Microstructural Characterization and Hardening Behavior of Reactive Magnetron Sputtered TiN/Si$_3$N$_4$ Multilayer Thin Films

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Cover figure: Interior view of the deposition chamber with both targets ignited. The titanium target is located in front whereas the silicon target can be seen in the background. For details see section 3.1.

Title page figure: Superlattice reflections observed with TEM. These originate from the highly ordered structure within a multilayer thin film. This specific sample has a wavelength of 7.3 nm (4.5 nm TiN/2.8 nm Si₃N₄).

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It doesn’t matter how beautiful your theory is, it doesn’t matter how smart you are. If it doesn’t agree with experiment, it’s wrong.
-Richard P. Feynman
Preface

The work presented in this licentiate thesis has been carried out during 2003-2004 at the Division of Engineering Materials at Luleå University of Technology (LTU) and to some extent also at the Thin Film Physics Division at Linköping University (LiU).

First of all to my supervisors, Professor Magnus Odén (LTU) and Professor Lars Hultman (LiU) to whom I owe a lot of thanks for giving me this chance and introducing me to the marvelous world of thin films, and also for their support and guidance, especially during those moments when my brain was out of order. Special thanks to Dr Jon Molina for his invaluable help during those long deposition runs and to Anders Hörling and Christian Schlauer for educating me in the delicate task of how to master an ion mill. I would also like to thank Dr Bill Clegg and Finn Giuliani at the Department of Materials Science and Metallurgy, University of Cambridge, for taking care of me during my visit and giving me the opportunity to use their FIB equipment. Additional thanks for inviting me to a very pleasant festivity, hopefully we will have the opportunity to do that again. To my fellow colleagues at the Division of Engineering Materials, thanks for being there and providing support when I have needed it. Finally I would like to thank Annica for her love and encouragement before and throughout this work, and particular for bearing with me during these final weeks when I have put this thesis together.

Hans Söderberg
Luleå, November 2004
Abstract

This licentiate thesis adds a new piece to the puzzle that describes how the microstructural characteristics influence the hardness behavior of a multilayer coating. It contains a presentation of the manufacturing and the subsequent characterization of multilayer thin films. These multilayers consist of alternating layers of crystalline titanium nitride (TiN) and amorphous silicon nitride (Si₃N₄), deposited with a physical vapor deposition technique referred to as reactive magnetron sputtering. The microstructure of as-deposited films was examined with cross-sectional transmission electron microscopy (XTEM) and x-ray diffraction (XRD).

XRD studies revealed a transition in preferred orientation for TiN, from a pure 002 orientation to a mixed 111/002 orientation as the TiN layer thickness increased from 4.5 nm to 9.8 nm. XTEM studies showed a microstructure consisting of equiaxed or elongated TiN grains, depending on layer thickness, limited in size by the amorphous interlayers. Selected area diffraction verified the observed transition in preferred orientation in TiN. For small silicon nitride layer thicknesses (~0.3 nm) an epitaxial stabilization of Si₃N₄ to the crystalline TiN lattice was observed through high resolution electron microscopy studies. Instead of amorphous interlayers a cubic silicon nitride rich phase (SiNx) was observed. This is to the present knowledge of the author the first time this phenomenon has been observed within this material system. In order to explain the observed behavior a model based on the involved energies were developed.

Nanoindentation was performed to evaluate the mechanical behavior of the coatings as the layer thicknesses varied. All multilayers were harder than the monolithic TiN film, which had a hardness of 18 GPa compared to 32 GPa for the hardest multilayer. An interesting observation was that the hardest multilayer corresponds to the presence of cubic silicon nitride. Curvature measurements were performed and showed that the residual stresses within the multilayers were compressive and relatively constant, 1.3±0.7 GPa. In addition to the XTEM studies of as-deposited samples, XTEM studies of deformed multilayers were also conducted. The 300 mN load produced plastic deformation in the substrate under the indent. Cracks within the multilayer normally propagated along TiN/Si₃N₄ interfaces, which suggest that a lower energy is needed for cracking along an interface compared to intralayer cracking.

The observed hardness increase can be ascribed to the multilayered structure of these films. By the interruption of TiN growth with intermittent Si₃N₄ layers the produced microstructure consisted of small TiN grains, separated in the growth direction by amorphous or crystalline interlayers. Small grains are known to contribute to hardening, but the interlayers also contribute, acting as dislocation obstacles either due to the amorphous tissue or to coherency stresses.
Appended papers

I. Nanostructure formation during deposition of TiN/Si$_3$N$_4$ nanomultilayer films by reactive dual magnetron sputtering
Hans Söderberg, Jon M. Molina-Aldareguia, Lars Hultman, and Magnus Odén
Submitted to Journal of Applied Physics

II. Epitaxial stabilization of cubic-SiN$_x$ in non-isostructural TiN/Si$_3$N$_4$ multilayers
Hans Söderberg, Jon M. Molina-Aldareguia, Tommy Larsson, Lars Hultman, and Magnus Odén
Manuscript in final preparation
List of symbols

CVD  Chemical Vapor Deposition
FIB  Focused Ion Beam
HRTEM  High Resolution Transmission Electron Microscopy
PVD  Physical Vapor Deposition
SAD  Selected Area Diffraction
SEM  Scanning Electron Microscopy
TEM  Transmission Electron Microscopy
UHV  Ultra High Vacuum
XRD  X-Ray Diffraction
XRR  X-Ray Reflectivity
XTEM  Cross-sectional Transmission Electron Microscopy

\(a\)  Lattice parameter (nm)
\(d\)  Lattice spacing (nm)
\(E\)  Elastic modulus, Young’s modulus (GPa)
\(E\)  Total lattice energy (J/m\(^3\))
\(E_{el}\)  Elastic energy (J/m\(^3\))
\(F(h)\)  Cross-sectional area of indenter at a distance \(h\) from its tip (m\(^2\))
\(G\)  Shear modulus (GPa)
\(H\)  Hardness (GPa)
\(h_{max}\)  Maximum indent depth (nm)
\(k\)  Incident wavevector (m\(^{-1}\))
\(k'\)  Scattered wavevector (m\(^{-1}\))
\(\Delta k\)  Change in wavevector due to scattering (m\(^{-1}\))
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>$L_{\text{max}}$</td>
<td>Maximum load (mN)</td>
</tr>
<tr>
<td>$r^{(A)}$</td>
<td>Deposition rate of compound A (Å/s)</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature (K)</td>
</tr>
<tr>
<td>$T_m$</td>
<td>Melting temperature (K)</td>
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<tr>
<td>$t_f$</td>
<td>Film thickness (µm)</td>
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<td>$t_s$</td>
<td>Substrate thickness (µm)</td>
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<td>$R$</td>
<td>Radius of curvature (m)</td>
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<tr>
<td>$\alpha$</td>
<td>Thermal expansion coefficient (K$^{-1}$)</td>
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<tr>
<td>$\gamma$</td>
<td>Surface energy (J/m$^2$)</td>
</tr>
<tr>
<td>$\gamma_{ch}$</td>
<td>Chemical contribution to surface energy (J/m$^2$)</td>
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<tr>
<td>$\gamma_{st}$</td>
<td>Structural contribution to surface energy (J/m$^2$)</td>
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<tr>
<td>$\delta$</td>
<td>Lattice misfit (%)</td>
</tr>
<tr>
<td>$\delta$</td>
<td>$1-\delta$ equals the real part of the volume average refractive index (-)</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>X-ray wavelength (nm)</td>
</tr>
<tr>
<td>$\Lambda$</td>
<td>Bilayer thickness (nm)</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Poisson’s ratio (-)</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Diffractometer angle (°)</td>
</tr>
<tr>
<td>$\theta_m$</td>
<td>Reflection angle for superlattice reflection number m (°)</td>
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</tbody>
</table>
Contents

1. Introduction ................................................................................................ 1
   1.1 Thin films ............................................................................................... 2
   1.2 Multilayers ............................................................................................. 2

2. Materials ..................................................................................................... 4
   2.1 Titanium nitride ....................................................................................... 4
   2.2 Silicon nitride ......................................................................................... 4

3. Experimental methods ................................................................................ 5
   3.1 Physical vapor deposition ........................................................................ 5
   3.2 X-ray diffraction ..................................................................................... 7
   3.3 X-ray reflectivity ..................................................................................... 10
   3.4 Nanoindentation ...................................................................................... 12
   3.5 Curvature measurements ....................................................................... 13
   3.6 Transmission electron microscopy ....................................................... 14
   3.7 Focused ion beam .................................................................................. 15

4. Experimental results ................................................................................. 17

5. Future work ............................................................................................... 25

References ..................................................................................................... 26

Paper I ........................................................................................................... 35

Paper II ......................................................................................................... 55
1. Introduction

Diamond has always been the hardest material known to man, and still is today. However, through the engineering of material at a nanometer level new promising materials have been manufactured. In the field of nano-engineering, surface coatings have been in the front line for decades, evolving from the classic monolithic titanium nitride coating to the advanced multilayer, nanocomposite coatings of today. In Fig. 1.1 a hardness comparison between several different materials is shown. In the low hardness region we find metals such as aluminum and steel. At slightly higher hardness, ceramic AlN and TiN coatings are located. With the deposition of alternating layers of materials, for instance TiN/Si₃N₄ and TiN/VN the hardness can be increased even further. Cubic boron nitride films have been reported with hardness values of 60 GPa. Finally, highest hardness is found for diamond (α-C). Hardness levels that previously were exclusive for diamond and cubic boron nitride can nowadays be reached by tailoring the microstructure and chemical composition of laminated and composite coatings.

![Hardness comparison graph](image)

Figure 1.1. Hardness values for various materials. Aluminum, steel, and diamond values are for bulk material, whereas the other values are for deposited films, AlN, TiN and TiN/Si₃N₄, TiN/VN, cubic−BN.

The remaining part of this chapter will be devoted to an introduction to thin films and multilayer structures. In chapter two the different materials used in this work will be introduced. Experimental equipment and methods are presented in chapter three. Chapter four will give a recapitulation of results obtained during this work. Thereafter the remaining part of this licentiate thesis is dedicated to the appended papers.
1.1 Thin films

The market for thin films is increasing year by year, and nothing indicates that this trend is about to change. A wide range of different applications exists, dedicated to enhance or modify the properties of a material or product. Possible modifications by thin film deposition quickly produce a long list, for example high or low friction, electrically conductive or non-conductive, different optical and magnetic properties, corrosion resistance, and finally high hardness and wear resistance.

By the deposition of a hard and wear resistant coating, the lifetime for a component exposed to contact wear can increase significantly. Reports of a more than 10 times increase in lifetime exist. This is only one example of the drastic change in properties possible by the deposition of a surface coating. Before continuing, a definition of a thin film is in order. How thin is thin? No well defined limit exists, but an adequate limit is from a couple of tens of a micrometer and below. A term frequently used to denote a thin film deposited in only one material is monolithic, which means constructed as one uniform piece, i.e. a single crystal or other single piece of material.

A wide variety of deposition techniques exist. Two main classes can be distinguished, physical vapor deposition (PVD) techniques and chemical vapor deposition (CVD) techniques. PVD has solid source material that is sputtered or evaporated, material that subsequently condenses on the substrate. CVD on the other hand utilizes gas phase source materials that are intermixed and heated whereupon reaction and deposition occurs. A deeper discussion of PVD and especially reactive magnetron sputtering follows in section 3.1.

1.2 Multilayers

Multilayers are a subclass of thin films where alternating layers of different materials are deposited. An illustration of a TiN/Si$_3$N$_4$ multilayer is shown in Fig. 1.2. Two consecutive layers are denoted bilayer, and its thickness is referred to as wavelength ($\Lambda$).

![Figure 1.2. Illustration of a multilayer thin film consisting of alternating layers of TiN and Si$_3$N$_4$. $\Lambda$ corresponds to the bilayer thickness.](image)

Through the combination of different materials and an optimization of the microstructure, hardness values well beyond the constituent materials can be obtained. The observed hardness enhancements appear as the layer dimensions shrinks and reach the nanometer region. This has been shown by researchers the last decades, and hardness increases
1. Introduction

exceeding 100% have been reported. The hardness enhancements are observed in a wide variety of material systems, e.g. metal/metal multilayers, metal/ceramic, and ceramic/ceramic. The common denominator with these studies is that hardness increases with a decrease in layer dimensions, and often this increase is followed by a decrease for a further reduction in wavelength.

