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A theoretical study of mass transport processes on TiN(001) and mechanical properties of TiN- and VN-based ternaries

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Abstract

This thesis concerns computer simulations, using classical molecular dynamics, of transport processes related to TiN(001) growth. It is motivated from the challenge to understand transport processes at the atomic scale responsible for crystal and film growth and their different growth modes. Not even the most advanced experimental techniques are capable of resolving the sub ps time and sub-Ångström length-scales required. TiN belongs to an important class of transition metal nitrides, and is chosen here as a model system for such fundamental studies of surface transport. The simulations show that on terraces, Ti adatoms exhibit much higher migration rates than N adatoms. For TiN_x complexes, as x increases from 1 to 3, rotation becomes increasingly more prevalent than translation. This leads to surprisingly high mobilities of TiN_2 trimers, higher than that of N adatoms. On islands, Ti adatoms experience a significant funneling effect, resulting in short residence times. TiN dimers and TiN_2 trimers exhibit surprisingly high diffusivities and residence times even shorter than Ti adatoms. TiN_3 trimers, however, are essentially stationary on both terraces and islands and serve as nucleation clusters. Overall, Ti adatoms and TiN_2 trimers are the most efficient carriers of Ti and N atoms with and between TiN(001) surface layers. These results indicate that Ti/N flux ratios close to one promote layer-by-layer TiN(001) growth, whereas lower ratios result in surface roughening. Understanding of these phenomena enables experimentalists to tune the growth processes to optimize material properties.

In this thesis I also carry out theoretical calculations to investigate the role of configurational order on the metallic sublattice in relation to toughness enhancement. My studies set out from the recent understanding that the toughness of transition metal nitrides can be enhanced by tuning the valence electron concentration. My results show that ordered alloys exhibit lower resistance to shear deformations than disordered alloys, and higher resistance to tensile deformation. The lower resistance to shear deformations is explained by the formation of fully bonding electronic states perpendicular to the applied stress. Using the Pugh-Pettifor criterion, it is shown that while configurational order has an effect on the ductility of the material, this is primarily governed by the valence electron concentration.

Preface

The work in this licentiate thesis has been carried out in the Thin Film Physics Group at Linköping University. The aim of the thesis is to provide an understanding of the processes related to the growth of transition metal nitride thin films, in particular TiN, by means of computer simulations. In addition, I investigate the mechanical properties of transition metal nitride ternary alloys.

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Included Papers

- Paper 1** **Dynamics of Ti, N, and TiN_x ($x = 1-3$) ad molecule transport on $\text{TiN}(001)$ surfaces**
D.G. Sangiovanni, D. Edström, L. Hultman, V. Chirita, I. Petrov, and J.E. Greene
Physical Review B **86**, 155443 (2012)
- Paper 2** **Ti and N adatom descent pathways to the terrace from atop two-dimensional $\text{TiN}/\text{TiN}(001)$ islands**
D. Edström, D.G. Sangiovanni, L. Hultman, V. Chirita, I. Petrov, and J.E. Greene
Thin Solid Films 558, 37-46 (2014)
- Paper 3** **The dynamics of TiN_x ($x=1-3$) ad molecule interlayer and intralayer transport on $\text{TiN}/\text{TiN}(001)$ islands**
D. Edström, D.G. Sangiovanni, L. Hultman, I. Petrov, J.E. Greene, and V. Chirita
In manuscript
- Paper 4** **Effects of atomic ordering on the elastic properties of TiN - and VN -based ternary alloys**
D. Edström, D.G. Sangiovanni, L. Hultman, and V. Chirita
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1. INTRODUCTION

Transition metal nitrides are a family of materials which possesses excellent material properties, such as electrical conductivity, high hardness and wear resistance, high melting temperatures, and chemical inertness [1,2]. Due to these properties, they are commonly deposited as thin films for diffusion barriers in microelectronics and wear-resistant coatings on cutting tools to increase their lifetime, and thereby enhancing performance and reducing costs.

1.1. Growth of transition-metal nitride thin films

Considering the industrial importance of transition metal nitride films, surprisingly little is known about the atomistic processes governing their growth. A detailed understanding of film growth would allow experimentalists to optimize deposition conditions in order to tailor the film properties.

