vacancy-induced toughening in hard single-crystal $V_{0.5}Mo_{0.5}N_x/MgO(001)$ thin films

H. Kindlund, D.G. Sangiovanni, J. Lu, J. Jensen, V. Chirita, J. Birch, I. Petrov, J. E. Greene, and L. Hultman

Submitted for publication

Paper V:

$V_{0.5}Mo_{0.5}N_x/MgO(001)$ layers grown at 100-900 °C: composition, nanostructure, and mechanical properties

H. Kindlund, G. Greczynski, E. Broitman, L. Martínez-de-Olcoz, J. Lu, J. Jensen, I. Petrov, J. E. Greene, J. Birch, and L. Hultman

In manuscript

Paper VI:

Microstructure and mechanical properties of $V_{0.5}Mo_{0.5}N_x(111)/Al_2O_3(0001)$ thin films

H. Kindlund, J. Lu, E. Broitman, L. Martínez-de-Olcoz, J. Jensen, I. Petrov, J. E. Greene, J. Birch, and L. Hultman

In manuscript

Paper VII:

Sputter-cleaned epitaxial $V_xMo_{(1-x)}N_y/MgO(001)$ thin films analyzed by x-ray photoelectron spectroscopy: 1. single-crystal $V_{0.48}Mo_{0.52}N_{0.64}$

G. Greczynski, H. Kindlund, I. Petrov, J. E. Greene, and L. Hultman

Surface Science Spectra 2013, **20**:68-73

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RELATED PAPERS

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G. Greczynski, H. Kindlund, I. Petrov, J. E. Greene, and L. Hultman

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Sputter-cleaned epitaxial $V_xMo_{(1-x)}N_y/MgO(001)$ thin films analyzed by x-ray photoelectron spectroscopy: 3. polycrystalline $V_{0.49}Mo_{0.51}N_{1.02}$

G. Greczynski, H. Kindlund, I. Petrov, J. E. Greene, and L. Hultman

Surface Science Spectra 2013, **20**:80-85

Hardening and toughening of $VN_x/MgO(001)$ ($0.80 \leq x \leq 1.36$)

A. B. Mei, H. Kindlund, D.G. Sangiovanni, E. Broitman, A. Rockett, L. Hultman, J. E. Greene, and I. Petrov

In manuscript

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CONTRIBUTIONS TO THE FIELD

Probably the two most important and highly desirable properties of structural materials are hardness and ductility. And, often, materials possess one or the other, but not both. As part of my doctoral work, I show that materials with both these properties *can* be prepared.

I show, for the first time, that cubic NaCl-structure pseudobinary alloys of VN with WN and MoN can be synthesized by reactive magnetron sputtering. By measuring hardnesses, elastic moduli of the as-grown VWN and VMoN alloy thin films, along with nano-indented morphologies, I demonstrate here that toughness is enhanced upon alloying.

I have grown cubic $V_{1-x}W_xN_y(001)$ alloys with the NaCl-structure on MgO(001) substrates within a temperature range $600\text{ }^{\circ}\text{C} \leq T_s \leq 900\text{ }^{\circ}\text{C}$. With this thesis I show that the hardness of these alloys increases with increasing WN concentration and that the elastic modulus of the alloys is lower than that of VN, indicative of enhanced toughness of $V_{1-x}W_xN$ due to WN alloying.

I have also synthesized, for the first time, $V_{1-x}Mo_xN_y$ alloys with the NaCl-structure on MgO(001) and $Al_2O_3(0001)$ substrates. It is shown here that $V_{0.5}Mo_{0.5}N_y(001)$ alloys exhibit not only higher hardness (more than 25% higher) than the binary compound VN(001), but also enhanced ductility and toughness. For comparison, I have also evaluated the ductility of a reference single-crystal TiN(001) sample with similar hardness and observed that while TiN(001) severely cracks, $V_{0.5}Mo_{0.5}N(001)$ films never crack and instead exhibit material pile-up typical of ductile materials. The high ductility observed in $V_{0.5}Mo_{0.5}N(001)$ is unusual and generally not expected in hard ceramic films.

In addition to the growth and characterization of stoichiometric films, I have also synthesized substoichiometric (N-deficient) alloys and studied the effect of N-vacancies

on the toughness enhancement in single-crystal $V_{0.5}Mo_{0.5}N_y(001)$ alloys. These results, I believe, are the first experimental demonstration of anion-vacancy-induced toughening in transition-metal nitrides.