Several explanations to the observed phenomenon have been proposed. Among the first was Koehler who 30 years ago theoretically showed that a hardness increase is expected within a material with a lamellar structure. This increase arises from image forces on the dislocations due to a shear modulus difference between the different layers. Koehler also suggested that the layer thickness should be kept small, so that a dislocation source cannot operate inside. Several other theories try to explain the observed hardness increase. In coherency stress hardening dislocation movement is restricted due to stress fields at coherent interfaces within the structure. Orowan-like strengthening, where plastic deformation occurs by dislocation movement and bowing inside layers. For Hall-Petch strengthening the hardness increase is a result of grain size reduction, thus an increase in grain boundary area, grain boundaries that subsequently act as dislocation obstacles. However there are reports indicating that Hall-Petch strengthening lose validity for small layer thicknesses. Finally, an epitaxial stabilization effect, where a metastable phase is grown, often occurring for thin layer thicknesses as a way to minimize the surface energy, e.g. a normally amorphous material that is stabilized into a crystalline structure for small layer thicknesses. All the theories mentioned above are originally designed for crystalline and polycrystalline materials, while the effect from amorphous layers are neglected. According to Koehler his theory is still valid, however this has not been confirmed.

A special case of multilayers are the superlattices, which also consist of a layered structure. However, in a superlattice the different materials grow as a single crystal, thus coherent interfaces, throughout the film. This is possible if the deposited crystalline materials have a small lattice mismatch, so that no large coherency stresses build up.

In this work crystalline titanium nitride (TiN) and amorphous silicon nitride (Si₃N₄) multilayer thin films of various wavelengths have been grown. The ternary Ti-Si-N system is interesting due to the extreme hardness enhancement reported within this material system for nanocomposite coatings, where the hardness of diamond is approached. In this work a multilayer configuration was chosen, as it results in a two-dimensional structure which simplifies the microstructural examination, and especially the interfacial analysis compared to a film grown as a nanocomposite. This system with a reduced dimensionality will aid in the effort of linking any hardness maxima with the microstructure of the multilayers, thus to test the present models describing superhardening effects in nanolaminate systems.

The repeated interruption of the TiN with the deposition of amorphous interlayers forces the subsequent TiN layers to renucleate, due to the lack of crystal registry with the underlying material. This should ensure small TiN grains throughout the film, which implies that if the classic Hall-Petch relation is applicable, a hardness increase will occur. Amorphous interlayers should also act as dislocation obstacles, thereby prohibiting the propagation of dislocations throughout the structure, thus contributing to hardness.

The microstructure is characterized with x-ray diffraction and transmission electron microscopy, whereas the mechanical properties are examined by nanoindentation and curvature measurements. For a detailed view of the experimental details see chapter 3.

Nanocomposite thin films are produced by co-deposition of immiscible materials, e.g. TiN and Si₃N₄, which results in a 3-D structure with nanocrystalline islands or columns within an amorphous matrix.
2. Materials

2.1 Titanium nitride

This transition metal nitride is one of the most diverse coatings, and its applications are found within a variety of technological areas, for example as wear resistant and hard coating on cutting tools and drills, as coating within the medical and health area due to its non-toxic nature, and as diffusion barrier in microelectronics. Titanium nitride (TiN) has also found a market as a decorative coating due to its golden color. Its usefulness is explained by the material properties. It has a rocksalt structure (FCC bravais lattice) with a unit cell consisting of four formula units, shown in Fig. 2.1. The lattice parameter is equal to 4.240 Å. On top of its high hardness of roughly 18 GPa it has a high melting temperature of 3290°C, and the density is 5.43 g/cm³.

![Figure 2.1. Illustration of a TiN lattice. It has a rocksalt structure with four formula unit in each lattice cell, 4 Ti and 4 N atoms.](image)

2.2 Silicon nitride

Silicon nitride (Si₃N₄) is polymorphic and therefore exists in several phases. Hexagonal α and β, amorphous, and also a high pressure, high temperature cubic polymorph. Si₃N₄ has excellent thermal shock resistance due to its low thermal expansion coefficient, and this property together with its high hardness of roughly 25 GPa makes Si₃N₄ suitable for wear resistance coatings. Other areas of use for Si₃N₄ is within electronics, e.g. as diffusion barriers in semiconductors and as an insulator layer. Within the amorphous Si₃N₄ network the Si-N distance is 1.74 Å, and each silicon atom is bonded to four nitrogen atoms. The melting temperature of Si₃N₄ is 1900°C, and the density 3.2 g/cm³.
3. Experimental methods

3.1 Physical vapor deposition

As mentioned in the introduction a vast number of different depositions techniques exist on the market. In this work a system based on a physical vapor deposition (PVD) technique was used. The equipment consisted of an unbalanced reactive dual magnetron sputtering apparatus, where the main component was an ultra high vacuum (UHV) chamber able to reach base pressures below $10^{-3}$ mTorr ($\approx 1.3 \times 10^{-4}$ Pa). A schematic interior view of the vacuum chamber is shown in Fig. 3.1. In the upper part of the chamber the two magnetrons were located, which are water-cooled copper cylinders that are able to produce magnetic fields, however, more of this later. The materials to be deposited are manufactured as high purity circular discs, 75 mm in diameter, also referred to as targets. These were mounted on the magnetrons. Underneath the targets a pair of computer controlled shutters was located. By opening and closing these shutters the material to be deposited was determined. In the lower part of the chamber a rotary substrate holder was positioned, where two substrates at a time can be deposited. In this work the substrates consisted of single crystalline silicon wafers (100), 10x10x0.5 mm$^3$ in size. Below the substrate holder a heater and a copper coil were located.

![Schematic view of the cylindrical deposition chamber](image)

When the base pressure was reached ($<10^{-3}$ mTorr), argon and nitrogen gas were introduced to the chamber at partial pressures of 4.0 and 0.5 mTorr respectively, i.e. a mixing ratio of 8:1. Constant currents of 0.8 A and 0.2 A were fed to the titanium and silicon targets respectively, which resulted in a negative potential of roughly 350 V over the targets. The applied voltage caused argon ions ($\text{Ar}^+$) to accelerate towards the targets, where they impinged. Despite being a noble gas, Ar ions are naturally occurring within the gas. If the impinging ions have enough energy (momentum) ejection of target material will occur$^b$, which is referred to as sputtering. The ejected material then propagates through the chamber and condenses on the substrate. A schematic view of the sputtering process is shown in Fig. 3.2, where one incident ion ejects a cascade of target material, e.g. secondary electrons, ions/neutrals, photons, but also backscattered incident ions/neutrals.

$^b$ The surface binding energy must be overcome in order for sputtering to occur.
3. Experimental methods

Figure 3.2. Illustration of the species involved in the sputtering process. An incident ion impinges with the target and ejects a cascade of different species.

The ejected electrons ionize additional Ar, which is subsequently accelerated towards the substrate, causing the process to repeat itself, thus the plasma becomes self sustaining. Nitrogen molecules are dissociated by the electrons, thus forming free ions, which in turn react with titanium and silicon forming TiN and Si₃N₄. The ejected material is spread throughout the chamber, and in order to achieve a higher degree of target material arriving at the substrate, the coil in the base of the chamber is used. A coil current of 5 A induces a magnetic field that will connect with the magnetic field from the exposed magnetron. This can be observed in Fig. 3.3 where the exposed Ti target is located in front and consequently the unexposed Si target can be seen in the background. In the lower part of the figure the substrate holder is located. The produced plasma is stretched out by the applied magnetic field, thus continuing down to the substrates. This increases the effectiveness of the process as the deposition rate increases due to higher ion current density at the substrate.

Figure 3.3. Deposition of TiN at which time the Si target’s line of sight is blocked by a shutter (seen in the background). The plasma is elongated down to the substrates due to the coupled magnetic fields produced by the magnetron at the top and the coil at the base.
3. Experimental methods

A negative potential called bias was applied over the substrate, which attract Ar⁺ in a similar fashion as the potential does at the magnetrons. However, the bias voltage was kept lower than the target voltage, resulting in a lower momentum transfer upon impingement. Voltages used in this work were roughly -350 V at the targets, compared to -50 V at the substrates. This low energetic bombardment was to promote ad-atom mobility resulting in a well defined layer-by-layer growth, i.e. a densification of the growing film and an elimination of voids. However, the bombardment can also induce compressive stresses in the film due to collision cascades resulting in atom entrapment. A deeper discussion of deposition induced stresses follows in section 3.5.

Further reading on this particular deposition system, including both plasma studies and current probe measurements can be found elsewhere.36

All films except the monolithic Si₃N₄ were grown on a 50 nm TiN bufferlayer. The deposition of a bufferlayer enhances the adhesion between substrate and film by forming a crystalline foundation for the multilayer to grow on. The multilayers were grown in two sets, one with constant TiN layer thickness, and one with constant Si₃N₄ layer thickness. See chapter 4 for details. The final film thicknesses were approximately 1 µm.

3.2 X-ray diffraction

X-ray diffraction (XRD) is a powerful technique to examine the crystallographic orientations within a material. In short, the process needs an x-ray source, a sample, and a detector, as shown in Fig. 3.4. Between source and sample and also between sample and detector, various slits and also a monochromator are located. In the source, electrons are emitted from a filament and subsequently accelerated towards a copper (Cu) anode. Upon impingement with the Cu anode both continuous radiation (bremsstrahlung) and characteristic radiation are produced. Bremsstrahlung is emitted when the impinging atoms deflects from their path due to electron-atom interactions, whereas characteristic radiation originates from electron transitions within the atom. This is why a monochromator is necessary, as it sort out specific energy intervals, i.e. wavelengths, so that the radiation used is as well defined as possible. The wavelength used in this work were CuKα, which consist of two narrow peaks Kα₁ and Kα₂, with intensity ratio 2:1 and wavelengths of 1.54056 Å and 1.54439 Å respectively.37

![Figure 3.4. Simplified figure of the diffractometer setup. X-rays are emitted from the source to the left, diffracted in the material, and subsequently collected in the detector to the right. Incident angle is θ, whereas the diffracted angle corresponds to 2θ. Different configurations regarding slits and apertures are possible, in this figure the divergence and receiving slits are included.](image)
3. Experimental methods

Upon impact with the sample the x-rays will interact with the atoms in the lattice, causing x-ray scattering in all directions. However, in specific direction constructive interference give rise to a diffracted signal, whereas in other directions, only the background noise will be present due to destructive interference. A schematic view of this process is shown in Fig. 3.5, where a lattice subjected to radiation is depicted.

![Figure 3.5. X-ray diffraction within a lattice. X-rays are incident from the left, and diffracted to the right. \( \theta \) corresponds to the incident angle, \( d \) to the interplanar distance, and 2\( x \) equals the path difference for the two x-rays.]

In Fig. 3.5 \( d \) corresponds to the interplanar atom spacing. For constructive interference to occur the difference in traveled path for two different x-rays must be equal to an integer number (n) times the x-ray radiation (\( \lambda \)), i.e. the path difference, \( \Delta \), between location A and location B in Fig. 3.5 must be equal to \( n\lambda \). From the geometry in Fig. 3.5 and the condition of constructive interference the following must apply,

\[
\Delta = n\lambda = 2x ,
\]

\[
x = d \cdot \sin \theta .
\]

Combining Eq. 3.1 and 3.2 results in the well known Bragg’s law,

\[
n\lambda = 2d \cdot \sin \theta .
\]

A three dimensional construction of Bragg’s law is shown in Fig. 3.6. Here the incident and scattered x-rays are described by wavevectors \( \mathbf{k} \) and \( \mathbf{k}' \) respectively. As complete elastic scattering is assumed the magnitudes \( |\mathbf{k}| = |\mathbf{k}'| = 2\pi/\lambda \), and the difference between incident and scattered beam is referred to as scattering vector, \( \Delta \mathbf{k} \), thus \( \mathbf{k} + \Delta \mathbf{k} = \mathbf{k}' \). The conditions that must be satisfied in order to obtain constructive interference is expressed by the three Laue equations,

\[
a_1 \cdot \Delta \mathbf{k} = 2\pi h , \quad a_2 \cdot \Delta \mathbf{k} = 2\pi k , \quad a_3 \cdot \Delta \mathbf{k} = 2\pi l
\]

where \( a_1 \), \( a_2 \), and \( a_3 \) are the primitive vectors of the lattice. A way to visualize this is through the use of a construction called Ewald’s sphere and by using the reciprocal lattice.38
3. Experimental methods

At specific angles $\theta$, all three Laue equations are fulfilled, which results in a peak in the diffractogram for that specific angle. In Fig. 3.7 a diffractogram from a monolithic TiN film is shown. The peaks originate from the crystalline Si substrate, and from TiN (111) and (002) planes. Once a peak position is established, i.e. $\theta$ is known, the corresponding interplanar distance $d$, can be calculated with Eq. 3.3. For a cubic lattice, the lattice parameter $a$ can subsequently be calculated using

$$d_{hkl}^2 = \frac{a^2}{h^2 + k^2 + l^2}, \quad (3.5)$$

where $d_{hkl}$ is the interplanar distance for a plane described by miller indices $h$, $k$, $l$.

