Linköping Studies in Science and Technology
Dissertation, No. 1901

Silicon Nitride Based Coatings Grown by Reactive Magnetron Sputtering

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Linköping 2018

ISBN 978-91-7685-374-0
ISSN 0345-7524

Printed by LiU-Tryck 2018

Silicon nitride and silicon nitride-based ceramics have several favorable material properties, such as high hardness and good wear resistance, which makes them important materials for the coating industry. This thesis focuses the synthesis of silicon nitride, silicon oxynitride, and silicon carbonitride thin films by reactive magnetron sputtering. The films were characterized based on their chemical composition, chemical bonding structure, and mechanical properties to link the growth conditions to the film properties. Silicon nitride films were synthesized by reactive high power impulse magnetron sputtering (HiPIMS) from a Si target in Ar/N₂ atmospheres, whereas silicon oxynitride films were grown by using nitrous oxide as the reactive gas. Silicon carbonitride was synthesized by two different methods. The first method was using acetylene (C₂H₂) in addition to N₂ in a Si HiPIMS process and the other was co-sputtering of Si and C, using HiPIMS for Si and direct current magnetron sputtering (DCMS) for graphite targets in an Ar/N₂ atmosphere. Langmuir probe measurements were carried out for the silicon nitride and silicon oxynitride processes and positive ion mass spectrometry for the silicon nitride processes to gain further understanding on the plasma conditions during film growth. The target current and voltage waveforms of the reactive HiPIMS processes were evaluated.

The main deposition parameter affecting the nitrogen concentration of silicon nitride films was found to be the nitrogen content in the plasma. Films with nitrogen contents of 50 at.% were deposited at N₂/Ar flow ratios of 0.3 and above. These films showed Si–N as the dominating component in Si 2p X-ray photoelectron spectroscopy (XPS) core level spectra and Si–Si bonds were absent. The substrate temperature and target power were found to affect the nitrogen content to a lower extent. The residual stress and hardness of the films were found to increase with the film nitrogen content. Another factors influencing the coating stress were the process pressure, negative substrate bias, substrate temperature, and HiPIMS pulse energy. Silicon nitride coatings with good adhesion and low levels of compressive residual stress were grown by using a pressure of 600 mPa, a substrate temperature

below 200 °C, pulse energies below 2.5 Ws, and negative bias voltages up to 100 V.

The elemental composition of silicon oxynitride films was shown to depend on the target power settings as well as on the nitrous oxide flow rate. Silicon oxide-like films were synthesized under poisoned target surface conditions, whereas films deposited in the transition regime between poisoned and metallic conditions showed higher nitrogen concentrations. The nitrogen content of the films deposited in the transition region was controlled by the applied gas flow rate. The applied target power did not affect the nitrogen concentration in the transition regime, while the oxygen content increased at decreasing target powers. The chemical composition of the films was shown to range from silicon-rich to effectively stoichiometric silicon oxynitrides, where no Si–Si contributions were found in the XPS Si 2p core level spectra. The film optical properties, namely the refractive index and extinction coefficient, were shown to depend on the film chemical bonding, with the stoichiometric films displaying optical properties falling between those of silicon oxide and silicon nitride.

The properties of silicon carbonitride films were greatly influenced by the synthesis method. The films deposited by HiPIMS using acetylene as the carbon source showed silicon nitride-like mechanical properties, such as a hardness of ~ 20 GPa and compressive residual stresses of 1.7 – 1.9 GPa, up to film carbon contents of 30 at.%. At larger film carbon contents the films had increasingly amorphous carbon-like properties, such as densities below 2 g/cm^3 and hardnesses below 10 GPa. The films with more than 30 at.% carbon also showed columnar morphologies in cross-sectional scanning electron microscopy, whereas films with lower carbon content showed dense morphologies. Due to the use of acetylene the carbonitride films contained hydrogen, up to ~ 15 at.%. The co-sputtered silicon carbonitride films showed a layered SiN_x/CN_x structure. The hardness of these films increased with the film carbon content, reaching a maximum of 18 GPa at a film carbon content of 12 at.%. Comparatively hard and low stressed films were grown by co-sputtering using a C target power of 1200 W for a C content around 12 at.%, a negative substrate bias less than 100 V, and a substrate temperature up to 340 °C.

Populärvetenskaplig sammanfattning

Tunna filmer och beläggningar med tjocklekar som sträcker sig från delar av en nanometer till flera mikrometer spelar en viktig roll i många avancerade tillämpningar. De används för att förbättra ytegenskaperna hos material eller för att lägga till en ny funktion till det underliggande substratet. Några exempel är isoleringsbarriärer i elektronik, reflekterande beläggningar i optik och skyddande beläggningar för skärverktyg. Givet de tunna filmernas tekniska betydelse utvecklas även syntesteknikern. Några av de mest populära metoderna för tunnfilmssyntes innefattar elektroplätning som används inom bilindustrin och olika typer av kemiska och fysikaliska metoder som används i stor utsträckning inom halvledarindustrin. Magnetronsputtring, en syntesteknik som tillhör de fysiska metoderna, beskrivs mer detaljerat i denna avhandling.

Arbetet som presenteras här har genomförts inom projekt LifeLongJoints, huvudsakligen finansierat av Europeiska unionen. Ett av projektets mål var att utveckla biokompatibla slitstarka kiselnitridbaserade beläggningar för ortopediska implantat. I denna avhandling har reaktiva magnetronputtringprocesser för kiselnitridbaserade beläggningar, innefattande kiselnitrid, kiseloxynitrid och kiselkarbonitrid studerats. En stor del av arbetet har varit att karakterisera de syntetiserade beläggningarna samt att koppla depositionsparametrarna till filmegenskaper. Plasmakarakterisering med hjälp av masspektrometri och Langmuirsondmätningar har utförts för att få ytterligare förståelse för de reaktiva magnetronputtringsprocesserna och att sammansätta processförhållanden till filmegenskaper.

Filmerna karaktäriserades baserat på deras sammansättning, kemisk bindingsstruktur och mekaniska egenskaper. Kiselnitridfilmer syntetiserades genom reaktiv hög-effektspulsadmagnetronsputtring (HiPIMS) från en kiselkälla i argon och kvävgas, medan kiseloxynitridfilmer syntetiserades med lustgas i stället för kvävgas. Kiselkarbonitridfilmer syntetiserades med två olika metoder. Den första metoden använde acetylen förutom kvävgas som reaktiva gaser och den andra samputtring av kisel och kol i argon och kvävgas.

Den primära tillväxtparametern som påverkade kvävekoncentrationen av kisel-

nitridfilmer var kvävehalten i plasmat. Filmer med kväveinnehåll av 50 % erhöles vid N_2/Ar flödesförhållanden av 0,3 och högre. Hårda kiselnitridbeläggningar med låga spänningar syntetiserades genom användning av ett processtryck av 600 mPa, en substrattemperatur lägre än 200 °C, pulsenergier under 2,5 Ws och negativa biaspänningar upp till 100 V.

Fördelningen mellan kväve och syre av kiseloxynitridfilmerna visade sig bero på effektsinställningarna av kiselkällan såväl som på lustgasflödes hastigheten. Kiseloxidliknande filmer syntetiserades med låg sputtringseffekt på kiselkällan och högt lustgasflöde, när kiseloxid bildades på källan. Kvävehalten i filmerna styrdes av gasflödes hastigheten och var oberoende av effekten på källan, när källan inte var förgiftad.

Egenskaperna av kiselkarbonitridfilmer påverkades starkt av syntesmetoden. Filmerna syntetiserade med HiPIMS och med acetylen som kolkälla visade kiselnitridliknande mekaniska egenskaper upp till kolinnehållet 30%. De samsputtrade kiselkarbonitridfilmerna uppvisade en skiktad kiselnitrid/kolnitrid struktur. Jämförelsevis hårda och lågstressade filmer syntetiseras med användning av en effekt 1200 W på grafitkällan för en kolhalt omkring 12%, en negativ substratförspänning lägre än 100 V, och en substrattemperatur upp till 340 °C.

Preface

This thesis presents the results of my doctoral studies at Linköping University, at the department of physics, chemistry, and biology (IFM), between the years 2013 and 2018. Parts of the work in this thesis have appeared in my licentiate thesis, *Silicon Oxynitride Thin Films Grown by Reactive HiPIMS*, Linköping Studies in Science and Technology, Thesis no. 1737, 2015.

The work has received funding from the European Union's Seventh Framework Program (FP7/2007-2013) under the LifeLongJoints Project, Grant Agreement No. GA-310477, and from the Swedish Government Strategic Research Area in Materials Science on Functional Materials at Linköping University (Faculty Grant SFO-Mat-LiU No. 2009-00971).

Acknowledgements

I want to express my gratitude to my supervisor Hans Högberg for his guidance during my studies. I am also thankful to my co-supervisors; Susann Schmidt for her invaluable help with the experimental work and article writing, and Lars Hultman for his insightful comments and questions.

In addition, I want to thank my co-authors and colleagues at the thin film physics division for their help, especially Thomas Lingefelt and Harri Savimäki for all the help with the equipment.

Lastly, I thank my family and Nina for their support.

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CHAPTER 1

Introduction

Thin films and coatings with thicknesses ranging from parts of a nanometer to several micrometers play an essential part in many modern day technologies. They are used to enhance the surface properties of materials or to add new functionalities to the underlying substrate. Some examples include insulating barriers in electronic devices, anti-reflective coatings in optics, and protective coatings for cutting tools. Due the technological importance of thin films, also the synthesis methods are being vigorously developed. Some of the most popular thin film synthesis methods include electroplating used in car industry, and various types of chemical vapor deposition (CVD) and physical vapor deposition (PVD) methods used extensively in semiconductor industry. Magnetron sputtering, a thin film deposition technique belonging to the PVD methods, is covered in more detail in this thesis.

1.1 Purpose and outline

The work presented in this thesis has been conducted within the LifeLongJoints project which was mostly funded by the European Union. One of the the goals of the project was to develop biocompatible wear-resistant silicon nitride-based coatings for joint implants. In this context, the reactive magnetron sputtering processes for silicon nitride-based coatings, including silicon nitride, silicon oxynitride, and silicon carbonitride, have been studied. A major part of the work has been characterizing the synthesized coatings and connecting the deposition parameters to the film properties. Some plasma characterization by using mass spectrometry and Langmuir probe measurements have been carried out to gain further understanding on the reactive magnetron sputtering processes and to link the growth conditions to the film properties.