My experimental studies of growth and mechanical properties of VMoN thin films validate the recent DFT predictions of toughness enhancement in these alloys. DFT calculations attribute this behavior to an optimal filling of the metallic $d-t_{2g}$ states resulting from a higher VEC of this alloy. XPS measurements of the valence band spectra presented in this thesis show an increase in the density of the $d-t_{2g}$ states of $V_{0.5}Mo_{0.5}N_y$ compared to VN, in agreement with the theory. For $V_{0.5}Mo_{0.5}N_y$ alloys, XPS data reveal that shear-sensitive $d-t_{2g}$ orbital occupancy increases with increasing N-vacancy concentration, and explains the N-vacancy-induced toughening phenomenon.

Finally, through a combination of detailed structural characterization and mechanical property measurements, I show that the observed toughness enhancement in $V_{0.5}Mo_{0.5}N(001)$ is inherent to this alloy and, in principle, independent of the atomic ordering. That is, my results indicate that an ordered structure is not necessary to achieve the combination of high hardness and ductility in these alloys.

Overall, I show that it is possible to synthesize transition-metal nitride films that are both hard and ductile, a highly desirable combination of mechanical properties aspired by material scientists for many years.

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FUTURE WORK

In this thesis, I have focused mainly on the growth and characterization of epitaxial and single-crystalline materials. I have investigated the effect of WN content on toughness enhancement in single-crystal $V_{1-x}W_xN$ alloys over a wide range of WN concentrations; I have shown that both 001- and 111-oriented single-crystalline $V_{0.5}Mo_{0.5}N_y$ films are tough; and that N-vacancy concentration and deposition temperatures influence their mechanical properties. The absence of grain boundaries facilitates interpretation of the results and comparison of the experimental results with theoretical predictions. However, in practical applications, for instance, in the hard coating industry, single-crystalline materials are rarely used, except for diamond. The fairly low deposition temperatures and high deposition rates, commonly employed for large-scale production of the coatings, typically result in polycrystalline films. Therefore, similar studies focused on the growth and characterization of polycrystalline alloy coatings could help successful transition from scientific discovery to practical technology.

It is possible, based on DFT calculations [65,121], that there exist other alloy combinations (e.g., TiN with TaN, MoN, etc.) that could exhibit similar or better mechanical properties, i.e. high hardness and high ductility. Future studies could focus on the growth and characterization of new alloys and explore their mechanical properties.

In Chapter 4 of this thesis and in *Paper VI*, I have presented results from the growth of $V_{0.5}Mo_{0.5}N_y(111)/Al_2O_3(0001)$ thin films. XRD data acquired from these films deposited at T_s between 100 and 700 °C suggest the presence of two phases, one of which is B1-structure VMoN. The exact structure and the composition as well as the origin of the second phase is not known and requires further investigation.

Measurement of the elastic constants C_{11} and C_{44} of thin films is possible, for example, by ultrasonic measurements [14]. In surface acoustic wave (SAW)

measurements, a laser pulse is used to obtain the sound velocity in the material. The elastic constants are given by:

$$C_{11} = \rho v_l^2 \quad (8-1)$$

and

$$C_{44} = \rho v_t^2, \quad (8-2)$$

where ρ is the film density v_l the material longitudinal sound velocity and v_t the material transversal sound velocity. It will be interesting to determine the elastic constants of $V_{0.5}Mo_{0.5}N_y$ and, specially, compare the C_{44} values with that of VN and other hard TM nitrides such as TiN and TiAlN. This is an ongoing project.

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APPENDIX

Copyrights of *Paper I*, *Paper II*, and *Paper VII* belong to the American Vacuum Society.

Author's contributions:

Paper I: I planned and carried out the growth experiments, acquired and interpreted XRD spectra, analyzed TEM and RBS data, and wrote the manuscript.

Paper II: I designed the experiments, deposited the thin films, carried out all the characterization (except TEM and RBS), analyzed and interpreted the experimental results, and wrote the manuscript.

Paper III: I planned the growth experiments and grew the thin films, characterized the as-grown films, except acquiring the TEM images and RBS data, analyzed and interpreted all the experimental results, and wrote the manuscript.

Paper IV: I conceived the study, designed and performed the growth experiments, most of thin film characterization experiments, analyzed the data, and wrote the manuscript.

Paper V: I conceived the study, designed and performed the growth experiments, most of thin film characterization experiments, analyzed the data, and wrote the manuscript.

Paper VI: I conceived the study, designed and performed the growth experiments, most of thin film characterization, analyzed the data, and wrote the manuscript.

Paper VII: I carried out the growth experiments and contributed to the writing of the manuscript.

Papers

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