UPPSALA
UNIVERSITET

Digital Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology 194

Hollow Cathode Deposition of Thin Films

LARS-ERIK GUSTAVSSON

ACTA
UNIVERSITATIS
UPSALIENSIS
UPPSALA
2006

ISSN 1651-6214
ISBN 91-554-6586-2
urn:nbn:se:uu:diva-6925

Dissertation presented at Uppsala University to be publicly examined in Häggsalen, Ångströmlaboratoriet, Uppsala, Wednesday, June 7, 2006 at 13:00 for the degree of Doctor of Philosophy. The examination will be conducted in Swedish.

Abstract
Gustavsson, L-E. 2006. Hollow Cathode Deposition of Thin Films. Acta Universitatis Upsaliensis. *Digital Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology* 194. 55 pp. Uppsala. ISBN 91-554-6586-2.

Thin films of metals and compounds have a very wide range of applications today. Many of the deposition methods used for the production of such films utilize plasma to support the growth the film, e.g. by the supply of energy and the enhancement of reactivity. This thesis focuses on the physical vapor deposition (PVD) of thin films by high density plasma sources based on hollow cathodes and aims to increase the understanding of the deposition process and its influence on the film properties.

Titanium nitride films reactively deposited by the low-pressure hybrid plasma (HYP LP) source exhibited excellent properties and was deposited at considerable higher rates than films deposited by conventional methods.

An original finding in this work is the influence of substrate material on the deposition process and consequently on the properties of the deposited film. In the deposition of TiN films by the HYP LP source it was found that the substrate temperature was higher for Si substrates than for steel substrates due to a more efficient absorption of microwave power in Si than in steel. Further, it was found that ferromagnetic substrates influence the film growth in magnetized plasma systems. An effect of the ferromagnetic substrates is the enhancement of ion bombardment that increases the growth temperature and affects the texture and morphology of the growing films. It was also found that a DC bias can change the TiN film properties considerably and compensate the effect of ferromagnetic substrates.

High rate depositions of chromium and chromium nitride films by the RF hollow cathode plasma jet (RHCPJ) source were studied. The performance of the reactive diffuse arc process and the CrN film properties indicates that the process can be transferred from small cylindrical cathodes to linear magnetized hollow cathodes which allow deposition on considerable larger areas and this is important for industrial applications.

Keywords: Hollow cathode, Hybrid plasma, PVD, TiN films, Ferromagnetic substrates, Magnetized plasma, CrN films

Lars-Erik Gustavsson, Department of Engineering Sciences, Solid State Electronics, Box 534, Uppsala University, SE-75121 Uppsala, Sweden

© Lars-Erik Gustavsson 2006

ISSN 1651-6214
ISBN 91-554-6586-2
urn:nbn:se:uu:diva-6925 (http://urn.kb.se/resolve?urn=urn:nbn:se:uu:diva-6925)

List of papers

I L. Bárdoš, H. Baránková, L-E. Gustavsson, and D.G. Teer, "New microwave and hollow cathode hybrid plasma sources", Surf. Coat. Technol. 177-178 (2004) pp. 651-656.

II L-E. Gustavsson, H. Baránková, L. Bárdoš, "Some properties of TiN films produced in hollow cathode and microwave ECR hybrid plasma system", Surf. Coat. Technol. (2006). In print.

III L. Bárdoš, L-E. Gustavsson, H. Baránková, "Effect of ferromagnetic substrates on the film growth in magnetized plasma systems". Surf. Coat. Technol. 200 (2005) pp. 1862-1866.

IV L-E. Gustavsson, H. Baránková, L. Bárdoš, "PVD of Films on Ferromagnetic Substrates in Magnetized Plasma Systems", SVC - 48th Annual Technical Conference Proceedings (2005) pp. 136-137.

V L. Bárdoš, H. Baránková, and L.-E. Gustavsson, "Effect of substrate material and bias on properties of TiN films deposited in the hybrid plasma reactor", J. Vac. Sci. Technol. A 24(4) (2006). In print.