Figure 1.1. The covalent bonding structure of silicon nitride.

1.2 Silicon nitride and silicon nitride-based materials

1.2.1 Silicon nitride

Silicon nitride was first synthesized in the 1800's. The industrial use of silicon nitride began in the 1950's as a refractory material. Naturally occurring silicon nitride can be found in meteorites in small quantities. [1] The chemical formula of stoichiometric silicon nitride is Si_3N_4 . It has three crystalline phases, the trigonal $\alpha\text{-Si}_3\text{N}_4$, the hexagonal $\beta\text{-Si}_3\text{N}_4$, and the high-pressure phase $\gamma\text{-Si}_3\text{N}_4$. [1, 2] Silicon nitride is extensively used in hard coating industry due to its favorable mechanical properties, such as chemical stability, high hardness, and high resistance to wear and corrosion. [1] It is also used in microelectronics as an insulator and in diffusion barriers, owing to its high resistivity and dielectric strength and resistance to water diffusion. [1] Silicon nitride has also been studied as a material for medical implants. [3]

Recently, there has been a growing interest for amorphous silicon nitride (SiN_x) coatings for metallic medical implants, in contrast to fully ceramic Si_3N_4 implants. [4–9] The use of a ceramic coating on a metallic implant would combine the ductility of the metallic implant with the biocompatibility of the ceramic, without the risk of a catastrophic failure of a fully ceramic implant. [8] It has been shown that a SiN_x coating can reduce implant corrosion and limit the metal ion release from metallic implants, thus reducing harmful inflammation in the surrounding tissue. [8] In addition to the favorable mechanical properties, such as high wear-resistance, SiN_x wear debris is soluble in aqueous solutions, further reducing the risk of undesired reactions between the host and the implant. [9–11]

The usual pathways to synthesize SiN_x thin films include the various types of CVD and PVD processes. Films synthesized by CVD often show hydrogen as the main contaminant due to hydrogen-containing precursor gases. [1] When SiN_x is synthesized by magnetron sputtering usually a Si target is sputtered in an Ar/N_2 atmosphere, although some studies have utilized a compound Si_3N_4 target. [12] Because the nonconducting nature of silicon nitride causes problems in direct current magnetron sputtering, radio frequency (RF) magnetron sputtering is often used. [12, 13]

The favorable mechanical properties of silicon nitride stem from its rigid covalent bonding structure consisting of SiN_4 tetrahedra, shown in Fig. 1.1. [1] Thin films of silicon nitride are usually amorphous or polycrystalline and can contain impurities such as hydrogen and oxygen from the residual water vapor and used precursors, depending on the synthesis method. The possible incorporation of contaminants makes the amorphous thin films often nonstoichiometric, with N/Si ratios deviating from the 4/3 ratio of the stoichiometric compound. [1] Large hydrogen concentrations in silicon nitride films have been shown to result in deteriorated mechanical and optical properties. [14, 15] The mechanical properties, such as density and hardness, show a large range of values due to the large number of synthesis methods and varying amounts of contaminants. The amorphous SiN_x films are usually less dense than crystalline Si_3N_4 (3.2 g/cm^3), up to $\sim 3 \text{ g/cm}^3$, depending on the processing conditions and amount of contaminants. [1] Mechanical properties, such as hardness, of amorphous SiN_x films also show a wide range of values, from under 10 GPa of understoichiometric contaminated films [16] to over $\sim 20 \text{ GPa}$ [12].

1.2.2 Silicon oxynitride

Silicon oxynitride is widely used in optoelectronics as graded-index layers [17, 18], waveguides [19, 20], and surface passivation layers, [21, 22] due to its favorable optical and electrical properties. Especially the tunable refractive index makes SiO_xN_y well-suited for optical applications. [23] Furthermore, also the mechanical properties, such as residual stress and hardness can be controlled through the elemental composition. [24–26] Lately, there has been a growing interest for the use of SiO_xN_y coatings in medical implants due to the good hemocompatibility of the material along with the suitable mechanical properties. [27, 28] The reason for such a wide range of applications for SiO_xN_y is the possibility to control its material properties by adjusting the amount and ratio of oxygen and nitrogen in the material. This yields properties ranging from those of amorphous silicon to amorphous silicon oxide and nitride, or such shown by mixed compositions between the three constituents. [29, 30]

Commonly SiO_xN_y thin films have been prepared by either CVD or magnetron sputtering. The CVD methods are limited by hydrogen-containing precursor gases, resulting in Si–H and N–H chemical bonding in the films, which causes absorption losses in the near-infrared wavelength range. [19, 29, 31] Two reactive gases, O_2 and N_2 , are usually employed when SiO_xN_y is synthesized by magnetron sputtering. [32–34] The two-gas approach results in nonlinear target effects due

Figure 1.2. A ternary plot of the Si–O–N system.

to the inherently different reactivities of oxygen and nitrogen, since oxygen as the more reactive element is more likely to form a compound on the Si target. [35] Additional equipment, such as a reactive gas pulsing process or a feedback loop based on monitoring the discharge current or voltage, can be employed to limit the O_2 flow during the process, and to reduce the nonlinear target effects caused by the different reactivities of oxygen and nitrogen. [32, 33, 36]

The Si–O–N system has only one thermodynamically stable ternary compound with the composition Si_2N_2O . [37, 38] A rare silicon oxynitride mineral known as sinoite can be found in some meteorites. [39] A ternary plot of the Si–O–N system is shown in Fig. 1.2. The chemical bonding in amorphous nonstoichiometric SiO_xN_y can be described by two bonding models, the random mixture model (RMM) and the random bonding model (RBM). [40, 41] In RMM, separate phases of SiO_2 and Si_3N_4 are randomly distributed in the material, whereas in RBM the central Si atom is randomly bond to four Si, O, and/or N atoms. [40, 41] Commonly, the growth of SiO_xN_y is more closely governed by RBM than by RMM, especially for sputter-deposited films, as the growth conditions are usually thermodynamically far from those required for the growth of separate SiO_2 and Si_3N_4 phases. [25, 42]

The material properties in the randomly bond SiO_xN_y mostly depend on the ratio of O and N in the Si-matrix. This can be achieved by changing the reactive gas flow ratios in reactive sputtering, for example. [43] The relative permittivity of stoichiometric SiO_xN_y can vary from 3.9 (SiO_2) to 7.4 (Si_3N_4). [44] The refractive index of SiO_xN_y can be tailored from that of SiO_2 ($n \sim 1.5$) to that of Si_3N_4

($n \sim 2.0$) by adjusting the O/N ratio in the material. [17, 18] Furthermore, the refractive index for understoichiometric SiO_xN_y are found to range from Si_3N_4 values to those recorded for amorphous Si ($n \sim 4$), depending on how much O and N is incorporated into the Si-matrix. [45–47] The total amount of O and N in SiO_xN_y affects the extinction coefficient (k) values, the stoichiometric compound is found to be transparent ($k \sim 0$) in the visible wavelength range, whereas for the understoichiometric compound the k values increase as the amount of Si in the compound increases, finally reaching values recorded for amorphous Si ($k \sim 0.2$). [46, 47]

Mechanical properties, such as density, residual stress, and hardness, depend on the O/N ratio of SiO_xN_y . The SiO_xN_y density can vary from that of SiO_2 ($\sim 2.1 \text{ g/cm}^3$) to that of Si_3N_4 ($\sim 3.0 \text{ g/cm}^3$). [48, 49] The residual stress in CVD-grown films can change from compressive to tensile, depending on if the material is oxide-like or nitride-like, respectively. [24] Moreover, both the hardness and elastic modulus of SiO_xN_y films with random bonding is found to increase as the film composition shifts from SiO_2 to Si_3N_4 , hardness from $\sim 10 \text{ GPa}$ to $\sim 20 \text{ GPa}$ and elastic modulus from $\sim 100 \text{ GPa}$ to $\sim 200 \text{ GPa}$. [12, 25]

1.2.3 Silicon carbonitride

Similar to silicon nitride and silicon oxynitride, silicon carbonitride (SiC_xN_y) has a wide range of applications. It is mostly known as a material for wear-resistant coatings due to its high corrosion and oxidation resistance, [50] but it also has uses in microelectronics and optics. [51, 52] As a ternary compound its material properties are highly dependent on the elemental composition. When it comes to medical applications, especially the favorable SiN_x -like mechanical properties and the potentially tunable dissolution rate make SiC_xN_y a prominent candidate for a coating material to be used in joint implants. [13, 53]

The synthesis methods most commonly employed are pyrolysis of pre-ceramic polymers, [54, 55], CVD, [51, 56] and PVD. [57, 58] Various target-reactive gas combinations are possible for magnetron sputtering of SiC_xN_y . Carbon can be introduced either by sputtering a SiC target, [50] by reactive co-sputtering of Si and C targets, [5, 59] or by using a hydrocarbon gas such as methane [60] or acetylene [61]. Silicon carbonitride films are mostly amorphous, presenting properties similar to those of SiN_x , CN_x , or SiC, depending on the composition. Possible crystalline phases in the SiC_xN_y system have been proposed, in particular Si_2CN_4 and SiC_2N_4 , but their existence remains debated. [62, 63]

The chemical bonding structure in amorphous films is heavily influenced by the elemental composition and the synthesis method. In magnetron sputtered films a distinctive Si–N component is often observed if nitrogen is abundant, [64] due to silicon preferably bonding to nitrogen rather than carbon [56]. Low film nitrogen contents favor the formation of Si–C bonds. [58] Films sputtered with a hydrocarbon gas as a carbon source often have a pronounced C–C component due to presence of amorphous hydrocarbon in the films. [59, 65] Similarly, co-sputtered films show a large C–C contribution. [59]

Due to the wide range of synthesis methods, the SiC_xN_y film properties vary

remarkably. Hardness values under 10 GPa are common for hydrogen-containing carbon-rich SiC_xN_y films, [66] whereas some films can have hardnesses over 30 GPa [51]. Similarly, mass density shows a wide range of values from under 2 g/cm^3 to $\sim 3 \text{ g/cm}^3$. [67] The same applies for optical properties, for example the refractive index can vary from 1.5 to 3.0. [68]

Thin film deposition and process characterization

Physical vapor deposition (PVD) methods, such as magnetron sputtering, are widely used both in research and in industry to grow a wide range of thin films for various applications. In PVD, the film material is ejected from a solid or liquid target and is transported to the substrate as a vapor. Usually PVD methods have a line-of-sight substrate coverage, unlike chemical vapor deposition (CVD) and atomic layer deposition (ALD) methods. The line-of-sight coverage limits the use of complex-shaped substrates in PVD deposition. Some advantages of PVD over CVD and ALD methods are, for example, off-thermal equilibrium film growth, allowing the use of heat-sensitive substrate materials, and higher deposition rates, respectively. Ionized PVD (IPVD) methods, such as high power impulse magnetron sputtering (HiPIMS), can be used to overcome shortages associated with common PVD methods, and open up possibilities to further tailor the film properties while still maintaining the favorable aspects of PVD. [69, 70]

2.1 Magnetron sputtering

Figure 2.1. A schematic drawing of a magnetron sputtering setup.