Thin film growth is inherently a complex process which is governed by the interplay of both thermodynamic driving forces and kinetic mechanisms. To fundamentally understand the processes controlling nanostructural and surface morphological evolution during growth, detailed information regarding the dynamics of atomic-scale transport on surfaces is required. Experimental techniques, such as scanning tunneling microscopy [3–5] and low-energy electron microscopy [6–8], cannot be used to resolve dynamics on the pico-second time-scale, necessitating the use of computational studies. First-principle techniques have been applied to small systems to study adatom diffusion on static transition-metal nitride surfaces [9–11]. However, the system sizes and time-scales required to study dynamics renders techniques such as Density Functional Theory (DFT) intractable. Classical molecular dynamics (CMD) is thus the primary computational method suitable to investigate the dynamics of atomic-scale processes on compound surfaces.

TiN is one of the most well-characterized transition metal nitride coatings and thin film materials. In addition to accurately determined bulk physical properties, different techniques have been used to study nucleation [9,12], growth [13,14], and surface morphological evolution of TiN surfaces [15]. With this information available, simulation results can be compared to experimental data and verified. This procedure allows for systematic improvement of TiN interaction potentials which can then be used to study film growth processes. Since transition metal nitrides, in general, have similar

properties and structures, TiN thus represents a model system for most transition metal nitrides.

I use CMD to investigate diffusion mechanisms of single adatoms and TiN_x ($x=1-3$) clusters, which have been shown experimentally to be the dominant diffusing species. Papers 1 to 3 as part of this thesis are dedicated to diffusion mechanisms of these species on TiN(001) surfaces and TiN/TiN(001) square islands. The implications for film growth are also discussed herein.

1.2. Toughness of transition-metal nitride alloys

In the last decades a significant amount of effort has been put into improving the protective properties of transition metal nitride coatings, primarily their hardness [16–18]. However, an increase in hardness is in general accompanied by increased brittleness. Brittle films may crack easily, hence lose adhesion to substrates and peel off, thus failing to provide the functionality for which they are designed. To combat this, it is desirable to create coatings with improved toughness. For designing tough coatings, their ductility must be increased, while maintaining their high hardness.

Studies have shown that tuning the valence electron concentration can play a central part in tailoring the mechanical properties of transition metal nitride alloys. This technique was employed to tune the total energies of nitride and carbide phases, thereby promoting stacking fault formation which hinders dislocation glide, resulting in an increase in hardness [19,20]. Similarly, it was demonstrated that precise tuning of the valence electron concentration allows for complete occupation of shear-resistant metal-N bonds, while leaving shear-sensitive metallic states empty [18], thereby maximizing the resistance to plastic deformation.

The technique of tuning the valence electron concentration can also be used to improve ductility. By increasing the valence electron concentration, metallic $d-t_{2g}$ states start to fill. This was shown to result in a layered electronic structure upon shearing which ultimately enhances ductility by promoting dislocation glide [21,22].

The analysis mentioned above was, however, carried out for highly ordered crystal structures, and it is unclear if the same phenomenon should occur in systems with a high degree of configurational disorder. Paper 4 included in this thesis details a study of the effects of configurational disorder on the metallic sublattice of TiN- and VN-based ternary alloys, which were previously predicted to be supertough.

2. METHODOLOGY

I use two computational techniques, CMD and DFT. CMD is computationally efficient, which enables the simulation of large systems, up to 10^5 atoms, for timescales of up to microseconds. This makes it ideal to study dynamic processes related to film growth. The suitability of CMD as a tool depends on the availability and accuracy of potentials for the material system under consideration. For TiN, interaction potentials have recently become available. However, no interaction potentials exist for the ternary systems studied in this thesis.

DFT is rooted in the quantum mechanical description of the system and is a highly reliable and accurate method. It is, however, much more expensive computationally and is thus limited to systems sizes of around 100 atoms and time-scales of, at best, a nanosecond. I use DFT strictly for the calculation of static properties.