Figure 3.7. XRD diffractogram from a monolithic TiN film. From left, the peaks correspond to the Si substrate, TiN 111, and TiN 002.
3.3 X-ray reflectivity

If the sample consists of a multilayer or in some other way, a periodic structure, X-ray reflectivity (XRR) scans can be performed in order to obtain the bilayer thickness, also referred to as wavelength ($\Lambda$). XRR measurements are done at grazing incident angles, in this work scans were performed between 1-6° 2$\theta$. Instead of diffraction from atoms, the x-rays reflect from the interfaces between different materials. This effect is caused by a change in refractive index due to fluctuations in electron density for the different materials. A typical XRR diffractogram is shown in Fig. 3.8, where intensity is plotted versus 2$\theta$.

Figure 3.8. XRR diffractogram from a sample with wavelength 6.9 nm. Peak numbers are assigned from left to right.

X-rays experiences total reflection for small angles (<1°), angles that is dependent on the refractive index, x-ray wavelength, and electron density of the material. Due to the presence of several materials a modified Bragg’s law is necessary:

$$ (m\lambda)^2 = 4\Lambda^2 (\sin^2 \theta_m - 2\delta - \delta^2) $$

where $m$ is the peak number, counted from the left, $\lambda$ is the x-ray wavelength, $\Lambda$ the unknown bilayer wavelength, $\theta_m$ is the angle position corresponding to peak $m$, and $\delta$ is related to the real part of the volume averaged refractive index, which is equal to 1-$\delta$. Data collected from Fig. 3.8 is shown in table 1.

<table>
<thead>
<tr>
<th>m</th>
<th>(m$\lambda$)$^2$</th>
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<th>$\sin^2\theta_m$</th>
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<td>1</td>
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<tr>
<td>4</td>
<td>3.79·10^{-19}</td>
<td>5.109</td>
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</tr>
</tbody>
</table>

Table 1. Data collected from XRR diffractogram in Fig. 3.8.
3. Experimental methods

According to Eq. 3.6 a linear fit to the data can be made by plotting \((m\lambda)^2\) versus \(\sin^2 \theta_m\). The slope of the resulting line is then equal to \(4\Lambda^2\), and from this \(\Lambda\) was derived. See Fig. 3.9 below. Numerical values are, \(4\Lambda^2 = 1.930 \cdot 10^{-16}\), yielding \(\Lambda = 6.9\) nm.

![Figure 3.9](image)

Figure 3.9. Linear regression of XRR data, yielding a slope from which the multilayer wavelength can be calculated. The data originates from a multilayer with wavelength equal 6.9 nm.

When the wavelengths from two multilayers (\(\Lambda_1\) and \(\Lambda_2\)) had been calculated, the individual layer thicknesses could be determined. The two deposited materials, A and B, had unknown deposition rates \(r^{(A)}\) and \(r^{(B)}\) respectively. However, the time \(t\) each layer was deposited was known. This information generates an equation system with two equations and two unknowns,

\[
\begin{align*}
\Lambda_1 &= r^{(A)} t_1^{(A)} + r^{(B)} t_1^{(B)} \\
\Lambda_2 &= r^{(A)} t_2^{(A)} + r^{(B)} t_2^{(B)}
\end{align*}
\]

(3.7)

where the unknown deposition rates, \(r^{(A)}\) and \(r^{(B)}\) could be determined. The individual layer thickness was subsequently obtained by multiplying the deposition rate with the deposition time of that layer. These calculations were afterwards controlled by cross-sectional transmission electron microscopy.
3.4 Nanoindentation

Due to the small dimensions for these films, 1 µm in total film thickness, no ordinary hardness test equipment can be used. Instead a nanoindentor equipped with a three sided diamond Berkovich indenter is used. A nanoindentor is a system that can produce loads in the mN region and measure displacement within the nm range. This is possible due to the load controlling coil and capacitive displacement sensors inside the instrument. During indentation both load and displacement are logged by the nanoindentor. In Fig. 3.10 a typical load-displacement plot is shown.

![Load-displacement curve obtained by nanoindentation. This particular curve belongs to the monolithic TiN film. The maximum load is 10 mN, and the maximum indentation depth is approximately 150 nm.](image)

The measurement was divided into several steps. First the sample was loaded to maximum load (L_max) and held there for 10 s. This was followed by an unloading to 10% of L_max and a 30 s hold period. Finally a second loading to L_max and a 10 s hold after which complete unloading took place. The hold periods at L_max and at 10% L_max were carried out in order to examine whether any thermal drift or time dependent plastic deformation, i.e. creep, was present.

The hardness and elastic properties of the film were calculated by using the theory developed by Oliver and Pharr. Due to the preceding loading/unloading segment the final unloading was approximately elastic in the beginning, and from this part Young’s modulus was extracted. The hardness was obtained from L_max and the projected area of the indent at L_max. L_max was known, whereas the projected area was calculated. The area is described by an area function F(h), which is dependent on the indent depth, h. For a perfect Berkovich indenter the area function is described by Eq. 3.8,

\[ F(h) = 24.5h^2, \quad (3.8) \]

where 24.5 is a geometrical term describing the three sided indenter. However, no indenter to this day has been atomically perfect, some blunting is always present. A correction term was therefore added to Eq. 3.8 yielding
3. Experimental methods

\[ F(h) = 24.5h^2 + \sum_{i=1}^{8} C_i \cdot h^{2i-1} \]  
(3.9)

where \( C_i \) is eight unknown coefficients that can be determined by performing repeated indentation series on fused silica (SiO\(_2\)), which is a well documented material suitable for calibration. Once the area function was known the hardness was obtained by dividing the maximum load (\( L_{\text{max}} \)) with the area function at the corresponding indent depth (\( h_{\text{max}} \)).

\[ H = \frac{L_{\text{max}}}{F(h_{\text{max}})} \]  
(3.10)

Throughout this work hardness measurements have been conducted by subjecting each sample to 45 indents. Six different loads were used (2, 5, 10, 15, 20, 40 mN). The average hardness value and its standard deviation were calculated using the indentation data from loads not influenced by the substrate.

3.5 Curvature measurements

Curvature measurements were carried in order to determine the residual stresses within deposited films. During deposition, compressive stresses can evolve in films due to the energetic deposition conditions, i.e. bombardment of energetic species (mostly Ar\(^+\)), which through impingement and the resulting collision cascades causes atoms to be entrapped under the growth front, thereby inducing compressive strain in the material. Another contribution to residual stresses is the difference in thermal expansion coefficient (\( \alpha \)) between the materials involved. If deposition is carried out at elevated temperatures the subsequent temperature decrease after deposition causes the materials to contract, however, due to the difference in \( \alpha \) the materials want to contract differently. The fact that they are adhered to each other results in a uniform contraction, and also formation of alternating thermal stresses within the layers. Residual stresses manifests as curvature on an initially flat substrate. If to large residual stress is produced delamination and spallation of the film may result.

The curvature of an initially flat substrate is proportional to the internal residual stress. In the case where film thickness (\( t_f \)) is much thinner then the substrate thickness (\( t_s \)), a good approximation of the residual stresses is obtained by the Stoney equation,

\[ \sigma = \frac{1}{6R} \frac{E_s t_s^2}{(1-\nu_s) \cdot t_f} \]  
(3.11)

where \( E \) equal Young’s modulus, \( R \) is the radius of curvature, \( \nu \) is Poisson’s ratio, and \( t \) equals the thickness as stated above. Subscripts \( s \) and \( f \) correspond to the substrate and film respectively. In this work \( t_s = 1 \) µm and \( t_f = 500 \) µm, and therefore it is possible to use the Stoney equation.

Measurements of the curvature have been performed in a WYKO NT1100 Optical Profiler, which uses interference to generate a topographical image of the surface. The residual stresses were subsequently determined using Eq. 3.11.
3.6 Transmission electron microscopy

The microstructural appearance of the deposited films where further examined using cross-sectional transmission electron microscopy (XTEM) and high resolution electron microscopy (HRTEM). These techniques, as their name implies, collect structural information by transmitting electrons through the material. For this to be possible the material must be electron transparent, i.e. very thin, and as a rule of thumb the figure 100 nm is used. To produce a XTEM sample the substrate was successively cut into smaller pieces as shown in Fig. 3.11a-c, where the final size is roughly 1.7x0.5x0.5 mm³. Thereafter the pieces were mounted, film sides against each other, within a 3 mm in diameter titanium TEM grid, Fig. 3.11d-e.

![Figure 3.11. Illustration of XTEM sample manufacturing. a-c) Successive cutting to produce pieces small enough to fit into the titanium TEM grid d). e) Pieces clamped together, film sides against each other.](image)

The grid was thereafter covered with a mixture of epoxy and carbon powder and subsequently heated. As the epoxy melted and hardened the voids present within the grid were eliminated. Electron transparency was achieved by initial polishing of the grid to a thickness of 30-70 µm, followed by ion milling in a BALTEC RES010 ion mill, where argon ions were used to mill material from the sample until electron transparency was achieved.

Throughout this work three different microscopes have been used. Ordinary XTEM studies were done on a Philips EM 400T and a JEOL JEM-2000EX with accelerating voltages of 120 kV and 200 kV respectively. For high resolution work a Philips CM20 UT with an accelerating voltage of 200 kV was used.

For further reading on various XTEM sample preparation techniques and electron microscope handling can be found elsewhere.⁴³,⁴⁴
3. Experimental methods

3.7 Focused ion beam

Focused ion beam (FIB) is an apparatus which can be used to mill material from very specific locations on a sample, hence it is suitable for XTEM sample preparation. With a FIB instrument XTEM samples of indented multilayers can be produced. This is not possible with ordinary sample preparation due to the lack of precision within an ion mill. The FIB instrument can be compared to a scanning electron microscope (SEM), but instead of emitting electrons, gallium ions are emitted. In a similar way as in a SEM the surface image can be collected in a FIB. The use of gallium ions is both the advantage and the disadvantage of this equipment. The heavier ions, compared to electrons, make it possible to mill material at a reasonable rate. However, this also induces beam damage to the sample just by observing it.

Indents were prepared in a pattern according to Fig. 3.12, with three rows and nine indents in each row. High load (300 mN) indents were placed on the edges and low load (20 mN) in the center. This setup was chosen with the following in mind, 20 mN indents are too small for the FIB to resolve, therefore the high load indents where used as a way to locate the smaller indents.