Sputter deposition is a plasma-based PVD technique commonly employed in thin film growth. A potential difference applied between the negative cathode and a grounded anode causes ionization of the process gas, most commonly Ar, yielding a glow discharge according to Paschen's law. The ignition of the plasma is possible due to the ions and free electrons naturally present in the gas. More ions are created through collisions of the gas atoms with the free electrons, i.e., by electron impact ionization. Positive ionized gas atoms or molecules are accelerated towards the negatively biased cathode, where they sputter away material from the target. The ejected material travels to the substrate in the gas phase and condenses into a film. The grounded chamber walls and the substrate table can act as an anode, though usually a negative bias voltage is applied to the substrate table to exceed the floating potential and to achieve reproducible deposition conditions. [71, 72]

In a magnetron sputtering setup electrons are confined into a magnetic field near the target surface. Increased amount of electrons near the target surface enhances the level of ionization of the working gas and results in greater plasma density in the target vicinity. The working pressure can be decreased due to the increased plasma density, resulting in decreased collisional energy loss of the target bombarding ions in the gas phase, and thus enhanced sputtering rates. [73] A simple schematic drawing of a magnetron sputtering setup is shown in Fig. 2.1. Typical gas pressures used in magnetron sputtering are in the range of 100 mPa – 10 Pa, depending on the dimensions of the sputtering system, affecting the pressure required to ignite and maintain a plasma. [74] Usually the magnets are arranged in a ring-like pattern, with one pole in the center and the opposite pole circling it. Figure 2.2 shows a balanced magnetron configuration, i.e., closed-loop magnetic field lines, which

Figure 2.2. A drawing depicting the orientation of magnetic field lines in a simple balanced magnetron sputtering setup.

results in a dense plasma contained in the target vicinity. Enhanced sputtering over a certain area of the target may result in a so-called racetrack target erosion pattern. Additionally, an unbalanced magnetron setup can be used, resulting in open magnetic field lines and an increased plasma density away from the target, promoting ion bombardment of the growing film. The applied magnetic field configurations affect the ion-to-metal flux ratio arriving at the substrate, and can be used to tailor the morphology and properties of the growing film. [71, 72]

2.1.1 High power impulse magnetron sputtering

High power impulse magnetron sputtering (HiPIMS) is an IPVD technique introduced in the 1990's. [75] In HiPIMS the power to the cathode is delivered in short unipolar pulses with a relatively long halt time between the pulses ($\sim 1 - 10$ ms). The pulse frequencies used in HiPIMS can range from a few tens of Hz to a few kHz, and the pulse on-time from a few microseconds to several hundreds of microseconds. The power on/off ratios during the cycle (duty cycle) vary from a few percent to a few tens of percent. The high energy delivered per pulse results in increased plasma densities in front of the target, which in turn leads to elevated amounts of ionized sputtered material due to electron impact ionization. In HiPIMS discharges the plasma density can reach values up to 10^{19} ions/cm³, for direct current magnetron sputtering (DCMS) discharges the peak plasma densities are two or three orders of magnitude lower. The use of high power pulses allows effective target cooling even when the power delivered to the cathode during the pulse on-time exceeds the time-averaged power by two orders of magnitude, and can reach values as high as several kW/cm². In DCMS processes the target powers usually fall in the range of some tens or hundreds of W/cm². An example of a HiPIMS target current and voltage waveforms recorded for a process done with an average target power of 2400 W, a frequency of 600 Hz, a pulse width of 200 μ s, and at a pressure of 400 mPa employing a N₂O/Ar flow ratio of 12.8% is shown in Fig. 2.3. The target

Figure 2.3. An example of target current and voltage waveforms with a 200 μs pulse.

voltage is not constant throughout the pulse due to depletion of the capacitor bank of the power supply. [76–78]

Thin film processing by HiPIMS mostly relies on the increased portion of ionized target material when compared to DCMS. The higher degree of ionization of the sputtered material results in increased ion bombardment of the substrate and the growing film. [75, 79, 80] For this reason, HiPIMS is found to yield denser films with a glass-like microstructure, when compared to films grown by DCMS that often have a more columnar appearance. [81, 82] The energy and direction of the ionized flux arriving at the substrate can be controlled by electric or magnetic fields, allowing off-axis deposition on complex-shaped substrates. [83, 84] For example, the energy of the ions impinging on the substrate and the growing film can be tuned by adjusting the substrate bias voltage, thus affecting the microstructure and the residual stresses of the growing film. [80] This opens up a possibility to tailor the electrical and optical properties of the films, as those properties depend on the microstructure. [80, 85–88]

HiPIMS also has its limitations. One major drawback is the low deposition rate

of some materials compared to DCMS, when both are operated at the same average target power. [89] The deposition rates for HiPIMS can be half of the DCMS rate or even lower for some metals, for example Ti, Al, and Cr, though for some oxides, e.g., ZrO_2 and Ta_2O_5 , the HiPIMS deposition rate can exceed that obtained by DCMS. [76, 81, 90] Some explanations proposed for lowered deposition rates include magnetic confinement of the sputtered species [84], non-linear energetic dependence of the sputter yield [91], the effects caused by plasma conductivity [92], and back-attraction of charged target metal ions [93]. Another concern is the existence of multiply charged target metal ions, which are accelerated into higher kinetic energies by the substrate bias and can cause undesirable effects, such as ion implantation and higher residual stresses in the films. [94]

2.1.2 Reactive sputtering

In reactive sputtering, the target is sputtered in the presence of one or more reactive gases, either mixed in with the neutral gas or completely replacing it. When a reactive gas, for example O_2 , N_2 , or a hydrocarbon gas such as C_2H_2 , is introduced to the chamber it is likely to react with the target surface by chemisorption and reactive ion implantation, and with the sputtered target material at the substrate as well as with the chamber walls, forming a compound. [95, 96]

The compound film formation at the target surface is known as target poisoning. [97] The transition between the metallic and poisoned target surface conditions is often observed as sudden changes in the cathode voltage and current, gas pressure, and deposition rate. [98, 99] The target current is made of the ion current to the target and partly due to the secondary electron emission from it, according to equation (2.1): [77]

$$I = I_i + I_{\text{SE}} = (1 + \gamma_{\text{SE}})I_i, \quad (2.1)$$

where I_i is the ionic current, I_{SE} is the secondary electron current, and γ_{SE} is the secondary electron emission yield of the target. The secondary electron emission yield can be estimated by using the following empirical relation: [100]

$$\gamma_{\text{SE}} = 0.032 (0.78E_P - 2\phi), \quad (2.2)$$

where E_P is the potential energy of the arriving ion, which is often the first ionization energy, and ϕ is the target surface work function. Thus the changes in plasma composition and the compound formation on target surface affect the discharge current.

Reactive sputtering processes often show hysteresis in relation to the reactive gas flow and the change in target surface conditions. This means that once the poisoned surface conditions have been achieved the reactive gas flow has to be lowered significantly to reach metallic surface conditions again. The magnitude of hysteresis is dependent on the sputter yields of the clean target material and the compound, and also on the pumping speed of the system. [101] The high peak powers used in HiPIMS allow better control over the onset of target poisoning by efficiently removing the poisoned surface layer during the pulse. [102, 103] Moreover, target poisoning by reactive gas ion implantation between the pulses

is limited, reducing the compound formation on the target. [76, 102] This is an advantage compared to DCMS, as growth of stoichiometric compound films often requires the deposition process to be run in the transition regime between metallic and poisoned target surface conditions, to achieve both the desired composition and an ample deposition rate. [102, 104]

2.1.3 Sputtering with different reactive gases

The reactive gases employed in reactive sputtering have a major role defining the behavior of the sputtering process. The gases not only provide the element of interest for compound formation, but due to their inherent chemical and physical properties, such as reactivity and ionization energy, the whole sputtering process is greatly affected by the choice of reactive gas. The following discussion focuses on the three gases that were used in the work presented in this thesis, N_2 , N_2O , and C_2H_2 .

Nitrogen

Nitrogen is commonly used in magnetron sputtering of metal nitrides, especially in the hard coating industry. Once nitrogen is introduced to the sputtering system, several reactions between the nitrogen molecule (N_2) and the plasma electrons can take place. The picture is more complicated than in the case of a monoatomic gas, since the N_2 molecule can also dissociate and in addition it has vibrational and rotational states that can be excited. [105]

The N_2 molecule has an ionization energy of 15.6 eV and can be ionized by electron impact according to the following reaction: [106]

Another possible electron impact reaction is dissociative ionization with an energy threshold of 24.3 eV: [107]

The N_2 molecule can also dissociate without ionization, yielding two N atoms. [108] Another contributing factor to the dissociation and ionization of N_2 is the neutral gas, in this case Ar, allowing for example Penning ionization of N_2 by metastable Ar species and charge transfer reactions. [109, 110] In HiPIMS plasmas, however, the electron impact reactions can be expected to dominate over the other mechanisms due to the high plasma density and high electron energy. [111]

The nitride compound growth on a silicon target surface is seen as a decrease in discharge current. [112] This is due the high surface work function of the compound (~ 7 eV) [113] compared to that of a clean Si surface (4.6 eV) [114], resulting in a decreased secondary electron emission from the target according to equation (2.2). In PAPER III, target poisoning due to nitride compound growth was observed at a comparably high N_2/Ar flow ratio of 0.5, due to low reactivity of nitrogen with silicon. [112] At lower N_2/Ar flow ratios of 0.3 a small increase in peak target

current was observed, which was associated a larger number ions in target vicinity as a result of dissociation of N_2 , rather than being caused by the slightly lower ionization energy of N_2 (15.6 eV) to that of argon (15.8 eV) [115].