2.1. Classical Molecular Dynamics

In CMD atoms are treated as point particles obeying Newton's equations of motion. The interactions between the atoms in the system are modeled using a semi-empirical potential which yields the forces needed to integrate the equations of motion. In my simulations I use the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) software distributed by Sandia National Laboratories [23]. LAMMPS employs the velocity Verlet algorithm to integrate the equations of motion,

$$\vec{r}(t + \Delta t) = \vec{r}(t) + \vec{v}(t)\Delta t + \frac{\vec{f}(t)}{2m}\Delta t^2 \quad (1)$$

$$\vec{v}(t + \Delta t) = \vec{v}(t) + \frac{\vec{f}(t + \Delta t) + \vec{f}(t)}{2m}\Delta t. \quad (2)$$

Here $\vec{r}$, $\vec{v}$, and $\vec{f}$ are the position, velocity, and force, respectively, and Δt is the timestep. The MD-loop is illustrated in Figure 1. For accurate results, the time-step must be short enough to capture the relevant dynamics of the system. I use a time-step of 1 fs. Initial atom positions are set to correspond to the structure that is to be investigated and initial velocities randomly generated to correspond to a Maxwell-Boltzmann distribution at the set temperature.

Figure 1: The Molecular Dynamics loop.

One must also define the statistical ensemble in which the simulation will be carried out. A typical choice is the micro-canonical (NVE) ensemble, in which case the number of particles, volume, and energy are conserved [24,25]. This is the ensemble I use. However, to keep the temperature at the desired value, I also impose a periodic rescaling of the atom velocities to the desired temperature. Other possible ensembles are, for example, the canonical (NVT) and the isothermal-isobaric (NPT) ensembles [24,25]. In order to simulate the true NVT ensemble, it is necessary to use more sophisticated thermostats than velocity rescaling. One option is the Andersen thermostat, in which atoms in the simulation are randomly subjected to elastic collisions with a heat bath prepared at the desired temperature [24,25]. Another possibility is the Nosé-Hoover, which enables deterministic simulation of the NVT ensemble by introducing additional, artificial coordinates and velocities and rewriting the equations of motion [24,25]. A similar approach is required for the sampling of the NPT ensemble [24,25].

2.2. Modified Embedded Atom Method

The behavior of the simulated system will depend on the interaction potential chosen to represent the system. Several interaction potentials of different forms and

complexity have been developed over the years. The arguably simplest potential is the Lennard-Jones potential, a pair potential which depends only on the interatomic distances. The Lennard-Jones potential has two tunable parameters: the position and depth of the potential well. For many systems, more complex potentials that also account for bond angles and screening effects, in addition to interatomic distances, are required.

The potential I employ here is known as the Modified Embedded Atom Method (MEAM) [26]. This potential, which depends on interatomic distances, bond angles, and screening effects, has been shown to reproduce the properties of several fcc, bcc, and hcp metals. MEAM has also been extended to binary and ternary systems, enabling the simulation of transition metal nitride compounds and alloys. The energy of the system in MEAM is given as

$$E = \sum_i \left[F_i(\bar{\rho}_i) + \frac{1}{2} \sum_{j \neq i} \varphi_{ij}(r_{ij}) \right], \quad (3)$$

where $F_i(\bar{\rho}_i)$ is the energy required to embed an atom i within the background electron density $\bar{\rho}_i$ and $\varphi_{ij}(r_{ij})$ is the pair interaction between atoms i and j at distance r_{ij} . This functional form of the potential accounts for many-body interactions via the embedding function, which is of utmost importance when simulating metals.

MEAM was developed from its predecessor, the Embedded Atom Method (EAM) [27], with which it shares the same functional form. The key difference lies in the treatment of the background electron density, $\bar{\rho}_i$. In EAM, the background electron density is given as a sum of spherically averaged atomic electron densities. Because of this spherical averaging, no directional bonding can be included in the model. In MEAM, however, the background density is augmented with angular dependent terms, allowing for the simulation of materials with covalent bonding [26].

The implementation of screening effects in MEAM is presented next. In a many-body system, the interaction between two atoms may be partially, or completely, masked by atoms occupying positions between them. In MEAM, this screening is realized by multiplying the electron density and the pair interaction with a screening function S_{ij} [28]. The screening function is a product of the screening caused by all atoms k . In mathematical terms,

$$S_{ij} = \prod_{k \neq i, j} S_{ijk}. \quad (4)$$

The factors S_{ijk} are determined by constructing an ellipse which passes through the atoms i, j and k . The vector from atom i to atom j defines the x-axis of the ellipse. This ellipse can be expressed as

$$x^2 + \frac{y^2}{C} = \left(\frac{R_{ij}}{2}\right)^2. \quad (5)$$

The amount of screening is determined by two MEAM parameters, C_{min} and C_{max} . If $C \leq C_{min}$, $S_{ijk} = 1$ and if $C \geq C_{max}$, $S_{ijk} = 0$ corresponding to total and no screening, respectively. For $C_{min} \leq C \leq C_{max}$, S_{ijk} is a smoothly varying function from 1 to 0. This is illustrated in Figure 2.