![Figure 3.12. Indentation pattern for FIB work. 300 mN high load indents at the edges and 20 mN low load indents in center. The distance between consecutive indents was 25 µm.](image)

Before the samples were placed in the FIB a thin layer of gold was deposited on the surface with an ordinary sputter coater. This was to protect the film during the initial moments of ion bombardment in the FIB. In Fig. 3.13 the different stages leading to an XTEM sample is shown. First of all platinum (Pt) strips were deposited on top of each indent, Fig 3.13a. This was to provide a more resistant protection to the indents during the following process. The deposition of platinum is feasible by the introduction of a platinum compound near the ion beam where it breaks down, resulting in the deposition of platinum whereas the volatile products are pumped away. After the indents were covered with platinum, the material next to them was milled away, Fig. 3.13b-c, thus producing a thin cross-section. This cross-section must be thinner than approximately 100 nm in order to be electron transparent. When this was achieved and the trenches had reached a sufficient depth (~10 µm) the sample was tilted approximately 45°, Fig. 3.13d. From this position the ion beam was scanned along the edges of the cross-section, thus cutting it loose from the

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5 SEM can also produce beam damage, but this is not comparable with the damage produced by a FIB.
rest of the substrate. In Fig. 3.13e the four cross-sections are shown. The final step consisted of the delicate task of moving these small (~20x10x0.1 \( \mu m^3 \)) electron transparent pieces from the trenches to a Cu TEM grid. This was achieved by using an optical microscope equipped with high magnification, long working distance lens, and a micromanipulator equipped with a sharp glass needle. When the tip of the glass needle was moved into the trench and close to a cross-section piece electrostatic forces will attach the two to each other. Thereafter the needle with the cross-section was carefully moved over to a grid where the cross-specimen was attached. To further secure the cross-section on the grid the FIB was used and a small slab of platinum was deposited to weld the two together, Fig. 3.13f. Finally the XTEM sample was finished and could be inserted into the TEM.

![Image](image_url)

Figure 3.13. Figures describing the different steps to produce a XTEM sample. a) Deposition of platinum strips to protect the indents from the ion bombardment. b-c) Successive milling of deeper trenches and closer to the indents. d) Sample tilted 45° and subsequently cutting of the cross-section. e) Four “free” cross-sections. f) Cross-section moved to a Cu TEM grid, and thereafter welded in place with a platinum weld.
4. Experimental results

This chapter consists of a recapitulation of the results from the appended papers. Also included here is XTEM work on deformed multilayers, which are not included in any of the papers.

Two sets of multilayer thin films were deposited. The first set was grown with a constant TiN layer thickness of 4.5 nm and with Si$_3$N$_4$ layer thicknesses varying between 0.1 nm and 2.8 nm. In the second set the opposite was applicable, with a constant Si$_3$N$_4$ layer thickness of 1.7 nm whereas the TiN layer thickness was varied between 2 and 100 nm. The layer thicknesses have been deduced from XRR studies and XTEM/HRTEM observations. In addition to the multilayers, monolithic TiN and Si$_3$N$_4$ films were also grown. The final film thicknesses were approximately 1 µm.

The XRD diffractograms corresponding to the set of multilayers grown with constant Si$_3$N$_4$ layer thickness is shown in Fig. 4.1. Added as a reference is a diffractogram from the monolithic TiN film. Fig. 4.1 shows how the diffractograms for multilayers with thick TiN layers resembles the monolithic TiN. However, as the TiN layer thickness decreases the peaks broaden, suggesting that a decrease in grain size occurs. This was also expected as the amorphous interlayers should force TiN to renucleate for each consecutive layer, thus limiting the TiN grain size. XTEM studies verified this observation (below). Fig. 4.1 also indicates that TiN nucleates by forming 001 oriented islands, and that 111 appears at a later stage. The sample with the thinnest TiN layers (2 nm) display an extraordinary broadening and the subsequent HRTEM examination revealed small, in the order of the layer thickness, equiaxed TiN grains explaining this broadening.

![Figure 4.1](image)

Figure 4.1. XRD diffractograms over the set of samples with a constant Si$_3$N$_4$ layer thickness. A monolithic TiN film is added as reference.
4. Experimental results

In Fig. 4.2 the diffractograms from the set of multilayers grown with a constant TiN layer thickness is shown. A monolithic TiN film is added as a reference. For the thicker Si$_3$N$_4$ layers a pure 002 TiN texture is observed, which are consistent with the earlier observation that TiN nucleates by forming 001 oriented grains. Thus at this TiN layer thickness (4.5 nm) still no 111 TiN texture is visible, which suggest that a thickness for TiN transition from a pure 002 orientation to a mixed 111/002 orientation can be encircled between 4.5 and 9.8 nm. TiN layers nucleate by forming 001 oriented island, however, the growth conditions favors growth on 111 orientation and thus a transition in preferred orientation can be observed as the layer thickness increases. Similar changes have been reported earlier.46,47

The thinnest (0.1 and 0.3 nm) interlayers exhibits a mixed 111/002 orientation but also a noteworthy decrease in peak broadening. No layering could be discern with XRR for the sample with the lowest nominal thickness of ~0.1 nm (i.e. thinner then a monolayer), instead the layer thickness is approximated by using the deposition time. Due to the lack of a multilayer structure this sample can therefore be considered as a dilute TiN:Si alloy. The sample with a thickness of 0.3 nm displayed a different behavior, to explain this, HRTEM studies were necessary and the results is described below.

Figure 4.2. XRD diffractograms over the set of samples with a constant TiN layer thickness. A monolithic TiN film is added as reference.

Extensive TEM and HRTEM studies have been carried out on the present films. The microstructure of the monolithic TiN film exhibits columnar growth originating from competitive growth conditions during the deposition. Thus some grains grow, and survive at the expense of others (see Fig. 11e in paper I). This kind of growth morphology is common within TiN.48,49 Studies of the multilayer films confirm the microstructural picture obtained by XRD. Multilayers with a broad 002 XRD peak display correspondingly small 002 oriented TiN grains, enclosed between the amorphous layers. An example of this is the sample with a wavelength of 6.9 nm (4.5 TiN/2.4 nm Si$_3$N$_4$) shown in Fig. 4.3, where the selected area diffraction (SAD) pattern inset supports XRD data, i.e. a clear 002 preferred orientation (Fig. 4.2).
4. Experimental results

The grains are equiaxed and the layering is flat, and no cracks or voids are present. Also included in Fig. 4.3 is a HRTEM inset which clearly shows the amorphous and crystalline layers. The HRTEM micrograph is in accordance with earlier XRD and SAD results, i.e. displaying a 002 preferred orientation. Also shown in the figure are the 111, and 020 orientations at angles of 55° and 90° respectively from the 002 orientation.

An increase in TiN layer thickness to 9.8 nm results in the microstructure shown in Fig. 4.4. Similar to the previous sample this also displays equiaxed grains, without any observable columnar growth morphology. This sample displays a mixed 111/002 preferred orientation (Fig. 4.1), which is supported by the SAD pattern. HRTEM inset shows an area with preferred 111 orientation, also indicated in the figure are the 111 and 200 orientations located at angles of 70° and 55° respectively from the (111) planes parallel to the interface. This crystallographic view implicate that a [110] direction is perpendicular to the image plane.

If the TiN layer thickness is increased even further the shape of TiN grains changes, from equiaxed to a more elongated shape, which is shown in Fig. 4.5. This sample exhibits columnar growth within each TiN layer. However at some location an apparent continuation of the columns are observed from one TiN layer to the next, despite the presence of amorphous interlayers. HRTEM studies reveal local non-planar TiN surfaces on each layer. In particular at the emerging grain boundaries surface cusps were observed, see HRTEM inset in Fig. 4.5. It is noteworthy that the deposition of amorphous Si$_3$N$_4$ on top of such non-planar sites results in a smoothening effect such that there is very limited accumulative coarsening as the multilayer grows thicker. To the extent that the Si$_3$N$_4$ layers are not healing the surface, the retained roughness may act as advantageous nucleation sites for the next TiN layer. The SAD pattern inset display a mixed 111/002 orientation in accordance with the XRD scan in Fig. 4.1. In addition the SAD pattern consists of discrete diffraction spots instead of more complete rings which indicate fewer but larger grains.
4. Experimental results

Figure 4.4. XTEM micrograph with corresponding HRTEM and SAD pattern inset, the individual layer thicknesses are 9.8 nm and 1.7 nm for TiN and Si$_3$N$_4$ respectively.

Figure 4.5. XTEM micrograph with HRTEM and SAD inset. Layer thicknesses are 100 nm and 1.7 nm for TiN and Si$_3$N$_4$ respectively.

If the Si$_3$N$_4$ layer thickness is decreased instead of the TiN thickness, a layered structure can still be achieved at very thin interlayer thicknesses. Fig. 4.6 shows a XTEM micrograph from the sample with an interlayer thickness of 0.3 nm. The interlayers are apparent from bright lines of contrast over a continuous TiN lattice, which suggest that no renucleation occurs within the TiN layers. HRTEM studies reveal the lack of amorphous interlayers and instead lattice fringes continuing throughout the structure is observed.
Thus crystalline silicon nitride rich (SiN$_x$) interlayers are formed through the epitaxial stabilization of Si$_3$N$_4$ on the TiN lattice. This results in larger areas of coherence which is the explanation to the observed decrease in peak broadening (Fig. 4.2). For an additional micrograph over epitaxial stabilized silicon nitride see Fig. 7 in Paper I. A transition to amorphous silicon nitride occurs as the layer thickness increases, and at 0.8 nm the layers are amorphous. Epitaxial stabilization for other material systems have been reported earlier.$^{27,50}$ According to Barnett et al.,$^{50}$ the presence of stabilized non-equilibrium phases can be explained by the minimization of interfacial energy at the early stages of layer nucleation. Instead of forming a high energy interface, in this case between crystalline TiN and amorphous Si$_3$N$_4$, the system stabilizes one of the materials to the other, thus forming a coherent, low energy interface. To conclude the microstructural characterization, these multilayers are of superior definition of this material system, with well-defined layers as concluded by XRR, XTEM/HRTEM studies.

Hardness values from the set of multilayers grown with a constant Si$_3$N$_4$ layer thickness is shown in Fig. 4.7 plotted versus TiN layer thickness. With decreasing TiN layer thickness the hardness increases. The maxima of 30 GPa are reached for a TiN layer thickness of 10 and 20 nm. For a TiN layer thickness of 2 nm a decrease in hardness can be observed. A thorough discussion of this behavior can be found in Paper I.
4. Experimental results

Figure 4.7. Hardness values from the samples with constant Si$_3$N$_4$ layer thickness (1.7 nm).

In Fig. 4.8 the hardness values corresponding to the set of multilayers grown with a constant TiN layer thickness are plotted versus Si$_3$N$_4$ layer thickness. An increase in hardness can be observed as the Si$_3$N$_4$ layer thickness decreases. The maximum is reached for an interlayer thickness of 0.3 nm which corresponds to the presence of crystalline silicon nitride rich layers, which are epitaxial stabilized on the TiN lattice below. The decrease in hardness for the sample of a nominal thickness of 0.1 nm is due to the lack of interlayers as described earlier.

Figure 4.8. Hardness values from the sample with constant TiN layer thicknesses (4.5 nm).
In Paper I a more in depth discussion of the hardness values is made. However, the conclusion drawn is that for larger wavelengths the hardness correlates to a Hall-Petch behavior, but with a generalized power of 0.4. The hardness enhancement for thinner layers is due to the presence of interlayers, either amorphous or crystalline. For the latter the presence of coherency stresses at the interfaces causes the high hardness.

In Paper II a model is presented that try to explain the observed crystalline-amorphous transition based on lattice strain, interfacial energy, and total lattice energy. *Ab initio* calculations have been performed on five different compositions of Ti$_{1-x}$Si$_x$N ($x = 0, 0.25, 0.5, 0.75, and 1$). In Fig. 4.9 a plot over the difference in total energies between Ti$_1$,$\_x$Si$_1$N and its phase separated parts, (1-x)TiN + xSiN, is shown.

![Figure 4.9. Total energy difference between Ti$_{1-x}$Si$_x$N and (1-x)TiN + xSiN for various compositions.](image)

All compositions display a positive energy difference, thus all mixtures of Si into a TiN lattice should be energetically unfavorable, neglecting entropy effects. This is in agreement with earlier phase diagram studies of the Ti-Si-N system.\(^{51}\) However, solid solution of Si into the TiN lattice is possible.\(^{52-55}\) Under thin film deposition, energetically unstable structures may form. The epitaxial stabilization of c-SiN$_x$ to the TiN lattice is due to the minimization of surface area energy at the early stages of growth, i.e. instead of forming a high energy crystalline/amorphous interface a low energy crystalline/crystalline interface is formed. Further details can be found in Paper II.