VI H. Baránková, L. Bárdoš, and L.-E. Gustavsson, "High-rate hot hollow cathode arc deposition of chromium and chromium nitride films", Surf. Coat. Technol. 188-189 (2004) pp. 703-707.

VII H. Baránková, L. Bárdoš, and L.-E. Gustavsson, "Hot Hollow Cathode Diffuse Arc Deposition of Chromium Nitride Films", J. Vac. Sci. Technol. A 23(4) (2005) pp. 959-963.

Comments on the author's contribution to appended papers

I Part of the experiments with the hybrid source and all film analyses (with help on ESCA).

II All film depositions in cooperation with co-authors. Major part of film analyses.

III All film depositions in cooperation with co-authors. All film analyses.

IV All film depositions in cooperation with co-authors. All film analyses.

V Major part of the experimental work in cooperation with co-authors. All film analyses.

VI Part of preparatory work. All film analyses.

VII Part of preparatory work. All film analyses except nanoindentation.

Contents

1 Introduction ... 7

2 Plasma ... 9
 2.1 Definition of a plasma ... 9
 2.2 Generation of plasmas ... 9
  2.2.1 Hollow cathodes ... 10
  2.2.2 Microwave ECR plasma sources ... 11

3 Deposition of thin films ... 12
 3.1 General characterization of the most common methods for thin film depositions ... 12
 3.2 Typical evaporation and sputtering based PVD methods ... 13
 3.3 Film growth ... 15
 3.4 Applications and materials for thin films ... 16
 3.5 Methods of film analysis ... 17
  3.5.1 Scanning electron microscopy ... 17
  3.5.2 Electron spectroscopy for chemical analysis ... 18
  3.5.3 X-ray diffraction ... 18
  3.5.4 The stylus profilometer ... 19
  3.5.5 Analysis of the mechanical properties of thin films ... 19
 3.6 Titanium nitride films ... 20
 3.7 Chromium films ... 22
 3.8 Chromium nitride films ... 23

4 Hollow cathode plasma sources for material processing ... 26
 4.1 Hollow cathode PVD ... 26
 4.2 The radio frequency hollow cathode plasma jet (RHCPJ) ... 27
 4.3 The hybrid plasma (HYP) source ... 28
 4.4 The special thermoprobe for temperature and current-voltage measurements ... 30

5 Summary of papers ... 32
 5.1 Summary of Paper I ... 32
 5.2 Summary of Paper II ... 33
 5.3 Summary of Paper III ... 35
 5.4 Summary of Paper IV ... 37

5.5 Summary of Paper V ... 39
5.6 Summary of Paper VI ... 42
5.7 Summary of Paper VII ... 45

6 Conclusions ... 47

7 Sammanfattning ... 49

Acknowledgements ... 51

References ... 52

1 Introduction

Thin films of metals are very common in different applications for example in the microelectronic industry where they are used for interconnections and contacts. Other applications for pure metal films are optics, e.g. mirrors, and protective coatings, e.g. oxygen barriers for food packaging. However, a much wider range of applications compound thin films such as metal oxides, metal nitrides and metal carbides have. These are used in a very wide range of applications: electronics, optics, and machinery. The latter application often utilizes the high hardness and high wear resistance of particular nitrides, oxides and carbides. One motivation for using thin films and coatings is that a small addition of material at the surface can make a big effect on the properties of the component where they are used. The coated component can also have unique properties that cannot be achieved in other ways. Deposition of thin films is a steadily growing technology and so is the related industry.

There are a number of different methods to produce thin films. Electrolytic and chemical methods are established since long ago but during the last century more sophisticated methods for deposition were developed, especially so-called atomistic methods where the film is formed from individual atoms/ions or molecules. Most of these methods can be classified as either physical vapor deposition (PVD) or chemical vapor deposition (CVD); however there exist combinations of the two. With these methods films with unique properties can be produced, particularly in low-pressure gas plasma, due to the possibility to deposit under thermal non-equilibrium conditions. In PVD the raw material is in solid phase that is either evaporated or sputtered to mostly atomic species that can be deposited and form a film. This can also take place in a reactive atmosphere for deposition of compound material films. In CVD the raw material is in gaseous phase and the film is formed through reactions on the surface that is to be coated. Regardless what deposition method is used the film properties are depending on the process parameters. To be able to control the film properties by controlling the process it is necessary to understand how the process influences the properties. In most cases this requires particular research work.