Figure 2: Illustration of the determination of the screening factors. The inner ellipse corresponds to C_{min} and the outer ellipse corresponds to C_{max} . In the illustrated example, the interaction between atoms i and j is partially screened by atom k .

The MEAM parameterization I employ reproduces bulk and surface properties of TiN to an excellent degree. In addition, the parameterization yields adatom formation energies, diffusion barriers and Ehrlich-Schwoebel barriers consistent with experimental results, which is of utmost importance when modeling processes related to film growth.

2.3. Nudged Elastic Band

The nudged elastic band method [29,30] is a technique to find the minimum energy path between two system states. The method entails preparing a number of

replicas, or images, of the system along an initial guessed path between the initial and final states. Typically, this initial guessed path is a straight line from the initial to the final states, with the images placed equidistantly along the line. The minimum energy path is found by minimizing the energy of all the images. To prevent all images from simply converging to the same energy minimum, the images are connected by artificial spring forces. In this way, the true minimum energy path between the two states can be found. I make use of the nudged elastic band method to compute energy barriers for adatom descent from TiN islands.

2.4. Density Functional Theory

In principle, any system can be described by the many-particle Schrödinger equation. When moving to large systems, however, the solution of this equation quickly becomes intractable. In DFT this is overcome by recasting the problem in terms of electron density instead of the many-particle wave-function. This is made possible due to the theorems of Hohenberg and Kohn [31], which state that: (1) the potential $v(\vec{r})$ of a system is uniquely determined, up to an additive constant, by the ground-state electron density $n(\vec{r})$, and (2) the ground state energy is given by the electron density $n(\vec{r})$ that minimizes the energy functional. In this way, the many-electron problem is recast into a minimization in a three-dimensional electron density.

The problem of finding the correct density is further facilitated in the Kohn-Sham scheme [32], in which an auxiliary system of non-interacting particles in an effective potential $v_{eff}(\vec{r})$ is studied. Kohn and Sham showed that for an effective potential given as

$$v_{eff}(\vec{r}) = v_H(\vec{r}) + v_{xc}(\vec{r}) + v(\vec{r}), \quad (4)$$

the non-interacting system will have the same ground state density as the fully interacting system. Here $v_H(\vec{r})$ is the Hartree potential, $v_{xc}(\vec{r})$ the exchange-correlation potential and $v(\vec{r})$ the ionic potential.

Although DFT is an exact reformulation of the Schrödinger equation, in practice several approximations are made which may be possible error sources. Crucially, no exact mathematical form of the exchange-correlation potential is known. However, several approximations exist. The two most common forms are the local density approximation (LDA) [32] and the generalized gradient approximation (GGA) [33,34]. In LDA, the exchange-correlation potential is a function of the local electron density. Specifically, the exchange-correlation is set as the exchange-correlation of a system with

uniform electron density equal to the electron density at that point. In GGA approximations, the exchange-correlation energy is a function of the local electron density, as in LDA, but also of the gradient of the electron density. There are several different GGA approximations available. In my work I use the PW91 GGA potential [34]. All calculations are performed using the Vienna Ab Initio Simulation Package (VASP) using projector augmented wave potentials [35] to describe electron-ion interactions. Further details may be found in the included papers.