XTEM studies of deformed multilayers were possible through the use of a FIB equipment where thin cross-sectional samples can be manufactured as described in section 3.7. Fig. 4.10a show a general view over a deformed multilayer exposed to a load of 300 mN. In the upper part of the micrograph the protective Pt layer is located. Underneath the Pt layer the deformed TiN/Si$_3$N$_4$ multilayer is visible, and in the lower part of the micrograph the silicon substrate with its oxidized surface layer can be observed. Massive plastic deformation can be discerned within the substrate directly underneath the indent. Cracks has nucleated and propagated under the high load. Cracks are also present within the multilayer.
Figure 4.10. a) General view of a deformed multilayer. The left and right square corresponds to figure b and c respectively.

Higher magnification micrographs of the deformed multilayer are shown in Fig. 4.10b-c. These are from the regions marked with squares in Fig. 4.10a. In Fig. 4.10b cracks are observed to have propagated along the interfaces between TiN and Si$_3$N$_4$ layers. Fig. 4.10c is directly under the indent, and here the cracks normally follow along a TiN/Si$_3$N$_4$ interface. However, at some locations the crack has turned, and propagated across a layer, and subsequently continued along its original path along an interface. This examination yields information of how a multilayer structure behaves under deformation. The interlayers deflect cracks so that they cannot propagate through the entire material at once. By the repeated deflections the movement of the crack is halted and resumed continuously, which consumes energy. Thus the presence of interlayers results in a tougher material.

Additional discussion regarding hardness and deformation of multilayers can be found in Paper I.
5. Future work

After this licentiate thesis the work will continue towards the goal of attaining a better understanding of how multilayer coatings obtain their interesting properties. That is to gain knowledge about deformation mechanisms within multilayered structures and which factors contribute to hardening. The final objective is the possibility to predict how the microstructural characteristics and deposition conditions affect the properties, and how to achieve the best possible result for a specific material system.

In order to obtain these goals more films have to be deposited. Hopefully this can be done with a deposition chamber equipped with \textit{in situ} curvature measurement capability, and thereby the stress history during the deposition can be monitored. More XTEM studies of deformed multilayers are also going to be carried out, either by the FIB technique described in section 3.7 or by \textit{in situ} deformation in a TEM equipped with a load cell. Additional \textit{ab initio} calculations are also necessary in order to further examine the energies and possible structures that form during deposition.
References


27 P. C. Yashar and W. D. Sproul, Vacuum 55, 179 (1999), and references therein.


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Appended papers
Paper I

Nanostructure formation during deposition of TiN/Si$_3$N$_4$ nanomultilayer films by reactive dual magnetron sputtering

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Nanostructure formation during deposition of TiN/Si$_3$N$_4$ nanomultilayer films by reactive dual magnetron sputtering

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ABSTRACT

Multilayer thin films consisting of titanium nitride (TiN) and silicon nitride (Si$_3$N$_4$) layers with compositional modulation periodicities between 3.7 and 101.7 nm have been grown on silicon wafers using reactive magnetron sputtering. Electron microscopy and X-ray diffraction studies showed that the layering is flat with distinct interfaces. The deposited TiN layers were crystalline and exhibited a preferred 002 orientation for layer thicknesses of 4.5 nm and below. For larger TiN layer thicknesses, a mixed 111/002 preferred orientation was present as the competitive growth favored 111 texture in monolithic TiN films. Si$_3$N$_4$ layers exhibited amorphous structure for layer thicknesses $\geq$0.8 nm, however, for the first time cubic crystalline silicon nitride phase was observed for layer thicknesses $\leq$0.3 nm. Formation of this metastable SiNx phase is explained by epitaxial stabilization to TiN. The microstructure of the multilayers displayed columnar growth within the TiN layers with intermittent TiN renucleation after each Si$_3$N$_4$ layer. A nano-brick-wall structure was thus demonstrated over a range of periodicities. As-deposited films exhibited relatively constant residual stress levels of 1.3±0.7 GPa (compressive) independent of the layering. Nanoindentation was used to determine the hardness of the films, and the measurements showed an increase in hardness for the multilayered films compared to the monolithic Si$_3$N$_4$ and TiN films. The hardness results varied between 18 GPa for the monolithic TiN film, up to 32 GPa for the hardest multilayer, which corresponds to the presence of cubic SiNx. For larger wavelengths, $\geq$20 nm, the observed hardness correlate to the layer thickness similar to a Hall-Petch dependence, but with a generalized power of 0.4. Sources to the hardness increase for shorter wavelengths are discussed, e.g. epitaxial stabilization of metastable cubic SiNx, coherency stress, and impeded dislocation activity.
I. INTRODUCTION

Growth of multilayer or superlattice thin films has shown various degrees of hardness enhancements often exceeding the individual hardness of the materials involved. Typically the hardness increases with decreasing wavelength until a maximum value is reached in the nm range, after which the hardness decreases with further decrease in wavelength. Different theories have been developed in order to explain the observed increase in hardness. Koehler showed theoretically a hardness increase for materials with a lamellar structure. This increase arises from image forces on dislocations due to a shear modulus difference between the layers. Koehler strengthening or modulus difference strengthening have been found experimentally. Other theories that try to explain the observed increase in hardness are, coherency stress hardening, where dislocation movement is restricted by the stress fields present at coherent interfaces within the multilayer. Also, the epitaxial stabilization effect has been demonstrated, where a metastable structure for one of the layer materials is formed by pseudomorphic forces to the surface of the other layer during nucleation and growth thus creating a coherent interface, e.g., a normally amorphous material assuming crystalline structure for small layer thicknesses. For Orowan-like strengthening, plastic deformation occurs by dislocation movement and bowing inside layers. Finally, in the case of Hall-Petch strengthening hardness increases due to a reduction in grain size and thereby an increase in grain boundary density, grain boundaries which acts as dislocation obstacles. The decrease in hardness for small wavelengths is often explained by incomplete layers and increased intermixing giving an imperfect multilayer. All of the above theories consider single crystal and polycrystalline multilayers, while the effect from amorphous layers are neglected, Koehler claims that his theory is still valid, however, it remains to be confirmed.

During the last decade, work on nanocomposites composed of amorphous and crystalline phases have been carried out. Herein nanocrystals are grown embedded in a matrix of amorphous material. The majority of the work listed above concerns the ternary titanium-silicon-nitride system. Veprek and co-workers revealed a hardness increase to 50 GPa on TiN/Si3N4 nanocomposites. In order to produce a superhard material according to Veprek and Reiprich certain factors should be fulfilled, namely that the materials should be immiscible, preferably even at high temperatures, and one component should be amorphous possessing high structural flexibility, i.e. the ability to accommodate coherency strain without forming dangling bonds. These factors are fulfilled for crystalline titanium nitride (TiN) and amorphous silicon nitride (Si3N4).

Purity is also important as shown by Veprek et al., who concluded that oxygen and other contaminants on the 1-2 at.% level act detrimental on film properties, lowering its hardness. Thus there is a need for well-defined phases for the constituents in a nanocomposite or nanolaminate (as here) with well-defined interfaces. Also, the results should be deconvoluted from any positive correlation with residual stress as this is a common phenomenon in thin film growth. In this work, the layers and interfaces are well-defined and pure by UHV processing conditions, and with a low, but relatively constant compressive stress level.

Growth studies for TiN and Si3N4 in a multilayered structure have been done to a lesser extent. In this paper we report on the influence of phase composition and thickness of Si3N4 interlayers in reactive magnetron sputtered TiN/Si3N4 multilayers. This system with a reduced dimensionality (2-D) was chosen to test the premises for present models for superhardening effects arising in nanocomposite and nanolaminate (superlattice) systems. By growing a multilayer the 2-D symmetry results in an easier interface analysis
compared to the 3-D structure in a nanocomposite. This will aid in the effort of finding a relationship between any hardness maxima and the Si$_3$N$_4$ tissue phase thickness, in nanocomposites referred to percolation threshold, which corresponds to an interlayer thickness of a few monolayers. The microstructure is characterized by XRD and TEM/HRTEM and the hardness by nanoindentation. The observed hardness variations are discussed in terms of layer thickness, crystallite size, and dislocation confinement.

II. EXPERIMENTAL METHODS

All films were grown in a dual unbalanced reactive dc magnetron sputtering system. As targets one titanium disc (purity 99.97%) and one silicon disc (purity 99.99%), both with a diameter of 75 mm were used. The computer controlled shutters in front of the two targets were maneuvered by compressed air with ≤0.1 s closing and opening time. A negative bias potential of 50 V over the substrates was used during all depositions. The base pressure reached before deposition was <10$^{-3}$ Torr (∼1.3*10$^{-4}$ Pa). Argon (purity 99.9999%) was used as working gas and nitrogen (purity 99.99999%) as reactive gas. Throughout the deposition runs the partial pressures were kept at 4.0 mTorr (∼0.5 Pa) and 0.5 mTorr (∼0.07 Pa) for argon and nitrogen respectively. All films were deposited on single crystal (100) silicon wafers (10x10x0.5 mm$^3$) with a top layer of 100 nm SiO$_2$. The substrates were thoroughly ultrasonically cleaned in trichloroethylene, acetone, and isopropanol baths and blown dried with nitrogen before being placed in the vacuum chamber.

The targets were fed with a constant current of 0.8 A and 0.2 A for the Ti and Si target respectively, which in both cases led to target voltages of 350 V. During the deposition the substrate holder was rotating with a revolution speed of 24 rpm. In order to raise the temperature of the substrates, and thereby the mobility of the impinging atoms, a heater was used to maintain a substrate temperature of 500°C during the depositions.

Two sets of TiN/Si$_3$N$_4$ multilayer samples were grown. The first set was made with a constant TiN thickness of 4.5 nm and with a varying Si$_3$N$_4$ thickness from 0.1 nm up to 2.8 nm. In a second set, the Si$_3$N$_4$ thickness was held constant at 1.7 nm whereas the TiN thickness varied between 2 and 100 nm. Periodicities (Λ) from 3.7 to 101.7 nm were thus prepared. In addition, monolithic TiN and Si$_3$N$_4$ films were also grown. All films except the monolithic Si$_3$N$_4$ were grown on a 50 nm bufferlayer of TiN. The final film thicknesses were approximately 1 µm.

The layering of the films was studied with low angle x-ray reflectivity (XRR) in order to determine the wavelength (Λ) of the samples. From the obtained data and a procedure described elsewhere the wavelengths were calculated. To examine the orientation and any possible preferred orientation of the TiN layers, high angle x-ray diffractometry (XRD) was carried out. All x-ray studies were performed on a Philips PW1729 diffractometer with 0-2θ geometry and CuK$_\alpha$ radiation.

To produce cross sectional samples for transmission electron microscopy (TEM), the substrates with their deposited films were cut and mounted with the film sides against each other in a titanium grid. Thereafter the grids were polished down to a thickness of approximately 30-70 µm and as a final step the samples were ion etched in a BALTEC RES010. When electron transparency was achieved three different microscopes were used to examine the cross sections of the films. The primary examinations were done on a Philips EM 400T and a Jeol JEM-2000EX with accelerating voltages of 120 kV and 200 kV respectively. For HRTEM a Philips CM20 UT operating at 200 kV were used.
The curvature of the sample was measured by a WYKO NT1100 Optical Profiler, which uses interference to generate a topographic image of the surface. Thereafter the stress was calculated using the Stoney equation\(^2\) and the curvature determined from the topographical image.

The hardness of the samples was obtained using a Nanoindentor II with a Berkovich diamond indenter and the theory developed by Oliver and Pharr.\(^3\) Each sample was subjected to 45 indents. 6 different loads (2, 5, 10, 15, 20 and 40 mN) were used. During the tests the samples were loaded to maximum load (\(L_{\text{max}}\)) and held there for 10 s. Thereafter they were unloaded to 10\% of \(L_{\text{max}}\) and held for 30 s. The test ended with a second loading to \(L_{\text{max}}\) and a 10 s hold after which complete unloading took place. The hardness was determined from the last unloading segment. From the indentation data generated for loads not influenced by the substrate, an average hardness value and its standard deviation were calculated.

III. RESULTS

Fig. 1 shows an x-ray reflectivity scan for the sample with a wavelength just above 50 nm. Apparent superlattice reflections can be observed, and the sharpness and periodicity shown support a well-defined multilayer.