Both PVD and CVD can use plasma to support the growth of the film, e.g. to increase the deposition rate or to allow lowering of the deposition temperature. Utilization of plasma can increase productivity and lower the costs and it allows also new combinations of films and substrate materials.

The role of plasma in coating technology is quite complex. For example one role is to supply energy to the growing film to promote the film quality and to allow a better control of the film growth. Another role is to supply energy to the film forming species to enhance their reactivity to increase the deposition rate, to improve adhesion to the substrate, etc. Big efforts have been devoted to develop plasma sources with high plasma densities to achieve a high reactivity and to allow the deposition conditions to be controlled within wide intervals, thereby controlling the properties of the films. In this work high density plasma sources based on hollow cathodes have been used for deposition of films.

Plasma is useful not only in deposition techniques but also in other techniques for etching, cleaning, and surface modification. This implies that many of the process techniques used e.g. in micro electronics industry, machinery, and biotech industry are based on plasma and hence a very big economic interest in plasma processing and plasma sources still has a growing tendency.

2 Plasma

2.1 Definition of a plasma

A plasma is a gas of charged particles (both ions and electrons) and neutrals (atoms and molecules) but also of photons. More specific it can be characterized as a fully or partly ionized gas that is electrically neutral as a whole, i.e. the number of positive and negative charges is equal. It is often considered as the 4th state of matter because it arises when supplying energy to a gas, though there is no abrupt phase transition like the transitions from solid to liquid and from liquid to gas. An alternative name for plasma is glow discharge owing to the characteristic glow from the plasma due to deexcitations of particles with the accompanied emission of photons. On Earth the plasma does not occur as a natural state, with exception of lightning flashes and flames, but in outer space plasma is the most common form of matter. Artificially generated gaseous plasmas have however numerous applications in the service of mankind. Plasma is found in so various applications as light sources, new kinds of television screens, in reactors for fusion experiments, etc. Probably the most common, and of the most economic importance, the plasma applications in material processing of solids, as well as of gases, are. Unlike the plasmas for fusion these plasmas are “cold”, i.e. not in thermodynamic equilibrium, where the gas is at low temperature while electrons have energies (temperatures) high enough to ionize, excite, dissociate, etc. part of gas particles.

2.2 Generation of plasmas

Plasmas for industrial applications in material processing are generated by different plasma sources; see e.g. [1]. This section will describe the basic principles of some of these sources.

A plasma can be generated by applying a voltage between two electrodes in a gas and at a certain voltage depending on the gas pressure and the distance between electrodes a breakdown will occur in the gas so that the gas becomes conducting due to the ionization. The ionization is caused by collisions between electrons, accelerated to the ionization energy by the electric field, and neutral particles, e.g. atoms. Every collision that generates one free electron can cause a new ionization but the first electron is also still free to

collide again, so the ionization appears as an avalanche process. Eventually this process reaches a steady-state between the generation and the loss of the charged particles. The loss of the ions and electrons from the plasma volume can occur by recombination and diffusion to the plasma boundaries. The start of the ionization is enabled by the primary ions and electrons that always are present in any neutral gas for example due to ionization by cosmic radiation. Electrons with not enough energy to ionize an atom can change its electronic structure and excite it and when the atom deexcites a photon can be emitted. Recombination of charged particles and deexcitations contribute to a glow characteristic for the plasma systems.

In the simplest type of a glow discharge the applied voltage is a DC voltage and the two electrodes represent a cathode and anode respectively. The electric field is not distributed evenly between the electrodes which causes differences in the brightness of the glow. The most intense part of the discharge is the "negative glow" near, but separate from the cathode. The region between this glow and the cathode is "the cathode dark space" or "the space charge sheath" where the potential drops drastically. Due to no or very few collisions and hence no photon emission in this region it appears dark. Positive ions will be accelerated by the potential drop through the sheath and collide with the cathode surface. This can cause emission of secondary electrons that are repelled from the cathode into the negative glow and enhance ionization there. The ions can also knock out atoms from the cathode material and this effect is used in sputtering as a source of material to be deposited. If the distance between the cathode and the anode is long enough with respect to the width of the discharge another glow region, "the positive column", can appear. At the anode there is also a dark space but very thin.