2.5. Calculation of elastic constants

Hooke's law states that for sufficiently small deformations of a material the strain is directly proportional to the stress, i. e. the strain components are linear functions of the stress components. This relation is quantified in the elastic stiffness constants C_{ij} . These constants are calculated by applying appropriate distortions to the material and fitting the energy as a function of the magnitude of the distortion. The elastic constants are then found from the second derivatives of these functions. I explicitly calculate the values of $C_{11} - C_{12}$, C_{44} as well as the bulk modulus, B , in this way. The values of C_{11} and C_{12} can then be extracted using the relation

$$B = \frac{C_{11} + 2C_{12}}{3}. \quad (5)$$

Shear modulus, Young modulus, and Poisson ratio can then be calculated according to

$$G = \frac{3C_{44} + C_{11} - C_{12}}{5}, \quad (6)$$

$$E = \frac{9BG}{3B + G}, \quad (7)$$

$$\nu = \frac{1}{2} \left(1 - \frac{E}{3B} \right). \quad (8)$$

The above relations are valid for cubic structures. Most of the crystal structures I study are not cubic. However, it is possible to project the elastic constants onto the closest elastic tensor with cubic symmetry [36,37], where these relations are valid. By calculating these properties, the mechanical behavior of a material can be predicted. Specifically, in relation to my work, the Pugh-Pettifor criterion [38,39] is used to predict whether a material will respond to shear in a ductile or brittle manner. Ductility is associated with values of $C_{12} - C_{44} > 0$ and $G/B < 0.5$.

3. RESULTS

3.1. Paper 1

Dynamics of Ti, N, and TiN_x (x = 1-3) ad molecule transport on TiN(001) surfaces

This paper reports the results of a CMD study on the dynamics of atomic-scale transport on TiN(001) surfaces at 1000 K. Ti and N adatoms are both found to favor adsorption at fourfold hollow sites, surrounded by two N and two Ti terrace atoms. Static energy calculations predict an energy barrier difference of only 0.1 eV between $\langle 100 \rangle$ and $\langle 110 \rangle$ directions. Despite this, Ti adatoms diffuse primarily via single jumps in $[100]$ and $[010]$ directions, with very few diffusion events along $\langle 110 \rangle$ directions observed. However, at finite temperatures terrace N atoms have large vibrational amplitudes and thus hinder diffusion along $\langle 110 \rangle$. In contrast, N adatoms diffuse along $\langle 110 \rangle$ directions through metastable positions atop Ti terrace atoms. Furthermore, diffusion of N adatoms is considerably less frequent than diffusion of Ti adatoms; the diffusion coefficients are determined to be $0.52 \times 10^{-6} \text{ cm}^2/\text{s}$ and $0.26 \times 10^{-6} \text{ cm}^2/\text{s}$, for Ti and N adatoms, respectively.

The stable configuration of TiN dimers is found to correspond to the Ti dimer atom residing in a fourfold hollow site and the N dimer atom on top of a nearest-neighbor Ti terrace atom. TiN dimer migration is observed to occur via three separate pathways: rotation, translation, and a combination of rotation and translation called roto-translation. During a rotation event, the N dimer atom remains anchored on top of a Ti terrace atom while the Ti dimer atom moves to a neighboring fourfold hollow site, passing over a N terrace atom in the process. A translation event proceeds with the dimer atoms simultaneously moving along $\langle 110 \rangle$ orthogonally to the dimer bond. During translation, the Ti dimer atom moves over a N terrace atom while the N dimer atom moves over a fourfold hollow site, before the dimer once again reaches its stable configuration. Roto-translation of TiN dimers, illustrated in Figure 3, is initiated with the rotation of the Ti dimer atom to a bulk position atop a N terrace atom, and followed by a secondary rotation, in which the N dimer atom moves to the vacated fourfold hollow site. The event is completed by translation to the stable configuration, with the Ti dimer atom in a fourfold hollow site and the N dimer atom atop a Ti terrace atom.

Figure 3: Roto-translation of TiN dimer. (a) From the stable configuration, the Ti dimer atom moves on top of a terrace N atom. (b) The N dimer atom moves into the vacated fourfold hollow site. (c) The Ti and N dimer atoms translate concertedly into (d) a new stable configuration.

TiN₂ trimers are found to favor a linear configuration in which the Ti trimer atom is in a fourfold hollow site and the two N trimer atoms on top of Ti terrace atoms. Trimers diffuse via rotation as well as via translation. In a rotation event, one N trimer atom remains anchored on top of a Ti terrace atom, while the two remaining trimer atoms move to bulk positions, so that the trimer is in a linear configuration with the N trimer atoms on top of Ti terrace atoms and the Ti trimer atom on top of a N terrace atom. Continuing the rotation, the non-anchored N trimer atom and the Ti trimer atom move so that the stable configuration is regained. In a translation event, the trimer atoms move simultaneously in a $\langle 110 \rangle$ direction orthogonal to the trimer bonds, so that the trimer remains linear throughout the translation.