![Figure 1. X-ray reflectivity scan for a TiN/Si\(_3\)N\(_4\) multilayer film. The bilayer composition is indicated in the figure and the number of bilayer repeats is 20.](image)

In Fig. 2 the diffractograms for the set of samples with constant TiN thickness are shown for different Si\(_3\)N\(_4\) layer thicknesses. For comparison reasons, the diffractogram from the monolithic TiN film is added to the figure. The two peaks belonging to TiN, 111 and 002, show similar intensity for the monolithic TiN film. For the Si\(_3\)N\(_4\) layer with the lowest nominal thickness of \(~0.1\) nm (i.e. thinner than a monolayer), no layering could be discerned with low angle XRD, instead the layer thickness is approximated using the deposition time. In the absence of a multilayer structure the film can be considered as a
dilute TiN:Si alloy. Its XRD-response resembles the one for the monolithic TiN, but with a more intense 111 peak. The sample with a SiN\textsubscript{x} layer thickness of 0.3 nm shows some broadening of the peaks, especially for the 002 peak. For the samples with Si\textsubscript{3}N\textsubscript{4} thickness of 0.8 nm and above, the diffractograms display similar appearance. As the Si\textsubscript{3}N\textsubscript{4} layers get thicker, the TiN 111 peak diminishes until it finally disappears for the sample with Si\textsubscript{3}N\textsubscript{4} thickness of 2.8 nm. At the same time, the TiN 002 peak gets broader. A small shift towards lower 2\theta values for the 002 peak can also be observed. The preferred TiN 002 orientation in the samples with a Si\textsubscript{3}N\textsubscript{4} layer thicker than 0.8 nm is evident.

Figure 2. High angle XRD scan from the set of TiN/Si\textsubscript{3}N\textsubscript{4} multilayer films with constant TiN layer thickness of 4.5 nm. A monolithic TiN film is added for reference.

Figure 3. High angle XRD scan from the set of TiN/Si\textsubscript{3}N\textsubscript{4} multilayers with constant Si\textsubscript{3}N\textsubscript{4} layer thickness of 1.7 nm. A monolithic TiN film is added for reference.
In Fig. 3 the diffractograms for the set of samples with constant Si$_3$N$_4$ layer thickness and varying TiN layer thicknesses are shown. For the sample with the thinnest TiN layer thickness (2 nm), the TiN 002 peak is broadened compared to the thicker TiN layer samples and the TiN reference. As the layer thickness of TiN increases, the TiN 002 peak becomes narrower and approaches the appearance of the monolithic TiN peak. For samples with a thin TiN layer, only 002 orientation is present. When the TiN thickness has reached 9.8 nm also the 111 orientation appears. Some broadening of the peaks exists, broadening that becomes less pronounced as the TiN thickness increases.

Cross-sectional TEM (XTEM) examination of the monolithic TiN film revealed a columnar structure. For the multilayer samples, the TiN layers are polycrystalline and exhibit columnar growth within each layer, analogous to a nanosized brick-wall structure. Fig. 4 shows a TEM micrograph of the multilayer with a TiN thickness of 9.8 nm. The structure of the layers appears flat and free from visible defects. No cracks or voids can be found. The different layers have distinct interfaces indicating that no or little interdiffusion has taken place between the as-deposited layers. This would be the expected due to the reported$^{31}$ immiscibility of TiN and Si$_3$N$_4$ at the low substrate temperature used. The SAD pattern from the film shows a mixed 111/002 texture in agreement with the XRD results. Multilayer samples with $l_{Si3N4} \geq 0.8$ nm show similar lack of flaws with distinct dense layers.

Figure 4. XTEM micrograph and SAD pattern from a TiN/Si$_3$N$_4$ multilayer sample with periodicity 11.5 nm and Si$_3$N$_4$ layer thickness of 1.7 nm.

In the monolithic TiN film, columns that proceed throughout the entire film were observed. This behavior is generally not displayed in the multilayer, however, shorter columns that advance over a few multilayer periods are found within the samples of Si$_3$N$_4$ layer thickness less or equal to 0.3 nm, see Fig. 5. In the 100 nm TiN/1.7 nm Si$_3$N$_4$ multilayer it is apparent that some of the TiN grains locally continue to grow past Si$_3$N$_4$ layers thereby forming columns that extend over some 5 wavelengths, Fig. 6. The broadest columns have a width of 50 nm. High resolution inset show a surface cusp at a TiN grain boundary. Included is also a SAD pattern verifying the observation from the micrograph as it shows
discrete diffraction spots instead of more complete rings which indicate fewer, but larger grains. Fig. 7 shows a high-resolution micrograph of the same sample in Fig. 5. Clear lattice fringes throughout the structure can be seen in the figure. Arrows indicate the location of the silicon nitride rich layers.

Figure 5. XTEM micrograph with higher-magnification inset and SAD pattern from a TiN/SiNₓ multilayer film with periodicity 4.8 nm and l_{SiNₓ} = 0.3 nm. Despite the presence of interlayers the columnar TiN growth mode is maintained over several periods.

Figure 6. XTEM micrograph with high-resolution inset and SAD pattern from the sample with layer thicknesses of 100 nm TiN and 1.7 nm Si₃N₄ respectively. Despite the presence of interlayers the columnar TiN growth mode is maintained over several periods.
Figure 7. HRTEM micrograph of the same multilayer as in Fig. 5. No amorphous interlayer is observed, instead lattice fringes are visible throughout the structure. Arrows indicate the silicon nitride layers.

The film/substrate curvature measurement revealed relatively constant compressive stresses of 1.3±0.7 GPa in the multilayers. For the set with constant TiN thickness, a change in compressive stress from -1.87 GPa to -1.15 GPa is observed as the Si₃N₄ layer thickness increases from 0.1 nm to 2.8 nm, which is expected based on the lower coefficient of thermal expansion of Si₃N₄.

Typical load-displacement curves for the monolithic TiN film and one of the multilayers are plotted in Fig. 8. The hold period at maximum load reveals a larger amount of creep within the TiN film compared to the multilayer. Also revealed by the load-displacement curves is a higher degree of plastic work generated during indentation of the TiN film, which is consistent with its lower hardness.
In Fig. 9 the hardness of the multilayer set with constant Si$_3$N$_4$ thickness is plotted versus TiN layer thickness. An increase in hardness can be seen in the multilayer films compared to the monolithic Si$_3$N$_4$ film (corresponding to TiN thickness 0 nm). A maximum hardness of 30 GPa is observed for the samples with TiN layer thickness of 10 and 20 nm. Thereafter as the TiN layers increase in thickness the hardness decreases. The nanoindentation results for the set with varying Si$_3$N$_4$ layer thickness can be seen in Fig. 10. An increase in film hardness is observed here as well as in the previous set. The highest hardness is found for the sample with a SiN$_x$ layer thickness of 0.3 nm where measurements yield a hardness of 32 GPa. As the silicon nitride layer thickness increases the hardness decreases.

![Figure 9](image9.png)

**Figure 9.** Hardness values from the samples with constant Si$_3$N$_4$ layer thickness (1.7 nm).

![Figure 10](image10.png)

**Figure 10.** Hardness values from the samples with constant TiN layer thickness (4.5 nm).
IV. DISCUSSION

The as-deposited TiN/Si$_3$N$_4$ multilayer films were noteworthy well-defined. This can be seen in the electron micrographs (see Fig. 4 and 6) and the x-ray reflectivity scan that showed up to 23 orders of superlattice reflections. Formation of such sharp interfaces between TiN and Si$_3$N$_4$ can be ascribed to several conditions, e.g., a well polished substrate, the choice of a relative low deposition temperature ($T/T_m^{TiN} = 0.22$) to avoid interface diffusion and coarsening, and a limited ion bombardment to promote ion-surface interaction for promoting ad-atom mobility required for layer-by-layer growth. Bias was, however, kept low in order to avoid recoil mixing in the collision cascades. These are factors contributing to maintain both flatness and the defect-free nature of the multilayers, including a relatively low level of compressive stress in all films.

In Fig. 11 a schematic description of the mechanism leading to the observed TiN nano- and microstructure evolution is shown. For each TiN layer in the multilayers there is nucleation, coalescence, growth, and eventual interruption by a subsequent Si$_3$N$_4$ layer. The case of monolithic TiN film shows that the material undergoes competitive columnar growth.

![Figure 11](image_url)

Figure 11. Illustration of the mechanisms leading to the nano-brick-wall structure observed within TiN layers of the TiN/Si$_3$N$_4$ multilayers with the stages. a) Nucleation of TiN on the Si$_3$N$_4$, b) coalescence, c) growth, and d) interruption by the deposition of the next Si$_3$N$_4$ layer. e) Competitive columnar growth between different crystallographic orientations within steady-state growth of TiN.

An illustrative example of the process that occurs in the majority of the multilayers is displayed in Fig. 4, where the Si$_3$N$_4$ layers interrupt the growth of TiN and thereby forces TiN to renucleate each time a new layer is deposited. For thicker TiN layers and in the case of a monolithic TiN film, the XTEM results show a columnar structure by competitive growth (Fig. 6 and 11e), the latter in accordance with findings done by others. Within the multilayers on the other hand, the effective TiN grain size can be controlled by
choosing the height of the TiN layer. For relatively small layer thicknesses the grains are equiaxed. Thus, we have fabricated a nano-brick-wall material. When the thickness of the layers increases the height of the grains surpass the width, e.g. for a TiN thickness of 100 nm the aspect ratio is 2. Another observation regarding the sample with 100 nm TiN layers (Fig. 6) is that a number of TiN grains continue with an apparent columnar growth morphology over several layers, indicating that TiN morphology is transferred over the Si$_3$N$_4$ layers. HRTEM examination reveals local non-planar TiN surfaces on each layer. In particular at the emerging grain boundaries there are surface cusps. It is noteworthy that the deposition of Si$_3$N$_4$ layers on top of such non-planar sites yields an apparent smoothening such that there is very limited accumulative coarsening of the multilayers over its periods. To the extent that the Si$_3$N$_4$ layers are not healing the surface, the retained roughness may act as advantageous nucleation sites for the next TiN layer.

From examination of the multilayers texture the resulting diffractograms (Fig. 2 and 3) indicate that the TiN layers nucleate by preferably forming 001 oriented islands. The subsequent growth is, however, favoring growth on 111-directed grains. This results in a texture transition 002 to 111 as the TiN becomes thicker in steady-state-growth mode. By interrupting the TiN growth in early stages and forcing it to repeatedly and controllably renucleate, the 002 preferred orientation can thus be maintained throughout the film. Similar conditions for the changes in preferred orientation in TiN films as a function of layer thickness has been observed by others.\textsuperscript{34-38} The present findings for multilayer films have useful implications for structural materials design purposes.

The repeated TiN growth interruption and renucleation processes are especially pronounced in samples with a TiN thickness $\leq 5$ nm. Samples that display a broad 002 XRD peak also have complete amorphous Si$_3$N$_4$ layers resulting in TiN renucleation and correspondingly small 002 oriented TiN grains. It is noteworthy that the multilayer samples with the smallest Si$_3$N$_4$ layer thickness display an abnormal decrease in peak broadening with decreasing $l_{\text{Si}_3\text{N}_4}$ from 0.8 nm to 0.3 nm. Fig. 5 shows the TEM micrograph of a sample with $l_{\text{Si}_3\text{N}_4} = 0.3$ nm where the interlayers are apparent from bright lines of contrast over a continuous lattice between TiN layers of the same orientation. HRTEM examination of this sample reveals a structure that exhibits lattice fringes that extend for several wavelengths, indicating SiN$_x$ strained into the cubic TiN lattice structure, Fig. 7. It is thus concluded that the silicon nitride layers do not form amorphous phase, but epitaxial strained layers of cubic phase. Thus, for such thin interlayers, instead of periodically causing the subsequent TiN layers to renucleate and grow in other orientations, the pseudomorphic crystalline silicon nitride layers intermittently retains and transfers the TiN structure. In the absence of TiN renucleation the columnar TiN structure may thus continue to evolve. The formation of relatively large areas of coherence explains why the XRD peaks show less broadening compared to samples with similar TiN thickness, but thicker amorphous Si$_3$N$_4$ layers. By controlling the individual layer thicknesses not only can the grain size of TiN be controlled, but also the silicon nitride phase.