Nitrous oxide

Oxygen as a highly reactive element is the major cause behind the effects that were observed for N_2O . First, as N_2O is introduced to the HiPIMS process, the N_2O molecule can be ionized or dissociatively ionized as a result of electron impact. The ionization energy of N_2O is 12.9 eV. [116] The dissociative ionization products of N_2O include NO^+ , O^+ , N_2^+ and N^+ . Both NO^+ and O^+ with a threshold of 15.3 eV are energetically more favorable than N_2^+ (17.3 eV) or N^+ (20.3 eV). [117, 118] In addition, the electron impact cross-sections of NO^+ and O^+ yielding reactions are larger. [117, 118] The N_2O molecule can undergo dissociative electron attachment to yield O^- ions, according to the following pathway:

The reaction occurs already at zero electron energies when the gas temperature is above the room temperature. [119] Additionally, the attachment cross-section increases with gas temperature and its values can reach the same order of magnitude as the electron impact ionization cross-section.[119] Based on the above discussion, it can be expected that ionized oxygen species are found in N_2O -containing HiPIMS plasmas.

The high reactivity of oxygen results in pronounced target poisoning, yielding highly unstable transition region conditions. Sputtering under poisoned target surface conditions often results in arcing of the target, and can produce undesirable macroparticles and decrease the film quality. [120, 121] Various reactive gas flow feedback systems, such as reactive gas partial pressure sensing and reactive gas pulsing, have been employed to maintain the process in the transition regime. [90, 122] Another possibility to achieve controllable deposition processes in the poisoned mode is to use arc suppression. [103, 123] The synthesis of oxynitrides by using both O_2 and N_2 as reactive gases is made more difficult by the nonlinear target effects caused by the different reactivities of O_2 and N_2 . [33, 35] Due to the higher reactivity of oxygen compared to nitrogen, it is more probable that the target is trapped into the poisoned state by oxygen if the reactive gas flows are not accurately controlled. [124] A pathway to achieve more controllable rHiPIMS deposition processes for SiO_xN_y by using nitrous oxide (N_2O) as a single-source precursor gas is presented in PAPERS I and II.

As an electronegative element, oxygen is found to yield O^- ions in rHiPIMS plasmas. [125, 126] These negative ions are repelled by the applied negative cathode potential and can have deteriorating effects on film quality, depending on their origin and energy. [125, 127, 128] Low energy negative ions can be generated via electron attachment to gas atoms or molecules, dissociative electron attachment to gas molecules, or by fragmentation of the sputtered target compound. [126] Ion energies corresponding to the applied cathode potential of several hundreds of volts have been measured for O^- ions originating from the target surface. [128] The O^-

ions existing in the afterglow of the rHiPIMS pulse can potentially contribute to the film oxygen uptake even during the pulse off-time. [125]

Figure 2.4. The evolution of the target current with N_2O flow.

The oxide compound formation at the target surface in the case of using silicon as target material is observed as a rise in peak target current due to higher secondary electron yield of silicon oxide compared to silicon. [100, 129] Figure 2.4 shows the target current waveform evolution as the percentage of nitrous oxide in the plasma is increased, using an average target power of 4000 W and a pulse frequency of 1000 Hz, at a pressure of 400 mPa. A noticeable delay in target current growth is seen as the N_2O flow is increased and the peak target current shifts later into the pulse compared to a nonreactive process. This behavior can be attributed to postponed breakdown of the process gas due energy loss of electrons in front of the target. [130] The energy loss is due to excitation of the N_2O molecules, owing to dissociation and excitation of the vibrational and rotational states of the molecule. [117, 118, 130, 131] Initially, the peak target current decreases as more nitrous oxide is introduced. This can be attributed to the decreasing plasma density in front of the target and thus decreasing plasma conductivity [132–134], and to reduced secondary electron emission from silicon suboxides [98], limiting the current that can be drawn to the cathode. After a certain threshold the peak current starts increasing, indicating poisoned target surface conditions, because the secondary electron emission yield from completely oxidized silicon surface is higher than that from clean silicon or suboxides. [98, 100, 129] Eventually the target current grows larger than that of the clean Si target, as is the case for a

N_2O flow of 100 sccm, shown in Fig. 2.4.

Acetylene

Hydrocarbon gases such as acetylene (C_2H_2) and methane (CH_4) are commonly used to synthesize amorphous carbon thin films and metal carbides by magnetron sputtering. [135–137] They have been used as the carbon source for SiCN films, where N_2 was used to supply nitrogen, resulting in a complex sputtering process with more than one reactive gas. [58, 60]

Several electron impact reactions are possible for the C_2H_2 molecule. Electron impact ionization has an energy threshold of 11.4 eV [105], which is significantly lower than that of Ar (15.8 eV) or N_2 (15.6 eV). In addition, the ionization cross-section of C_2H_2 is higher than those of Ar [138] or N_2 [106], implying that ionization of C_2H_2 favored in Ar/ N_2 / C_2H_2 mixtures. Also the dissociative ionization products C_2H^+ , C_2^+ , H^+ , and C^+ are possible, but have higher energy thresholds than pure ionization. [139] The C_2H_2 molecule can dissociate into C_2H and H radicals with a threshold energy of 7.5 eV, which further increases the number of reactive hydrocarbon species in the plasma. [140]

Figure 2.5. The Si target peak current as a function of C_2H_2 flow rate.

The reactive sputtering process with C_2H_2 is inherently different compared to those using O_2 or N_2 , because a hydrogen-containing carbon layer consisting only of the supplied gas can form on the target surface, whereas both oxygen and nitrogen need to form a compound with the target material. [135, 141]

This leads to some peculiar properties, such as a plasma CVD-like process where amorphous carbon films can be deposited from a heavily poisoned metal target. [137, 142] Similar behavior was observed in PAPER V for a Si target sputtered in Ar/N₂/C₂H₂ plasmas, where increasing C₂H₂ flow rates resulted in increasing film carbon contents, replacing equally both silicon and nitrogen. Here, the Ar/N₂ flow rate was fixed to 0.28 to yield a pressure of 400 mPa and pressure was allowed to increase as C₂H₂ was introduced. Figure 2.5 shows the Si target peak current versus the applied C₂H₂ flow rate. The initially increasing peak target currents were assigned to increased ion bombardment of the target, owing to the large number of ionized hydrocarbon species present in the plasma, and partly to altered target surface chemistry. Decreasing peak target currents seen for C₂H₂ flows higher than 20 sccm were linked to decreased secondary electron emission due to greater number of target-bombarding ions being hydrocarbon species. This results in lower secondary electron emission yield according to equation (2.2), as the ionization energy of C₂H₂ is lower than those of Ar or N₂. An amorphous carbon-rich target surface can also contribute to lower secondary electron emission [143], compared to silicon [114] or nitrogen-rich hydrocarbon [144].

2.2 Plasma characterization

2.2.1 Langmuir probe measurements

Plasma parameters in the HiPIMS discharge can be measured by using a Langmuir probe. [145, 146] The probe has to be small to minimize perturbations caused to the plasma. As the probe bias is swept from negative to positive voltages, both ions and electrons are collected by the probe and an $I - V$ curve is recorded. These curves can be measured dynamically to record the $I - V$ curves during different stages of the pulse. An ideal $I - V$ curve is shown in Fig. 2.6. At the floating potential (V_f) the ion and electron currents drawn by the probe are equal and probe current (I_p) is nil. At the plasma potential (V_p) the probe is in the same potential as the plasma itself, and the probe current is mostly resulting from electrons. [147]

Three different curve regions can be identified based on the applied probe bias (V_b). When $V_b < V_f$, electrons are repelled and I_p is mainly caused by ions, until the ion saturation current ($I_{i,sat}$) is reached at large negative V_b . At $V_b > V_p$, only negative charge carriers are being collected by the probe and eventually the electron saturation current ($I_{e,sat}$) is reached. [147]

Between V_f and V_p , increasing amount of electrons are being collected by the probe. At a certain V_b only those electrons that have enough energy to overcome the potential difference between the probe and the plasma are collected. In the case of a Maxwellian energy distribution of electrons, the electron current collected by the probe in this region follows equation (2.6):

$$I_e = I_{e,sat} \exp e \frac{V_b - V_p}{k_B T_e}, \quad (2.6)$$

where k_B is the Boltzmann constant and T_e is the average electron temperature. The slope of $\ln I_e$ versus V_p yields the electron temperature. It is convenient to

Figure 2.6. An ideal Langmuir probe $I - V$ curve, showing both V_f and V_p .

give T_e in electronvolts, by using the inverse of the slope. [147]

A custom built Langmuir probe system was used in PAPERS II and III to measure the electron temperature. Time-resolved measurements were performed to measure the $I - V$ curves during the peak target current of the HiPIMS pulse. The chosen $I - V$ curves were analyzed manually by extracting the electron temperature from the slope of electron current versus the probe current in a semilogarithmic scale. The main finding of the Langmuir study was that the electron temperature was increasing with the amount of N_2O in the plasma, as is presented in Fig. 2.7. The electron temperature was found to increase rapidly from 2.8 eV of the non-reactive process when only a small amount of N_2O was introduced. At a N_2O flow of 10 sccm, corresponding to a 2.3 % N_2O/Ar flow ratio, T_e rose to 4.6 eV, a 1.8 eV increase from 2.8 eV. An increasing T_e was observed though the studied flow range, T_e reaching a maximum of 7.2 eV at a N_2O flow of 60 sccm. The increase in T_e can be due to the removal of low-temperature electrons from the plasma due to dissociative electron attachment to the N_2O molecule, [148] or due to the excitation of the vibrational and rotational levels of the N_2O molecule, which increases the effective ionization energy of the working gas. [133, 134]