The TiN₃ tetramers frequently change shape between a T configuration, in which all tetramer atoms are at bulk positions, and a Y configuration, in which one N tetramer atom resides in a fourfold hollow site. In this way, tetramers rotate continuously. However, this process yields no net migration. Net migration of tetramers only occurs via translation. While the tetramer is in a Y configuration, all atoms move simultaneously in

a $\langle 110 \rangle$ direction so that the Y configuration is maintained until the tetramer has reached a new stable configuration.

In general for TiN_x clusters, it is found that as x is increased from 1 to 3, rotation becomes more frequent and translation becomes less frequent. This results in significantly increased mobility of TiN_2 compared to TiN dimers. DFT calculations reveal that the interaction between the Ti trimer atom and neighboring Ti terrace atoms is significantly weaker than that of Ti dimer atoms. As a result, trimer rotation becomes significantly easier to initiate than dimer rotation, which explains the observed trend.

Since TiN_3 rotation yields no net migration, and rotation is the primary diffusion pathway for these ad molecules, this translates into TiN_3 tetramers remaining essentially stationary. Consequently, TiN_3 tetramers, reside most of the time on epitaxial sites, and lead directly to island growth on $\text{TiN}(001)$.

3.2. Paper 2

Ti and N adatom descent pathways to the terrace from atop two-dimensional $\text{TiN}/\text{TiN}(001)$ islands

This paper reports the results of a CMD study on the descent mechanisms of Ti and N adatoms from 8×8 atom-sized, square, two-dimensional $\text{TiN}/\text{TiN}(001)$ islands. Ti and N adatom migration is found to proceed along the same pathways as on infinite TiN terraces. Ti adatoms diffuse between fourfold hollow sites along $[100]$ and $[010]$ channels, while N adatoms diffuse along $\langle 110 \rangle$ directions passing over metastable sites on top of Ti terrace atoms. As on infinite terraces, N adatoms on islands have significantly higher diffusion barriers than Ti adatoms. Consequently, N adatoms require longer times to reach the island edge and to descend onto the terrace. In addition, Ti adatoms experience a significant funneling effect on islands, which decreases the time required to reach the island edges.

Out of 50, 2 ns MD runs, Ti adatoms descend in 43 cases: 14 times at the island edges, 25 times at the N corner of the island, and 2 times at the Ti island corner. Ti adatoms are found to descend exclusively via the push-out/exchange mechanism. This mechanism is illustrated in Figure 4.

Figure 4: Ti push-out/exchange at island edge. (a) Ti adatom in fourfold hollow at island edge. (b) Ti at bridge position at the island edge, beginning to push out the underlying Ti atom. (c) Completion of push-out/exchange event.

The Ti adatom can move to a saddle-point between an island edge Ti atom and an adjacent N island atom. In this process, the underlying Ti-N bond is stretched and the Ti island edge atom is pushed out slightly. When the Ti-N bond is sufficiently stretched, the Ti adatom moves downward and pushes the Ti island edge atom into an epitaxial terrace site along the island edge. Double push-out/exchange events are also observed, but only at N island corners. When a Ti island atom adjacent to the N corner atom of the island is pushed-out, the N corner atom may be concertedly drawn out with the pushed-out Ti atom, resulting in island corner blunting. Calculations of energy barriers using NEB confirm that the energy barrier for descent via push-out/exchange is lower than that of direct hop over the island edge. On average, the residence time on islands of Ti adatoms is 1.15 ns.

N adatoms are found to descend from islands by both direct hopping over the island edge and by push-out/exchange, depending on the region of island where the descent event occurs. Direct hops dominate at the center of the island edges, whereas push-out/exchange is observed primarily at Ti island corners. At N island corners, both push-out/exchange and direct hopping are observed, with direct hops the more frequent mechanism. Descent by direct hopping proceeds along the following path: from a fourfold hollow site, the N adatom moves along $\langle 110 \rangle$ on top of a Ti island edge atom, after which it directly hops into an epitaxial terrace site adjacent to the island edge. Energy barrier calculations using NEB indicate that direct hopping is favored from all positions, seemingly contradicting the observations. At finite temperatures however, out-of-plane oscillation of island atoms hinders direct hopping. On average, the residence time on islands of N adatoms is 3.94 ns.