The hardness of the present multilayer films increases as the layer thicknesses decreases. At a specific point, depending on layer composition (cf. Fig. 9 and 10), a maximum hardness is found and thereafter the hardness decreases with a further decrease in layer thickness. This development of hardness versus wavelength ($\Lambda$) data is consistent with findings made by others for TiN/Si$_3$N$_4$ multilayers,\textsuperscript{26} and also for different material systems.\textsuperscript{1,2} The main reason for hardness increase over the individual materials hardness is due to different effects decreasing or hindering dislocation motion. According to Koehler,\textsuperscript{3} the theories of image forces on dislocations due to a modulus difference is valid for amorphous/crystalline structures. However, the theory does not take any layer thicknesses
into consideration which is needed. A calculation of the hardness increase results in an underestimation compared to the indentation measurements. The theory can, however, be used as a first approximation of what level of hardening to expect. Using the data obtained from the monolithic films (\(E_{\text{TiN}} = 356\pm50\) GPa, \(E_{\text{Si}_3\text{N}_4} = 250\pm15\) GPa) and Poisson’s ratio of 0.2 and 0.25 for TiN and Si\(_3\)N\(_4\) respectively the shear modulus can be calculated, yielding \(G_{\text{TiN}} = 148\) GPa and \(G_{\text{Si}_3\text{N}_4} = 100\) GPa. From these values one should expect a hardness increase of 5.4 GPa, which is less than observed. Most probable is that a single effect cannot explain the whole hardness increase and instead a combination of several effects is necessary to produce the observed hardening. Several additional sources for hardness enhancement have been suggested. Xu et al.\(^{25}\) conclude that TiN grain size is not the main effect causing the increase in hardness in TiN/Si\(_3\)N\(_4\) multilayers. Instead they suggest that one of the main reasons for the increase is the alternating stress fields caused by thermal mismatch between the layers. The critical resolved shear stress necessary to propagate a dislocation will be affected by the alternating compressive/tensile stress fields, i.e. hinder the movement of dislocations which leads to hardening. Following their calculation a compressive thermal stress of 0.9±0.1 GPa is present in the Si\(_3\)N\(_4\) layers whereas a small tensile thermal stress of 0.16±0.14 GPa is present in the TiN layers. For TiN, the stress increases as the layer thickness decreases. This could be a partial explanation to the decrease in hardness for thin TiN layers (2 nm). In addition, we demonstrated the existence of alternating coherency strain fields from the thinnest epitaxial Si\(_x\)N\(_{3-x}\) layers with epitaxial interfaces to TiN. Such effect has been reported to account for several GPa hardening in TiN/NbN superlattice films.\(^{39}\)

In an effort to take TiN grain size into consideration, which in itself is a hardening mechanism as the grain size decreases, the hardness of both series were plotted versus \(\Lambda^{-0.5}\) in Fig. 12. Keep in mind that these values are from two different sets, constant TiN and Si\(_3\)N\(_4\) layer thicknesses respectively, however it works as a survey. Fig. 12 reveals an almost straight line for the films with the largest wavelengths (TiN thickness \(\geq 20\) nm) thus indicating a Hall-Petch (H-P) dependence.

![Figure 12](image-url)

Figure 12. Hardness of the TiN/Si\(_3\)N\(_4\) multilayer films plotted versus \(\Lambda^{-1/2}\). Dotted line corresponds to a best fit to a Hall-Petch behavior, resulting in an exponent equal 0.4.
Upon closer examination the exponent in the H-P expression is corrected to 0.4 instead of 0.5. Deviations from an H-P exponent of 0.5 have been observed earlier in other material systems.\textsuperscript{40,41} For the samples where the majority of the film consists of crystalline TiN (TiN thickness $\geq$ 20 nm), the hardness increase is correlated to the H-P theory, i.e. shorter columns/grains within TiN yield a harder film. For smaller wavelengths, the hardness values deviates from the H-P relationship, producing a lower hardness than expected. This happens partly because the volume fraction of amorphous Si$_3$N$_4$ increases in the film and also due to the smaller layer dimensions. Similar results where H-P strengthening only is valid down to a certain wavelength have been reported by others.\textsuperscript{12,42,43} Additional factors that influence the hardening behavior in these films are changes in preferred orientation resulting in different plastic behavior of TiN,\textsuperscript{44} variation in the amorphous layer thickness, any inhomogeneities in the amorphous structure, and also the presence of crystalline silicon nitride interlayers.

Within these multilayers dislocations movement occur along glide planes in TiN. Upon impact with the amorphous Si$_3$N$_4$ layers, deformation displacement occurs through movement and rotation of the rather stiff covalent bonds, which may result in a weakening of the stress concentration associated with the dislocation, see Fig. 13. According to Veprek,\textsuperscript{45} the large structural flexibility within amorphous Si$_3$N$_4$ is capable of relaxing stresses at interfaces. As the deformation progresses more dislocations are transported. Since such a mechanical mixing between TiN and Si$_3$N$_4$ is unfavorable from a thermodynamic viewpoint, the process should contribute to hardening. An additional effect is that hardening of the Si$_3$N$_4$ is expected at some point as the deformation progresses, due to an increasing resistance to deformation of the amorphous structure. This effect is enhanced by the fact that TiN deforms in a planar manner with a tendency to form slip bands, resulting in a higher degree of deformation in Si$_3$N$_4$ locally adjacent to the slip planes. Thus the flexibility of Si$_3$N$_4$ may locally be exhausted, resulting in larger force required to deform Si$_3$N$_4$ and a hardening enhancement.

Figure 13. Schematic illustration of how dislocation movement inside TiN layers causes a mechanical intermixing between TiN and amorphous Si$_3$N$_4$ layers. The stress concentration associated with the advancing TiN edge is reduced through the amorphous network causing a lower stress concentration on the next TiN layer.
The hardness values obtained are somewhat lower than those reported by Xu" and Chen.\textsuperscript{26} Dissimilar deposition systems and parameters could explain this behavior. Xu et al. used an RF reactive magnetron sputtering system. Whereas Chen et al. deposited films using a pulsed bias, and for the hardest film a bias of -90 V was used. A lower bias, -50 V, used in this work is a probable explanation to the relatively low biaxial stresses observed here and consequently a lower hardness. Moreover, the multilayer hardening observed here is substantiated since the effect on hardness from the residual stresses in this work is almost constant throughout the samples due to the relative low and constant stresses measured.

For the set of multilayer films grown with constant Si\textsubscript{3}N\textsubscript{4} layer thickness, the peak hardness is obtained for the samples with 10 and 20 nm TiN layers, see in Fig. 9. These two samples and those with longer wavelength all exhibit a mixed texture. However, the grain size decreases as the layer thickness decreases, explaining the higher hardness for \( \Lambda=10 \) and 20 nm compared to 50 and 100 nm. A decrease in hardness is observed for the sample with a TiN thickness of 2 nm. Such thin layers are just barely continuous after the nucleation and coalescence stage on amorphous Si\textsubscript{3}N\textsubscript{4}. The corresponding inhomogeneities including any intermixing of Si into the first monolayers TiN by recoil mixing during the energetic deposition conditions (include ion bombardment and reflected neutrals from the target) may soften the TiN layers. A certain contribution to the apparent softening of such multilayer is also expected from the TiN anisotropic hardness characteristics\textsuperscript{44} (\( H_{111}>H_{001} \)). If the theory of thermal stresses suggested by Xu et al.\textsuperscript{25} (described above) is correct the softening can also, at least partly, be explained by increased tensile thermal stresses for these thin TiN layers. The set grown with constant TiN thickness also display hardness variations (Fig. 10). As the Si\textsubscript{3}N\textsubscript{4} layer thickness decreases the hardness increases. The maximum is reached for a SiN\textsubscript{x} layer thickness of 0.3 nm. As shown earlier this sample differs from the others, due to lack of homogenous amorphous Si\textsubscript{3}N\textsubscript{4} layers. Instead, the epitaxial stabilization of crystalline silicon nitride within the TiN lattice produces local high stresses that will act as areas effective at obstructing dislocation movement. A higher lattice resistance to dislocation movement compared to pure TiN may cause the observed hardness increase.

From the discussion above it is clear that multilayers of TiN and amorphous or crystalline silicon nitride layers exhibit increased hardness compared to monolithic TiN. As the amorphous layer thickness decreases hardness increases until the maximum is reached as crystalline silicon nitride interlayers are formed. This seems to be the most favorable case as it allows dislocations to move, but at an increased energy cost compared to monolithic TiN film without interlayers.
V. CONCLUSIONS

Multilayer thin films consisting of crystalline TiN and amorphous Si$_3$N$_4$ have been fabricated by reactive magnetron sputtering. The resulting multilayers are of superior definition for this materials system. XRD diffractograms show a clear 002 preferred orientation for TiN layers with a thickness of 4.5 nm and below. As the TiN thickness increases also the 111 orientation appears. The broadened XRD peaks indicate small TiN grains. This was confirmed by TEM/HRTEM studies showing a nano-brick-wall structure. The grain size and to some extent also the preferred orientation of TiN can be controlled by choosing the appropriate thickness of the TiN layers. Curvature measurement reveals a relatively constant compressive residual stresses of 1.3±0.7 GPa. This rather low stress level is a plausible explanation to the somewhat lower hardness results obtained here compared to cases where the multilayers were under significantly higher stress levels.²⁶

The hardness of all the multilayers is higher than that for monolithic films grown under the same conditions. The higher hardness obtained for the multilayers has its origin in smaller grains and the fact that dislocations cannot propagate unaffected throughout the film due to interlayers. For wavelengths larger then 20 nm the hardness scales with wavelength similar to a Hall-Petch relationship, but with a generalized power of 0.4. TEM/HRTEM examination of the hardest multilayer (32 GPa), with a SiN$_x$ thickness of 0.3 nm show no amorphous interlayers, instead lattice fringes continuing throughout several wavelengths are observed. Thus, growth of cubic silicon nitride by epitaxial stabilization to the TiN lattice is demonstrated. The coherency stresses between the two lattices effectively hinder dislocation movement resulting in the apparent superhardening.

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Paper II

Epitaxial stabilization of cubic-SiN$_x$ in non-isostructural TiN/Si$_3$N$_4$ multilayers

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Epitaxial stabilization of cubic-SiN$_x$ in non-isostructural TiN/Si$_3$N$_4$ multilayers

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ABSTRACT

Titanium nitride/silicon nitride multilayer films have been deposited by reactive magnetron sputtering. XTEM/HRTEM examination reveals a transition from amorphous silicon nitride interlayers to epitaxial stabilized cubic silicon nitride rich layers as the interlayer thickness decreases from 0.8 nm to 0.3 nm. A model describing this morphological transition based on lattice strain, and interfacial energies is presented.
The ternary Ti-Si-N system is an interesting system to exploit in order to study and test superhardening effects in nanocomposites and nanolaminates (multilayers and superlattices). Extensive studies have been devoted on nanocomposites with extreme hardness consisting of nanocrystals or nanocolumns within an amorphous matrix, e.g. Veprek and Zhang, and references therein. Numerous nanocomposite studies have been devoted to the Ti-Si-N system. According to Veprek and Niederhofer a maximum hardness should be obtained with small crystallite sizes (~10 nm and below) separated by a thin amorphous matrix in the order of a monolayer, a thickness also referred to as percolation threshold. The hardness enhancements are explained by small crystallite sizes, producing grain boundary hardening, and possibly also obstructing dislocation nucleation below a critical size (~10 nm). Deformation through grain boundary sliding and microcrack formation should also be inhibited to a larger extent due to the three dimensional microstructure. However, the 3-D structure is a disadvantage when it comes to microstructural and interfacial analysis.

Multilayers are useful as a model system since they allow the design and study of interfaces not readily studied in a 3-D nanocomposite. Thus, we studied the TiN/Si3N4 system and found that for thin (~0.3 nm) SiN_x layers an epitaxial stabilization to the crystalline TiN lattice occurred. Crystalline silicon nitride rich interlayers were formed and as the layer thickness increased a transition to amorphous layers followed.