2.2.2 Mass spectrometry

The properties of sputtered thin films are strongly dependent on the type and energy of the species arriving at the substrate during film growth. Mass spectrometry can

Figure 2.7. The average electron temperature HiPIMS Ar/N₂O plasmas measured at the moment of peak target current versus the applied N₂O flow.

be used to identify these species and to determine their quantity and energy. In the case of pulsed sputtering, also the temporal evolution can be recorded. A mass spectrometer is an instrument consisting of several stages. A probe with an orifice is immersed in the plasma, in this case inside the sputtering chamber, to collect the species to be analyzed. An ionization stage inside the orifice is used to ionize the neutral species being studied. The ions are then filtered based on their kinetic energies to choose the desired energy range. The remaining ions are further filtered based on their mass-to-charge ratio by using a quadrupole mass filter. Finally the ions are detected by using a secondary electron multiplier, which transforms the counts into an electrical signal. [149]

Mass spectrometry was used in PAPERS III and IV to study the composition and temporal evolution of Si/Ar/N₂ plasmas, with N₂/Ar flow ratios up to 0.50. In PAPER III it was observed that increasing N₂/Ar flow ratios resulted in decreasing ion count rates and energies compared to the nonreactive discharge. It was concluded that during pulse on-time the prevailing ion species in the plasma were Si⁺ and N⁺/Si₂⁺, where the effect of Si₂⁺ to the N⁺/Si₂⁺ signal was assumed to be low as it was not detected for the nonreactive discharge. The heavier species such as SiN/Si₂ and 2 Ar reached their maximum intensity after the pulse due to their higher probability of collisions and low kinetic energies after forming in the plasma. The difference between these two groups of ions was most pronounced at an N₂/Ar flow ratio of 0.30. The effect of gas rarefaction was seen in the ³⁶Ar

signal up to N_2/Ar flows of 0.16.

In PAPER IV, mass spectrometry was used to investigate the effect of pressure, pulse energy, and target power on the composition and energy distribution of the $\text{Si}/\text{Ar}/\text{N}_2$ discharge to connect the plasma properties to residual stresses in the films. Increasing ion energies were observed for lower pressures and larger pulse energies, while increasing pulse frequencies were found to result in larger overall ion count rates.

2.3 Experimental details of thin film deposition

An industrial coating unit CC800/9 ML (CemeCon AG, Germany) was used for thin film synthesis and plasma characterization presented in this work. The unit is equipped with six cathodes of which two can be run in either HiPIMS or DC mode and four in either DC or mid-frequency mode. A schematic view of the substrate table and the cathodes is shown in Fig. 2.8. In the case of noncombustible gases Ar and N_2 in PAPERS III, IV, and VI, the process gas was let in between the front heater and the closest DC cathodes. With combustible gases N_2O and C_2H_2 , the inlets behind the cathodes on both sides of the chamber were used.

A fixed target-to-substrate distance of 6 cm was used in all depositions. No substrate rotation was applied in processes studied in PAPERS I-V, while in PAPER VI the substrate table was rotated as multiple targets were used. The applied substrate bias was synchronized with the cathode pulses for thin film deposition in all studies, except in PAPER VI, where a DC bias was used. A constant pulse width of 200 μs was applied for the HiPIMS pulses, with frequencies ranging from 100 Hz to 4000 Hz. The average target power at the Si HiPIMS target ranged between 400 W and 4000 W. The processes were conducted at substrate temperatures from no applied heating, i.e., only plasma heating, to 530 °C.

Figure 2.8. A schematic top view of the deposition chamber.

Several analysis methods are required to characterize thin film properties. A set of techniques used to determine chemical composition, chemical bonding, mechanical properties, and optical properties of the films are presented in this chapter.

3.1 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is used to determine both the elemental composition and chemical bonding in the films. The operational principle of XPS is based on the photoelectric effect caused by soft X-rays, commonly Al K_α radiation ($h\nu = 1486.6$ eV). XPS is a surface sensitive technique, as the inelastic mean free path of photoelectrons is in the order of $\sim 5 - 10$ nm. The measurements have to be performed under ultra-high vacuum conditions to suppress adsorption of residual gas during analysis. [150]

Binding energies (E_b) of the emitted photoelectrons can be determined according to equation (3.1), as their kinetic energies (E_k) are measured and the photon energy ($h\nu$) is known:

$$E_b = h\nu - E_k - \phi, \quad (3.1)$$

where ϕ is the spectrometer work function. [150]

Both the elemental composition and chemical bonding structure of the sample can be determined by the core level electron binding energies. The detection of hydrogen by XPS is virtually impossible, because it only has one valence electron and no inner electrons. The signal from the H valence electron would be lost within the signal from all the other valence electrons of the surface atoms in the sample. [151] Different elements have distinct core level binding energies that can be slightly influenced by the chemical environment of the atom, a phenomenon known as the chemical shift. For example, the core level electrons of an atom bonded to a more

electronegative atom will have a stronger Coulomb interaction with the nucleus, as valence electrons are drawn towards the more electronegative element. Charge compensation can be applied in the case of dielectric samples, such as SiO_xN_y films, because charge accumulation on the sample results in a shift of measured binding energies. [150]

The sample surface can be sputter cleaned with an ion beam etch to remove the oxidized surface layer and adventitious carbon occurring on most materials. A significant oxygen surplus in the elemental composition would be observed if the elemental composition was to be determined from this oxidized surface layer. The energetic ions used for the sputter cleaning can, however, damage the chemical bonding structure and alter the composition in some amorphous materials. In such cases the chemical bonding structure can instead be determined from as-received films, without applying sputter cleaning, thus avoiding possible alterations to the chemical bonding structure. [152]

Figure 3.1. A XPS Si 2p core level spectrum recorded for a SiO_xN_y film containing 27 at.% and 17 at.% of N and O, respectively. Five peaks can be fitted to the spectrum.

A peak fitting procedure has to be implemented to obtain information about the chemical bonding in the films. In compound films, the number of different chemically shifted contributions in the core level spectra of elements partaking in chemical bonding can be up to five, or even more in some cases. [153, 154] An example of a Si 2p core level spectrum obtained before a sputter clean for a SiO_xN_y film containing 27 at.% of N and 17 at.% of O, and fitted with a peak fit model consisting of five distinct peaks is shown in Fig. 3.1. Here, the different chemical

bonding contributions can be assigned to Si–Si bonds at 99 eV, Si–N_x bonds at 99.7 eV, Si–O_xN_y contributions at 100.9 eV and 101.9 eV, and Si–O_x bonds at 102.9 eV. The Si–O_xN_y contributions have the largest FWHM values, as much as 1.8 eV, while for the Si–Si bonds the peak FWHM is under 1 eV.

In SiO_xN_y films, the number of different bonding contributions in the Si 2p core level spectra depends on the bonding model of the films. In the case of the film shown in Fig. 3.1, deposited at a relatively low temperature ($\lesssim 350$ °C) by HiPIMS, both N and O are randomly distributed in the Si matrix. [153, 154] As silicon can form four bonds, multiple different bonding configurations with varying x and y in SiO_xN_y are possible. This results in large peak widths for the components corresponding to SiO_xN_y compositions. [153, 154]

Figure 3.2. The XPS C 1s core level spectra recorded for a SiCN films containing ~ 20 at.% C, a) deposited by using acetylene as the carbon source and b) by co-sputtering from C and Si targets.

The bonding of carbon in SiCN films depends on the carbon source, as was

found out in PAPERS V and VI. As seen in Fig. 3.2 the C 1s core level spectra are slightly different for films co-deposited from C and Si targets than films deposited with C_2H_2 as the carbon source. Both films contain ~ 20 at.% of C and 33 at.% Si, the N content in the co-sputtered films is higher (43 at.%) than in the C_2H_2 films (29 at.%) that also contain 14 at.% hydrogen. In the co-sputtered films the area of the C–Si component 283.4 eV [64] corresponds to 24% of the total C 1s peak area, while in the C_2H_2 films it amounts for 22%. A larger difference is observed for the C–C component at 284.5 eV [155], in the co-sputtered films it amounts for 42% of the total C 1s area and for 54% in C_2H_2 films. The co-sputtered films have a higher amount of C–N and C–N/O bonded carbon (34%), at 285.8 eV and 287.3 eV, respectively, than the C_2H_2 -based films (28%). The components in the co-sputtered films are also shifted towards higher binding energies by 0.2 – 0.3 eV when compared to the C_2H_2 films as a result of their higher N content and more electronegative bonding environment.

3.2 Elastic recoil detection analysis

Elastic recoil detection analysis (ERDA) is an ion beam analysis method used to obtain thin film sample's elemental concentration depth profiles. In ERDA, high energy ion beam, such as 36 MeV $^{127}I^{8+}$ used in PAPER I, is collided with the sample and the energies of forward-directed elastic recoils are measured. A time-of-flight (ToF) spectrometer can be used to differentiate between recoils having the same energy but different mass. The use of a ToF spectrometer allows the determination of element depth profiles, as ions originating from below the sample surface lose some of their energy in collisions. [156]

The energy of a target atom with mass M_2 after an elastic collision with a projectile with mass M_1 and energy E_1 is given by equation (3.2):

$$E_2 = \frac{4M_1M_2 \cos^2 \theta}{(M_1 + M_2)^2} E_1 = K_R E_1, \quad (3.2)$$

where θ is the scattering angle and K_R is the kinematic factor for elastic recoil. The maximum scattering angle depends on the ratio of the masses of the projectile and the target atom. The maximum scattering angle is given by equation (3.3): [157]

$$\phi_{max} = \arcsin \left(\frac{M_2}{M_1} \right). \quad (3.3)$$

As can be seen from (3.3), the amount of detectable elements for a certain sample depends on the system geometry and the choice of projectile. For film elemental compositions measured in PAPERS I and V a 36 MeV $^{127}I^{8+}$ ion beam at an angle of 22.5° relative to the sample surface was used.