Post-descent, atoms are never observed to diffuse along the island edges. Atoms are however observed to move around island corners. Ti atoms can pass N corners by corner rounding and Ti corners by a one-dimensional push-out/exchange mechanism. N adatoms are also observed to pass Ti corners by corner rounding. The corner rounding barriers are relatively easy overcome by one-dimensional push-outs, in the case of adatoms rounding a corner of the same atom type, or by direct rounding in the case of adatoms rounding a corner of the opposite type. This is a consequence of the ionic nature of TiN bonding.

The results show that Ti adatoms on TiN/TiN(001) islands have high mobilities at 1000 K, a reasonable growth temperature, and rapidly descend onto the terrace. Conversely, N adatoms have much lower mobilities and are likely to encounter other adspecies before descending, forming either N₂ molecules, which desorb, or TiN_x admolecules, promoting multilayer growth.

3.3. Paper 3

The dynamics of TiN_x (x=1-3) admolecule interlayer and intralayer transport on TiN/TiN(001) islands

This paper builds on the studies in Papers 1 and 2 by studying admolecule transport on TiN/TiN(001) islands. Diffusion of the studied admolecules on TiN/TiN(001) islands is found to proceed mainly via the same pathways as on infinite terraces. TiN dimers however, diffuse primarily by translation, as opposed to on terraces where rotation is the dominant mechanism. In addition, TiN dimers on islands exhibit a diffusion mechanism not observed on terraces: concerted roto-translation, in which the translation step is parallel to the dimer bond axis.

TiN dimer diffusion events are considerably more frequent on islands than on terraces, and the average residence time of TiN dimers, 0.99 ns, is lower than that of Ti adatoms, 1.15 ns. TiN dimers descend from islands via direct hopping, push-out/exchange, and a combination of the two where the Ti dimer atom pushes out an underlying Ti island atom, and the N dimer atom hops over the island edge. Direct hopping primarily occurs at island edges, while descent via mixed Ti push-out – N hopping mostly occurs at Ti island corners. Descent events involving push-out/exchange of both Ti and N atoms are only observed at N island corners.

TiN₂ trimers are highly mobile adspecies and exhibit the shortest average residence time of the studied admolecules, 0.72 ns. Trimers always descend by hopping over the island edges. From a stable configuration near the island edge, the trimer rotates so that all trimer atoms are in epitaxial sites above island edge atoms, a position from which the trimer atoms concertedly hop over the island edge. Trimer descent from islands may be hindered if they reach N island corners, where they are trapped by the strong interaction between the N corner atom and the Ti trimer atom. The trimers never escape this configuration, which is illustrated in Figure 5.

Figure 5: TiN₂ trimer trapped at island corner.

TiN₃ tetramers are essentially stationary on TiN/TiN(001) islands, as they are on infinite terraces. Throughout the study, a total of only two diffusion events were observed, and tetramers are never observed to descend. Generally, it is thus clear that TiN₃ tetramers, on terraces as well as on islands, lead directly to island growth and are primary promoters of multilayer growth.

Overall, TiN₂ trimers are found to be the most efficient carriers of both Ti and N atoms in terms of interlayer mass transport. TiN₂ trimers are also the most efficient carriers of N atoms in terms of intralayer mass transport on both 8 x 8 islands and infinite flat terraces. With respect to intralayer mass transport of Ti atoms, TiN dimers are the most efficient carriers on 8 x 8 islands, while on infinite flat terraces, the migration of Ti

adatoms is the most efficient form of transport. This demonstrates that Ti adatoms and TiN_2 trimers are the main contributors to promoting two-dimensional growth. In contrast, the formation of TiN_3 tetramers, which are stationary on both terraces and islands, favors multilayer growth. These results indicate that Ti/N flux ratios close to 1:1 promote layer-by-layer $\text{TiN}(001)$ growth, whereas lower ratios may result in surface roughening.