For the case of multilayers there are several studies performed on transitional metal nitride systems for isostructural and non-isostructural crystalline systems. However, for crystalline/amorphous multilayer systems, fewer studies have been presented. To conclude how microstructural characteristics affect the mechanical behavior of multilayer thin films, there is a need to determine the layer structure as a function of layer thickness over the dimensions found to yield a superhardening. This has not been done for the interesting thicknesses of less than a few nanometers.

In this paper we report on the formation of epitaxial stabilized cubic-SiN_x in c-TiN/a-Si3N4 multilayers at layer thicknesses corresponding to 1.5 monolayers of SiN_x. Further, the multilayers with crystalline SiN_x exhibits a higher hardness compared to multilayers containing amorphous Si3N4. This implies that a higher hardening effect is obtained with crystalline interlayers when coherent stresses are present than compared to the case with amorphous interlays.

All depositions were carried out in a reactive dual magnetron sputtering system where the 50 V negatively biased Si(100) substrates where placed on a heater maintained at 500°C. The two targets consisted of high purity Ti(99.97%) and Si(99.99%) discs. Argon and nitrogen was used as working and reactive gas respectively, the purity of the gases was 99.99999%. The deposited samples were cut and thereafter mounted with a mixture of epoxy and carbon powder, film surfaces against each other, within titanium TEM grids. Electron transparency was achieved by initial polishing of the grids followed by ion etching in a BALTEC RES010 apparatus. Cross sectional transmission electron microscopy (XTEM) studies were carried out on a JEOL JEM-2000EX, whereas for high resolution microscopy a Philips CM20 UT was used.

Ab initio calculations on a cubic lattice cell at different compositions were also carried out. Properties examined were the lattice parameter, and the total lattice energy for a number of different compositions. The different compositions were achieved by assuming a NaCl-type structure consisting of 4 Ti and 4 N atoms. Thereafter Ti atoms were exchanged for Si atoms, resulting in five different compositions (Ti1-xSi_xN, where x = 0, 0.25, 0.5, 0.75, and 1). The calculations were performed using a full potential muffin tin orbital method.
(FP-LMTO) within the local density approximation (LDA) of density functional theory (DFT).

Fig. 1 show XTEM micrographs from two multilayers, included are also the corresponding SAD patterns and HRTEM micrographs. XTEM micrograph in Fig. 1a shows equiaxed TiN grains separated by amorphous Si\textsubscript{3}N\textsubscript{4} interlayers. Layer thicknesses are 4.5 and 2.4 nm for TiN and Si\textsubscript{3}N\textsubscript{4} respectively. A clear distinction between the amorphous and crystalline structure can be seen and the interfaces are flat. The included HRTEM micrograph displays TiN 002 orientation perpendicular to the growth direction, corresponding well to previous reported data on the early growth morphology of TiN.\textsuperscript{13,14} Also shown are the 111 and 020 orientations at angles of 55° and 90° from the 002 orientation.

Figure 1. XTEM micrographs of two multilayers with different wavelengths, included are also the corresponding SAD patterns and HRTEM micrographs. a) Multilayer with a wavelength composition of 4.5 nm TiN and 2.4 nm a-Si\textsubscript{3}N\textsubscript{4}. b) Multilayer with crystalline SiN\textsubscript{x} interlayers of 0.3 nm thickness.
If the Si₃N₄ layer thickness is decreased the columnar growth is not interrupted by the layering. Fig. 1b shows a XTEM micrograph from the sample with an interlayer thickness of 0.3 nm. The interlayers are seen as bright lines of contrast passing through the columnar TiN growth morphology, i.e. no renucleation occurs within the TiN layers. HRTEM reveals the lack of amorphous interlayers and instead lattice fringes continuing throughout the structure is present, which suggest epitaxial stabilization of SiNₓ on TiN, or epitaxial stabilization of a silicon nitride rich compound on TiN. The interlayers are slightly uneven (Fig. 1b), which is understandable as strained (metastable) growth becomes unstable at a critical thickness. Similar observations have been reported earlier for TiN/NbN.⁷

In Fig. 2a the x-ray reflectivity (XRR) curve for a multilayer with 0.3 nm SiNₓ is shown. An increase in the silicon nitride layer thickness to 0.8 nm results in the XRR curve shown in Fig. 2b. Both XRR curves are plotted with the square root of the intensity along the ordinate in order to enhance low intensity peaks.

![Figure 2. XRR curves. a) Multilayer with 0.3 nm SiNₓ. b) Multilayer with 0.8 nm Si₃N₄.](image)

Fig. 3a shows the calculated lattice parameter for the five different compositions. The lattice parameter (a) is normalized with respect to a₀ which is equal to 4.240 Å, corresponding to the equilibrium lattice parameter for TiN.¹⁵ LDA within DFT is known to overestimate the bond strength, thus yielding lattice parameter values slightly (<3%) lower than expected,¹⁶ thereby explaining a(x=0)/a₀<1. Introducing Si atoms into the pure TiN lattice results in a decrease of the lattice parameter until a minimum is reached at approximately 66 at.% Si, whereupon the a/a₀ increases. Fig. 3b shows the total energy difference between the compound structure Ti₁₋ₓSiₓN and its phase separated counterparts (1-x)TiN and xSiN at different compositions. Consequently the energy difference for TiN (x=0) and SiN (x=1) is equal to zero.

The observed crystalline SiNₓ layers suggest that a Si-N thickness greater than 0.3 nm is necessary to form amorphous Si₃N₄. Sambasivan and Petuskey reported immiscibility within this system at low temperatures (<1000°C) and under equilibrium conditions.¹⁷ This is further corroborated by the calculated differences in total energy shown in Fig. 3b, where the positive energy difference suggests that all mixtures of Si into the cubic TiN lattice are energetically unstable and could result in decomposition into two different phases, neglecting the effect of entropy. However, studies exist where a solid solution of Si in the TiN lattice is present.¹⁸⁻²¹
H. Söderberg, J. M. Molina-Aldareguia, T. Larsson, L. Hultman, and M. Odén

Figure 3. a) Calculated lattice parameter of $\text{Ti}_{1-x}\text{Si}_x\text{N}$ compound within a TiN lattice, normalized with $a_0 = 4.24$ Å, corresponding to the lattice parameter of TiN. The model slightly overestimates bond strength, explaining $a(x=0)/a_0<1$. b) Calculated total energy difference between $\text{Ti}_{1-x}\text{Si}_x\text{N}$ and its phase separated counterparts, i.e. $(1-x)\text{TiN}$ and $x\text{SiN}$. Values higher than 0 indicates energetically unstable compound.

Experimental data from TEM/HRTEM prove a transition from crystalline to amorphous as the Si-N layer thickness increases. Epitaxial stabilization of non-equilibrium phases in thin films and multilayers has been well documented for a number of materials systems, not the least the nitrides, and references therein. The stabilization of non-equilibrium phases results from pseudomorphic forces and the minimization of interfacial energy at the early stages of layer nucleation.

In this study two growth modes are possible for the silicon nitride, either epitaxially stabilized and thus coherent with the TiN layer below, or amorphous and incoherent. For both cases a complete coverage is assumed due to the low deposition temperature used when depositing these high $T_m$ materials, thus resulting in a layer of Si-rich compound of thickness $t$ over an area $s^2$. In the coherent case the bulk energies involved are the total lattice energy ($E_{\text{TiN-SiN}}$), and the elastic strain energy ($E_{\text{el}}$) due to the lattice misfit ($\delta$) between TiN and $\text{Ti}_{1-x}\text{Si}_x\text{N}$. Additional energy contribution originates from the interface between $\text{Ti}_{1-x}\text{Si}_x\text{N}$ and TiN, being a coherent interface only a chemical interface term is present ($\gamma_{ch}^{\text{coh}}$). For the amorphous and incoherent case the involved energies consist of the total lattice energy ($E_{\text{Si}_3\text{N}_4}$) and an interfacial term consisting of two parts, one chemical ($\gamma_{ch}^{\text{in}}$) and one structural ($\gamma_{st}$). Compiling and equating the energies for a critical thickness $t_c$, yields

$$
(E_{\text{TiN-SiN}} + E_{\text{el}}) \cdot t_c s^2 + s^2 \gamma_{ch}^{\text{coh}} = E_{\text{Si}_3\text{N}_4} \cdot t_c s^2 + s^2 (\gamma_{ch}^{\text{in}} + \gamma_{st}).
$$

Rearrangement and cancellation of $s^2$ yields

$$
(E_{\text{TiN-SiN}} + E_{\text{el}} - E_{\text{Si}_3\text{N}_4}) \cdot t_c = \gamma_{ch}^{\text{in}} + \gamma_{st} - \gamma_{ch}^{\text{coh}}.
$$

The two chemical interfacial energy terms should be approximately equal, and can therefore be cancelled. The elastic strain energy term is proportional to $G\delta^2$ ($G=$ shear modulus) which are several order of magnitudes lower than the total energies present. However, since the lattice energies are subtracted the elastic strain energy may influence the result. For $t$=0.3 nm the layers are crystalline, whereas for $t$=0.8 nm amorphous. Fitting these numbers in Eq. 3 yields two inequalities,
\[
\begin{align*}
\Delta E \cdot 0.3 \cdot 10^{-9} &< \gamma_{st}, \\
\Delta E \cdot 0.8 \cdot 10^{-9} &> \gamma_{st},
\end{align*}
\]  
(3)

which results in a crude estimate of the structural interfacial energy present between TiN and a-Si$_3$N$_4$, 

\[
\Delta E \cdot 0.3 \cdot 10^{-9} < \gamma_{st} < \Delta E \cdot 0.8 \cdot 10^{-9}.
\]  
(4)

The stabilization occurs in order to avoid the structural interfacial energy, which can be seen from Eq. 2. An increase in $\gamma_{st}$ causes an increase in $t$, which is the expected as a transformation to a structure with a higher interfacial energy is what the system tries to avoid. An increase in elastic energy ($E_{el}$) due to increased misfit causes a decrease in $t$, as expected. Based on the calculated lattice parameters in Fig. 3a an approximation of the lattice misfit, $\delta$, can be obtained,

\[
\delta = \frac{a_{PL-xSi,N} - a_{TiN}}{a_{TiN}} \approx 0.5\%|_{x=1},
\]  
(5)

which suggest a small compressive strain within the silicon nitride rich interlayers. The small strain is a plausible explanation to the lack of misfit dislocations observed with HRTEM. Also, the lack of misfit dislocations at the interfaces suggests that the strain energy term never reaches a critical level to form misfit dislocations before it transforms into amorphous Si$_3$N$_4$. Thus the transition is governed by the removal of the energetically unstable Ti$_{1-x}$Si$_x$N and formation of the more stable a-Si$_3$N$_4$.

For multilayer with epitaxial stabilized crystalline silicon nitride rich interlayers the increase in hardness can be explained by stresses. Coherent stress fields are present at the interfaces due to the lattice mismatch between TiN and Ti$_{1-x}$Si$_x$N (0.5% for SiN, Eq. 5). Another stress contribution is from the Peierls stress. Within the interlayers Ti and Si atoms are randomly located at the different lattice positions, giving rise to a directional bonding force in the lattice, which in turns causes an increase in Peierls stress, i.e. a higher lattice resistance to dislocation movement compared to pure TiN where the bond forces are less anisotropic. A higher resolved shear stress is therefore necessary to propagate a dislocation through the interlayer compared to pure TiN. Since the exact force displacement relation between the atoms in the layers is unknown an accurate description of the Peierls stress contribution to hardness enhancement cannot be carried out. However, a higher resistance to dislocation movement should be present in accordance with the discussion above.

In this work evidence for epitaxial stabilization of cubic-Si$_N$ on a TiN lattice is presented. The formation of crystalline interlayers is explained by a minimization of surface energies for small layer thicknesses (~0.3 nm). For thicker interlayer thicknesses (>0.8 nm) amorphous Si$_3$N$_4$ are obtained. Finally, one question should be raised: If silicon nitride can stabilize into a crystalline phase for small layer thicknesses, should this phase not be able to exist within nanocomposite coatings where the amorphous matrix approaches monolayer thicknesses?
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