The use of ERDA was necessary to study the elemental composition of the films in PAPER V, deposited with acetylene as the carbon source, since XPS can not be used to detect hydrogen. A concern however associated with ERDA measurements for films of low- Z elements is the possible film alteration due to ion bombardment. [158] As the density of some films in PAPER V was under 2.0 g/cm^3 and the carbon

Figure 3.3. The elemental composition SiCN:H films versus the applied acetylene flow as measured by ERDA, from PAPER V.

content was expected to be as high as 80%, caution was taken to avoid too long measurement times and potentially causing damage to the samples during the measurement. Figure 3.3 shows the elemental composition of the SiCN:H films studied in PAPER V as a function of the applied C_2H_2 flow rate. As expected, the amount of C increases as the C_2H_2 flow rate is increased, and at the same time the Si concentration decreases. The amount of N is decreasing with increasing C_2H_2 flows as C_2H_2 is more readily ionized in the plasma. [105, 106, 139]

The film hydrogen content does not follow a similar pattern, but rather seems to reach a plateau at ~ 15 at.%. Based only on the level of acetylene in the plasma one could expect increasing film H contents with increasing C_2H_2 flows. The potential causes behind the leveling of film H concentration include removal of H by ion bombardment either at the target or the growing film during the synthesis, [159–161] or potentially by the beam during the ERD measurement. Further investigations are required to precisely identify the cause behind the leveling of film H concentration.

3.3 X-ray reflectivity

X-ray reflectivity is a technique based on specular reflection of X-rays from surfaces and interfaces. The reflection is based on the different electron densities of the layers. The method can be used to determine thin film thickness, density, surface

roughness, and multilayer structures in a glancing angle $\theta/2\theta$ configuration, where the incident and reflected angle are equal ($\omega = \theta$). Below the critical angle θ_c , the incident beam undergoes total external reflection. For $\theta > \theta_c$ the reflected intensity starts to fall due to absorption in the material. A double critical angle can be observed if the film is less dense than the substrate. [162] In this case the X-rays first penetrate the film when the incident angle exceeds the film critical angle and are reflected at the film–substrate interface. Above θ_c the reflections from different interfaces interfere and give rise to interference fringes. The period of the fringes along with the fall in intensity can be used to determine the thickness and roughness of the layers. [163]

For a monolayer film, equation (3.4) can be used to obtain the film thickness: [164]

$$n\lambda = 2t \sin \theta \sqrt{1 + \frac{\eta^2 - 1}{\sin^2 \theta}}, \quad (3.4)$$

where n is an integer, λ is the wavelength of incident X-rays, t is the film thickness, and η is the film's complex refractive index. To assess properties such as density and surface roughness, the recorded data can be iteratively fitted with a suitable theoretical model of the sample, if the film composition is known. [163]

Figure 3.4. Two examples of experimental XRR curves obtained for films studied in PAPER V.

The method was used in PAPERS I, II, III, and V to obtain the film density. Figure 3.4 shows an example of two experimental XRR curves obtained for SiN and SiCN:H films in PAPER V. A clear double critical angle is visible in the SiCN:H

film in the example, containing ~ 80 at.% carbon, due to the film being less dense (1.6 g/cm^3) than the silicon substrate (2.3 g/cm^3). Double critical angles were observed for SiCN:H films containing ~ 50 at.% or more carbon. The experimental XRR curves were fitted with the PANALYTICAL X'PERT REFLECTIVITY software to obtain the film density. A model consisting of the surface oxide layer, the film, and the native oxide on a Si substrate was used. The densities of co-sputtered SiCN films in PAPER VI could not be resolved reliably by XRR, probably due to the laminate-like structure of the films.

3.4 Raman spectroscopy

Raman spectroscopy is a vibrational spectroscopy method commonly used for determining the molecular and lattice vibrations in materials. It is based in the inelastic scattering of monochromatic light, usually from a laser, by the target material, which can be solid, liquid, or even gaseous. Most of the signal consist of light that scatters elastically from the sample, giving rise to a strong signal at the same frequency as the incident light, the so-called Rayleigh scattered light. Some of the photons however interact with the sample molecule or crystal, resulting in a vibrational transition and the frequency of the emitted photon is shifted by the energy required to excite the transition. The Raman spectrum of the sample is made of the inelastically scattered light. The Stokes line corresponds to light with a lower frequency than the incident light, as the target molecule or lattice is excited to a higher vibrational state. In anti-Stokes scattering the sample is on an excited vibrational state and the interaction with the light results in a return to the ground state, and a photon with a larger energy is emitted. The Stokes line is often more pronounced as the sample is in thermodynamic equilibrium. Raman spectroscopy is complementary to infrared spectroscopy and often they are combined to map the vibrational modes of the sample being studied. The Raman scattering requires the molecule or the lattice vibration to have a nonzero change in polarizability upon irradiation, while infrared activity requires a change in dipole moment during vibration. Some of the vibrational modes satisfy both selection rules. The intensity of Raman scattered light is low, only $\sim 10^{-5}$ of the intensity of the incident light, meaning that the signal needs to be filtered to cut off the Rayleigh scattered light. This can be done by using interference filters or by having multiple dispersion stages. [165, 166]

The Raman signal of carbon-containing materials shows characteristic features at $\sim 1360 \text{ cm}^{-1}$ and $\sim 1560 \text{ cm}^{-1}$, named the *D* and *G* peaks, respectively. [167] The origin of both *D* and *G* peaks is the sp^2 hybridized carbon. The *G* peak arises from bond stretching of sp^2 atoms in rings and chains, while the *D* peak is due to breathing modes in rings. [168] The shift of peak positions and their relative intensities, the $I(D)/I(G)$ ratio, tell about the ordering of film carbon network. [167] Increasing $I(D)/I(G)$ ratio and decreasing *G* peak linewidths are signs of ring-like ordering of the sp^2 carbon network. [168] Raman spectroscopy was used to study the chemical state of carbon in SiCN:H films deposited by HiPIMS in PAPER V. An example of Raman spectra obtained for two films deposited at different

Figure 3.5. Raman spectra of two SiCN:H films deposited at different substrate temperatures by HiPIMS in PAPER V.

substrate temperatures is shown in Fig. 3.5. It was observed that the G peak FWHM decreased from $\sim 200 \text{ cm}^{-1}$ to $\sim 180 \text{ cm}^{-1}$ as substrate temperature was raised from no additional heating to 510°C . At the same time the $I(D)/I(G)$ ratio rose from 0.44 to 1.10. Similar ring-like ordering of film sp^2 carbon network is often seen for carbon-containing thin films as the substrate temperature is increased or after annealing. [169, 170]

3.5 Transmission electron microscopy

In transmission electron microscopy (TEM) a beam of electrons is accelerated towards a thin sample. Due to small sample thickness of $\sim 100 \text{ nm}$ part of the electron beam is transmitted through the sample unaffected while some of the beam is scattered by the atoms, either elastically or inelastically. The acceleration voltages used in materials science TEM imaging are usually around 200 kV . Magnetic lenses and apertures are used to focus the beam on a desired spot on the sample. Similarly, after the beam passes the sample lenses and apertures are used to select and steer the desired signal to form an image by a CCD camera. The most straightforward TEM imaging mode is the bright field (BF) mode, where only the directly transmitted beam is used to construct the image. In a BF image the sample areas that are thick, have high mass and density appear darker as they scatter more electrons, which are filtered away from the image. The inverse imaging mode

to BF is dark field (DF) imaging, where the directly transmitted beam is filtered away and the scattered parts are selected, thus the areas with higher scattering probability appearing brighter in the image. Both signals can be selected to obtain a phase contrast image. Phase contrast imaging is used in high resolution TEM (HRTEM) to achieve atomic resolution.

The electron beam can be used to study the sample structure by means of diffraction, as the diffracted electrons satisfy Bragg's law. The major advantage of using electrons for diffraction studies is their short wavelength compared to X-rays. By selecting a correct aperture a diffraction pattern can be obtained from a certain spot of the sample, creating a selected-area diffraction (SAED) pattern. The SAED pattern can be used to determine the local sample microstructure rather than having the signal from a larger volume as in XRD. For crystalline samples the diffraction pattern consists of discrete dots, while for amorphous samples broad and diffuse rings are observed due to lack of ordering. The distance of the diffraction features from the central spot can be used to calculate the associated lattice spacing.

Figure 3.6. a) A TEM image of a layered SiCN film deposited by HiPIMS/DCMS co-sputtering from PAPER VI, b) a SAED pattern from the given SiCN film and the Si substrate.

A multistep preparation procedure needs to be carried out in order to obtain electron transparent cross-sectional TEM samples. For ceramic materials a procedure involving mechanical polishing followed by ion beam thinning is often used, as in PAPER VI. In this procedure, two small pieces of the sample are fitted in a grid with the film sides against each other. The grid is then tightened so that the pieces are firmly secured and glued with a mixture epoxy resin and carbon on a heating plate. After that the sandwich is mechanically polished by using diamond grinding paper to obtain a scratch-free surface and a thickness of under 100 μm . After the mechanical polishing step the final thinning is done by ion milling. During the ion milling two Ar^+ ion beams of 1 – 5 keV at an angle of $\sim 5^\circ$ to the surface plane are used to thin the sample. For cross-sectional samples a higher energy of ~ 5 keV is

first used to create a hole through the sample and after that the final polishing is carried out at beam energies around 1 keV to clean off the damaged portion of the specimen.

A TEM image of a SiCN film from PAPER VI is shown in Fig. 3.6 a), and its respective SAED pattern along the diffraction pattern of the Si substrate in Fig. 3.6 b). The layered SiN/CN structure is clearly visible in the image, the thicker SiN layers appearing darker due to the larger mass of silicon. The SAED pattern gives away the sample's amorphous structure as broad and diffuse rings are observed rather than discrete diffraction spots.

3.6 Residual stress measurement

The residual stresses in amorphous thin films can be determined by the wafer curvature method, using X-ray diffraction to obtain the substrate curvature after deposition. An assumption made here is that the residual stresses in the film have only uniform in-plane components, which is a reasonable approximation for amorphous films. [171]

Figure 3.7. A measured shift in the angle between the X-ray beam and the sample surface, while maintaining the 2θ -reflection, versus sample displacement.