3.4. Paper 4

Effects of atomic ordering on the elastic properties of TiN- and VN-based ternary alloys

This paper reports the results of a DFT study on the elastic properties of selected TiN- and VN-based ternary alloys as a function of atomic ordering on the metallic sublattice. $\text{Ti}_{0.5}\text{Mo}_{0.5}\text{N}$, $\text{Ti}_{0.5}\text{W}_{0.5}\text{N}$, $\text{V}_{0.5}\text{Mo}_{0.5}\text{N}$, and $\text{V}_{0.5}\text{W}_{0.5}\text{N}$ are alloys that have previously been predicted to be significantly more ductile, and hence tougher, than their parent binary alloys. These results, however, were based on calculations of highly ordered structures and the precise effect of the atomic ordering had not been investigated.

The elastic properties of the studied alloys were calculated for five different atomic arrangements: three highly ordered, one fully disordered, and one of intermediate order. The degree of ordering was characterized using the Warren-Cowley short-range order parameter.

The results of the study show that the resistance to shear deformation is reduced considerably upon alloying with Mo or W, as compared to the parent binaries, for all studied atomic arrangements. Comparing the atomic arrangements, ordered structures consistently exhibit lower values of the C_{44} elastic constant than disordered structures, hence lower resistance to shear deformation, and higher values for the bulk modulus and the C_{11} elastic constant, thus higher resistance to tensile deformation.

The low resistance to shear deformation of ordered alloys is explained by the formation of fully bonding metallic states perpendicular to the direction of the applied stress. This effect is illustrated in Figure 6.

Figure 6: Charge density map of a strained ordered structure. The scale is expressed in electrons/ $\text{\AA}^3$.

A similar, but reduced, effect is observed in disordered structures, wherein metallic bonds are formed between every second neighboring $Me - Me$ pair, resulting in a partially bonding metallic state.

The ductility of the studied alloys was evaluated using the Pugh – Pettifor criterion, which associates ductility with positive Cauchy pressures and ratios of $G/B < 0.5$. Results show that while different ordering on the metallic sublattice induces variations in the values of these parameters, all ternary alloys possess ductility superior to the reference binaries. This demonstrates that the experimentally verified toughness enhancements in $V_{0.5}Mo_{0.5}N$ and $V_{0.5}W_{0.5}N$ alloys are primarily an effect of the increased valence electron concentration induced upon alloying.

4. CONCLUSIONS AND FUTURE WORK

In this thesis I have presented results from my studies on the dynamics of Ti and N adatoms and TiN_x ($x=1$ to 3) ad molecules on $\text{TiN}(001)$ terraces and on $\text{TiN}/\text{TiN}(001)$ islands. The results show that Ti adatoms are highly mobile and diffuse along $[100]$ and $[010]$ channels, whereas N adatoms diffuse along $\langle 110 \rangle$ channels and are much less mobile. TiN_x dynamics are characterized by a combination of translation and rotation diffusion pathways, with rotation becoming more prevalent as x increases from 1 to 3. This trend results in surprisingly high mobilities for TiN_2 trimers, on both terraces and islands. Conversely, TiN_3 tetramers are essentially stationary and serve as precursors of multilayer growth. Ti adatoms and TiN_2 trimers are found to be the most efficient carriers of Ti and N atoms within and between surface layers. Hence, the formation of these species promotes two-dimensional growth. The results indicate that Ti/N flux ratios close to one promote layer-by-layer growth, whereas lower ratios result in surface roughening and columnar growth.

Currently, I am performing large scale simulations of TiN growth under two sets of incident energies and two sets of Ti/N flux ratios. The aim of these simulations is to provide a clear picture of how the growth mode of $\text{TiN}(001)$ is affected by altering Ti/N flux ratios and incident energy, by varying the nitrogen partial pressure and substrate bias, respectively. The results presented herein will be used to interpret and analyze the findings of these growth simulations.

The theoretical study of ductility reported herein provides an insight into how the elastic properties of ternary transition metal nitride alloys are affected by variations in ordering on the metallic sublattice. Results show that ordering on the metallic sublattice promotes lower resistance to shear deformation, as well as higher resistance to tensile deformation. The lower resistance to shear deformation is explained by the formation of bonding states perpendicular to the applied stress upon shearing. It is thus shown that the ductility of the studied alloys, while affected by ordering on the metallic sublattice, is superior to the reference binaries. The calculations demonstrate that the experimentally observed toughness enhancement in these alloys is primarily an effect of the increased valence electron concentration, which is induced upon alloying.

A possible extension of this work is to proceed with studying ductility enhancement in transition metal carbides, which are also well known hard materials.

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