The curved crystallographic planes in the stressed silicon substrate cause the angle of diffraction to shift along the rigid translation of the sample. When displacing the sample along the x -axis and maintaining the 2θ -reflection, the radius of curvature of the substrate can be determined from the measured shift of the ω -angle (the angle between the beam and the sample surface) as a function of the

x -displacement. A typical measurement for a SiO_xN_y film is shown in Fig. 3.8. The specimen curvature is related to the change in orientation of the diffracted beam after displacement in the x -axis by equation (3.5): [172]

$$\frac{1}{R} = \frac{d\omega}{dx}, \quad (3.5)$$

where R is the radius of curvature of the specimen, $d\omega$ is the change in the orientation of the diffracted beam, and dx is the sample displacement along the x -axis.

Figure 3.8. A linear fit to the measured displacement–angle pairs to yield the radius of substrate curvature for a SiO_xN_y film, from PAPER I.

The effect caused by intrinsic substrate curvature and possible erroneous stage translation can be determined by measuring the curvature of an uncoated substrate. The obtained value is subtracted from the curvature value measured for the coated specimen to obtain the true curvature:

$$\frac{1}{R} = \frac{d\omega}{dx} - \frac{d\omega}{dx}_{\text{uncoated}}. \quad (3.6)$$

The radius of substrate curvature is then given by the slope of x -displacement versus the ω -angle in radians, as shown in Fig. 3.8. [172]

The measured substrate curvature can be related to the residual film stress by using the Stoney formula for anisotropic single crystal $\text{Si}(001)$ lattice:

$$\sigma_f t_f = \frac{h^2}{6(s_{11}^{\text{Si}} + s_{12}^{\text{Si}})R}, \quad (3.7)$$

where σ_f is the in-plane stress component of the film, t_f is the film thickness, h is substrate thickness, and the term $1/(s_{11}^{\text{Si}} + s_{12}^{\text{Si}})$ is the biaxial modulus of Si(001) ($1.803 \cdot 10^{11}$ Pa). [171, 173] An example of the ω -angle versus sample displacement is shown in Fig. 3.8. With a film thickness of ~ 420 nm the residual stress can be calculated to be approximately -680 MPa, indicating compressive residual stress in the film.

3.7 Nanoindentation

Nanoindentation is a method commonly used in measuring the hardness and elastic modulus of thin films. In nanoindentation, a sharp diamond tip of known geometry is pressed against the sample surface with a steadily increasing load and then released. The applied load and indentation depth are monitored to construct a load–displacement curve. Typically a Berkovich tip with a three-sided pyramid shape is used to maximize the contact area. In the case of thin films the indentation depth has to be limited to $\sim 10\%$ of the films thickness, or otherwise the substrate will influence the measurement. The most common method used in analyzing the nanoindentation data is the one suggested by Oliver and Pharr. [174] In the model the load deformation is assumed to be both elastic and plastic, and the unload deformation being only elastic. An example of a load–displacement curve recorded for SiCN:H studied in PAPER V is shown in Fig. 3.9.

Figure 3.9. A typical load–displacement curve measured for the SiCN:H studied in PAPER V, where $P_{\max}$ is the maximum load, $h_{\max}$ is the maximum displacement, h_f is the final displacement, and $\frac{dP}{dh}$ is the elastic unloading stiffness.

The hardness (H) of the films can be calculated from the effective contact area of the tip (A) and maximum applied load ($P_{\max}$) according to equation (3.8):

$$H = \frac{P_{\max}}{A}. \quad (3.8)$$

The contact area can be estimated by using a tip-specific area function. The required area function on the other hand can be calibrated by performing a series of indents on a sample with a known hardness and elastic modulus, such as fused quartz. [174]

The elastic unloading stiffness $\frac{dP}{dh}$, which can be determined from the tangent of the first part of the unloading curve as shown in Fig. 3.9, and the effective contact area can be connected to the elastic modulus E by using equation (3.9):

$$\frac{dP}{dh} = \beta \frac{2E_{eff}\sqrt{A}}{\sqrt{\pi}}, \quad (3.9)$$

where β is a tip specific constant (~ 1 for a Berkovich tip) and E_{eff} is the effective elastic modulus. Effective elastic modulus is defined as:

$$\frac{1}{E_{eff}} = \frac{1 - \nu^2}{E} - \frac{1 - \nu_i^2}{E_i}. \quad (3.10)$$

Here, ν is the Poisson ratio and of the specimen, E is the elastic modulus of the specimen, ν_i is the Poisson ratio of the indenter, and E_i is the elastic modulus of the indenter. [174]

Nanoindentation was used in PAPERS III, IV, V, and VI to study the hardness and elastic modulus of SiN and SiCN thin films.

3.8 Spectroscopic ellipsometry

Spectroscopic ellipsometry is a technique widely used for structural and optical characterization of thin films and surfaces. In the case of standard ellipsometry, the measured parameters are the ellipsometric angles Ψ and Δ . In reflection mode the state of polarization of light reflected from the sample is analyzed, when the incident light has a known polarization. The complex reflectance ratio ρ between the p and s polarization planes can be linked to the measured angles by equation (3.11): [175]

$$\rho = \frac{r_p}{r_s} = \tan \Psi \exp i\Delta, \quad (3.11)$$

where r_p and r_s are the complex reflection coefficients for p - and s -polarization, respectively.

A dual rotating compensator ellipsometer setup can be used to measure the full Mueller matrix $\mathbf{M}$ of the sample. A Mueller matrix is a 4×4 matrix describing the polarization properties of an optical element interacting with the incident light. Measuring the Mueller matrix allows determination of depolarization effects, caused by, for example, nonuniform film thickness. A simple schematic of a dual rotating

Figure 3.10. A schematic drawing of a dual rotating compensator spectroscopic ellipsometer.

compensator ellipsometer setup is shown in Fig. 3.10. Unpolarized light is passed through a polarizer and a rotating compensator modulating the polarization, before being reflected from the sample. After being reflected, the light passes through a second rotating compensator and an analyzer before being detected. [175]

In the case of isotropic reflecting samples, such as amorphous SiO_xN_y films, the number of nonzero elements in $\mathbf{M}$ decreases to 8 and $\mathbf{M}$ takes the following form: [175]

$$\mathbf{M} = \begin{bmatrix} 1 & -N & 0 & 0 \\ -N & 1 & 0 & 0 \\ 0 & 0 & C & S \\ 0 & 0 & -S & C \end{bmatrix}. \quad (3.12)$$

The elements N , C , and S can be related to the ellipsometric angles by relations (3.13) a-c:

$$N = \cos 2\Psi, \quad (3.13a)$$

$$C = \sin 2\Psi \cos \Delta, \quad (3.13b)$$

$$S = \sin 2\Psi \sin \Delta. \quad (3.13c)$$

For N , C , and S it holds that

$$N^2 + C^2 + S^2 = 1.$$

The N , C , and S can also be connected to equation (3.11) by equation (3.14): [175]

$$\rho = \frac{r_p}{r_s} = \frac{C + iS}{1 + N} = \tan \Psi \exp i\Delta. \quad (3.14)$$

In most cases the ellipsometric measurement is indirect, and does not yield the sample's structural properties, but they have to be obtained by iteratively fitting

the data with a suitable model including the possible layers and interfaces in the sample. In the case of amorphous SiO_xN_y films, the Tauc–Lorentz (TL) dispersion model was used to model the complex dielectric function ($\epsilon = \epsilon_1 + i\epsilon_2$) of the films to obtain their refractive indexes n and extinction coefficients k . [176, 177] Both n and k can be calculated from ϵ , as $\epsilon_1 = N^2 - k^2$ and $\epsilon_2 = 2nk$. In TL model, ϵ_2 has the following expression above the band gap energy:

$$\epsilon_2 = \frac{1}{E} \frac{AE_0C(E - E_g)^2}{(E^2 - E_0^2)^2 + C^2E^2}, E > E_g, \quad (3.15)$$

where E is the photon energy, A the peak amplitude, E_g is the band gap energy, E_0 is the peak transition energy, and C is a broadening term. Below the band gap energy $\epsilon_2 = 0$. The real part of the dielectric function, ϵ_1 , can be calculated from ϵ_2 by using Kramers–Kronig integration. [176]

The measure of how well the model fits the measured data is quantified by mean squared error (MSE). The MSE is minimized by iteratively fitting the constructed model to the measured data. However, the smallest MSE does not necessarily implicate that the used model is correct. The model has to yield physically meaningful results for the layer thicknesses, for example. [175]

Figure 3.11. Refractive indexes of SiO_xN_y films from PAPER II.

Spectroscopic ellipsometry was used in PAPERS I and II to measure the refractive indexes and extinction coefficients of SiO_xN_y films. Values ranging between those of silicon nitride and silicon oxide were measured for films where no Si–Si bonds

were detected in the XPS core level spectra. Films with Si–Si chemical bonding showed values that were nearing those of amorphous silicon, depending on the film chemical composition. An example of refractive indexes measured for SiO_xN_y films versus the applied target power and nitrous oxide flow rate is shown in Fig. 3.11. At low average powers the films show lower values of n due to more oxide-like film chemical composition. Also the pulse frequency affects the n , but to lesser extent than the average target power. Higher N_2O flow rates resulted in lower values due to more stoichiometric film composition.

Summary of included publications

Paper I

A new synthesis route for SiO_xN_y thin films by rHiPIMS, using N_2O as a single-source precursor gas, was presented. The films were characterized based on their chemical, optical, and mechanical properties. The elemental compositions of the films are shown in Fig. 4.1 along with those studied in PAPER II as a ternary plot. The changes in film elemental composition were related to the used deposition parameters through target poisoning. The film elemental composition was controlled by the target power, either by having a fixed pulse energy or increasing the target power, and by the N_2O -to-Ar flow ratio. Increasing N_2O flow ratios resulted in larger film O and N concentrations, while the O/N ratio could be controlled by the average target power. The effect of target power was studied both by using a constant energy per pulse and changing the pulse frequency, and by using a fixed pulse frequency and changing the average target power. The O/N ratio varied between 0.8 – 1.9, while the largest film O content was ~ 13 at.%. Nitrogen concentrations were not affected by the power settings, but mainly responded to the applied N_2O flow rate.

Film mechanical properties did not show large variations with respect to deposition parameters. The films showed dense and featureless cross-sections as studied by scanning electron microscopy. Residual stresses from -650 to -960 MPa were measured, and the average film density was 2.45 g/cm^3 .

The film chemical bonding structure was studied by XPS. Increasing Si–N and Si–O bonding was seen for larger N and O contents, respectively. The percentage of Si–Si bonding in the spectra was decreasing with increasing N_2O flows and decreasing target power. Film optical properties were in agreement with the chemical composition. Decreasing values of both n and k were measured for films

Figure 4.1. The chemical composition of SiO_xN_y films studied is PAPERS I and II.

with low silicon contents. The values were still high compared to those measured for stoichiometric silicon oxynitrides ($n < 3, k = 0$), with n above 3 and nonzero k .

Paper II

Effectively stoichiometric SiO_xN_y thin films, meaning no observable Si–Si chemical bonding contributions the XPS Si 2p spectra, were synthesized by rHiPIMS. The optical properties of these stoichiometric were shown to fall in between those of SiO_2 and Si_3N_4 . Favorable film deposition conditions were established in the transition and poisoned target surface regimes, based on the analysis of the target current behavior and plasma properties upon the introduction of N_2O . Large N_2O -to-Ar flow ratios were shown to result in mainly SiO_x -like films with low nitrogen concentrations.

The film chemical compositions are shown in Fig. 4.1 As in PAPER I, the film chemical composition was tuned by N_2O flow rate and the applied power settings. Now, a larger span of different SiO_xN_y compositions were covered than in PAPER I, with $x = 0.2 - 1.3$, $y = 0.2 - 0.7$, due to larger N_2O flow rates used. The film morphology was dense and featureless, as shown in Fig. 4.2. Film density was found to range between $2.6 - 3.2 \text{ g/cm}^3$. As in PAPER I, here the film stress did not show correlation with the studied synthesis parameters, but ranged from -500 MPa to -1600 MPa .

Figure 4.2. A cross-sectional SEM image of a SiO_xN_y film, from PAPER II.

Paper III

Silicon nitride coatings were deposited by rHiPIMS. The influence of N_2 -to-Ar flow ratio (from 0 and 0.3), pulse frequency, target power, and substrate temperature on the SiN_x film nitrogen content was investigated. Mass spectrometry and Langmuir probe analysis were used to characterize the discharge properties. The N_2 -to-Ar flow ratio was found to be the main factor influencing both the coating properties and the discharge.

Film nitrogen concentrations up to ~ 50 at.% were achieved by using flow ratios of ~ 0.3 , which corresponds to a discharge operated in the transition region between the metallic and poisoned target surface conditions. These films also showed a high density of $\sim 3 \text{ g/cm}^3$ and a hardness up to 27.5 GPa. Average target power had a negligible effect on film nitrogen concentration in the transition mode, whereas under metallic surface conditions an increase in average target power was found to yield larger film silicon contents. Plasma characterization showed increased plasma densities at a N_2 -to-Ar flow ratio of 0.16 due to dissociation and ionization of N_2 . In the transition regime at a flow ratio of 0.3 both the plasma density and film growth rate decreased. At the same time the film hardness, elastic modulus, density, and the compressive residual stress increased.

Paper IV

The paper focused on residual stress in SiN_x coatings synthesized by rHiPIMS. Depending on the deposition parameters, the coatings showed a wide range of compressive stresses, from 0.2 GPa to 2.1 GPa. The main parameters affecting the coating stress were the process pressure, pulse energy, substrate bias, and substrate temperature. The physical mechanisms behind the stress formation were identified as forward sputtering due to energetic ion bombardment, which was

controlled by process pressure, energy per pulse, and substrate bias. Another contributing factor was ad-atom mobility, evident at low substrate temperatures and increased deposition rates per pulse. Additionally, the difference in thermal expansion coefficients between the film and the substrate caused increasing coating stresses. The parameters that were found to yield coatings with low levels of compressive residual stress and good adhesion (HF1) were a pressure of 600 mPa, substrate temperatures below 200 °C, pulse energies lower than 2.5 Ws, and negative substrate bias voltages up to 100 V.

Paper V

Silicon carbonitride films were synthesized by reactive HiPIMS by using silicon targets with acetylene and nitrogen as reactive gases. The characteristics of the deposition process were found to be affected by the applied C_2H_2 flow rate. Physical process conditions were identified for C_2H_2 flow rates up to 10 sccm, while higher flow rates resulted in increasingly chemically driven process conditions. The transition between the different regimes was seen as an increasing target current and was noticeable in the film properties. Carbon replaced both Si and N equally in the films as more C_2H_2 is employed in the process. The films also contained hydrogen, up to 16 at.%, as confirmed by ERDA.

Figure 4.3. The peak target current of the Si target and hardness plus residual stress of SiCN:H films versus, the applied C_2H_2 flow rate, from PAPER V.

The films showed silicon nitride like mechanical properties up to film carbon concentrations of ~ 20 at.%, particularly compressive residual stresses below 1.5 GPa and hardnesses of 21 – 22 GPa. Figure 4.3 shows the evolution of the film mechanical properties with the applied C_2H_2 flow rate. At 10 sccm the peak target current

risks sharply and both the residual stress and hardness decrease. The transition was visible in cross-sectional SEM, with film morphologies being increasingly granular as more C_2H_2 was used in the process. Film densities decreased accordingly, from 3.0 g/cm^3 measured for the SiN_x films down to 1.6 g/cm^3 at a film carbon concentration of $\sim 80 \text{ at.}\%$. Both the substrate temperature and bias affected the film mechanical properties to a lower extent. Both increasing substrate temperatures and bias voltages resulted in larger film stresses and slightly higher hardness.

The chemical bonding in the films was studied with XPS and Raman spectroscopy. Silicon in the films was shown to preferably bond with nitrogen rather than with carbon. Films with carbon contents above $30 \text{ at.}\%$ showed no C–Si bonding and the C 1s spectra were close to that of amorphous hydrocarbon. Raman spectroscopy showed that the film carbon bonding network was slightly more ordered in the films deposited at higher substrate temperatures.

Figure 4.4. The hardness and residual stress of SiCN films as the function of film carbon content , from PAPER VI.

Paper VI

Silicon carbonitride coatings were deposited by reactive HiPIMS/DCMS co-sputtering from elemental Si and C targets. The films showed columnar morphologies in cross-sectional SEM due to substrate rotation. The composition of the films was controlled through the graphite target power, while the power at Si targets was fixed. Cross-sectional TEM showed that the films are amorphous. The alternating SiN and CN layered structured showed as an increasing C–C bonding contribution as the CN layers grew thicker. Simultaneously the amount of C–Si

bonding decreased.

Improved film mechanical properties were seen when the film carbon content exceeded 9 at.%, as is seen in Fig. 4.4. Film H/E ratio had a maximum of 0.105 at a C concentration of 12 at.%. Increased residual stress and hardness were observed at elevated substrate temperatures and bias voltages. Also a lowered pulse frequency resulted in a slightly increased film hardness. Additionally, a lowered pulse frequency was accompanied by an increased film average surface roughness from 5.4 nm at 4000 Hz to 7.8 nm at 1000 Hz. Parameters that showed the most promise for production of biocompatible SiCN coatings with low surface roughness were a film carbon content of ~ 12 at.%, substrate temperatures up to 340 °C, a negative substrate bias up to 100 V, and a large HiPIMS pulse frequency of 3000 Hz or above.

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List of publications

I Silicon oxynitride films deposited by reactive high power impulse magnetron sputtering using nitrous oxide as a single-source precursor

T. Hänninen, S. Schmidt, J. Jensen, L. Hultman, and H. Högberg
Journal of Vacuum Science and Technology A **33**, 05E121 (2015)

II Stoichiometric silicon oxynitride thin films reactively sputtered in Ar/N₂O plasmas by HiPIMS

T. Hänninen, S. Schmidt, J. Wissting, J. Jensen, L. Hultman, and H. Högberg
Journal of Physics D: Applied Physics **49**, 135309 (2016)

III SiN_x coatings deposited by reactive high power impulse magnetron sputtering: process parameters influencing the nitrogen content

S. Schmidt, T. Hänninen, C. Goyenola, J. Wissting, J. Jensen, L. Hultman, N. Goebbels, M. Tobler, and H. Högberg
ACS Applied Materials and Interfaces, **8**, 20385 (2016)

IV SiN_x coatings deposited by reactive high power impulse magnetron sputtering: Process parameters influencing the residual coating stress

S. Schmidt, T. Hänninen, J. Wissting, L. Hultman, N. Goebbels, A. Santana, M. Tobler, and H. Högberg
Journal of Applied Physics, **121**, 171904 (2017)

V Silicon carbonitride thin films deposited by reactive high power impulse magnetron sputtering

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Surface and Coatings Technology, **335**, 248 (2018)

VI Mechanical properties of SiCN thin films deposited by HiPIMS/DCMS co-sputtering

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Submitted for publication

Author's contribution

Paper I

The author designed the study and performed thin film synthesis. The author did the thin film characterization and data analysis, except XPS measurements and ERD analysis. The author wrote the manuscript.

Paper II

The author designed the study and performed thin film deposition. The author did the thin film characterization and data analysis, except XPS measurements. The author performed the Langmuir probe measurements and data analysis in cooperation with co-authors. The author wrote the manuscript.

Papers III-IV

The author took part in thin film deposition and residual stress measurements. The author participated in discussing the results and provided comments for the manuscripts.

Paper V

The author designed the study and performed thin film synthesis. The author did the thin film characterization and data analysis, except XPS, Raman, and ERDA measurements. The author wrote the manuscript.

Paper VI

The author designed the study and performed thin film deposition. The author did the thin film characterization and data analysis, except XPS measurements, TEM, and surface roughness measurements. The author wrote the manuscript.

Papers

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