If the cathode is surrounded by a non-conducting material a plasma can not be sustained by a DC voltage because of charging of the electrode surface. In this case it is possible to power the electrode with radio frequency (RF) voltage to allow the discharge to be generated. The RF-discharges have usually more efficient ionization than the DC-discharges. The electrons have very low mass and they can easily follow the RF oscillations while the ions just follow the time average field. In the case of a conducting cathode a blocking capacitor between the cathode and the power supply can be used to build up a negative DC bias on the cathode (actually on both electrodes) and a space charge sheath can be formed between the electrodes and the plasma. In an RF-discharge the ions will be accelerated through this sheath like in the DC case.

2.2.1 Hollow cathodes

Existence of sheaths in hollow electrode geometries can give rise to an "extra" discharge - the hollow cathode discharge (HCD) - that is utilized in the hollow cathode sources. In a two-electrode system with a hollow negative

electrode (cathode) and a larger counter electrode (anode) the HCD can arise within the cavity in the cathode simultaneously with the "ordinary" discharge between the cathode and the anode if the distance of opposite walls in the cavity is roughly equal to the width of the negative glow. The origin of the HCD is an entrapment of electrons inside the hollow cathode when energetic electrons emitted from one cathode wall are accelerated across the sheath towards the opposite wall. When they reach the identical sheath on the opposite side with the same but opposite electric field they are reflected back. The electrons are trapped and forced to oscillate between the opposite sheaths. This mechanism is called the "hollow cathode effect". During these oscillations electrons can undergo inelastic collisions with gas atoms and increase the probability for ionization giving a very dense plasma inside the cathode. This plasma is forced out of the cathode by flowing gas. The hollow cathode can also be powered by an RF power supply. The electrons can oscillate many times during one RF cycle giving a high plasma density. The hollow cathodes can have different geometries: tubes, arrays of tubes, or parallel plates (linear hollow cathodes) [2].

2.2.2 Microwave ECR plasma sources

Another type of high density plasma is based on a very high frequency (microwave) power. A unique plasma source is the microwave electron cyclotron resonance (ECR) source [3]. It is an electrodeless source in a magnetic field where the discharge intensifies substantially when the conditions for electron cyclotron resonance are fulfilled. The electron cyclotron frequency, ω_c, is given by $\omega_c = 2\pi f_c = eB/m_e$, where e = electron charge, B = magnetic field strength, and m_e = electron mass. For the microwave power from a commercial microwave power supply with f = 2.45 GHz the resonance condition ($f = f_c$) is fulfilled for a magnetic field strength of 0.0875 T. The microwave power absorption will reach maximum where the magnetic field reaches this value and a discharge will be generated mainly in this area.

3 Deposition of thin films

3.1 General characterization of the most common methods for thin film depositions

As was already mentioned in the introduction, there are two main groups of methods for thin film deposition, chemical vapor deposition (CVD) and physical vapor deposition (PVD). As the methods for producing the films in this work were PVD methods, the CVD is described only briefly in the beginning of this section.

Chemical vapor deposition is a method where a solid film is deposited via chemical reactions at an elevated temperature. The reactants are gaseous and any other reaction products than the film must be gases. The reaction is thermally activated, i.e. heated to a temperature often exceeding 1000 ºC, what many substrates cannot endure. Note that there is possible to avoid external heating of substrates in CVD methods assisted or induced by plasma. This use of plasma in CVD processes is however out of scope of this work. Advantages of CVD are the possibility for batch processing and mostly a very good film adhesion and the step coverage, i.e. the ability to cover substrates with complicated shapes.

Physical vapor deposition (PVD) is a concept that gathers a great number of different deposition methods where the initial material is in solid phase and then it is turned into vapor phase during the process. A common feature for almost all methods is that they require a low pressure (vacuum) to avoid impurities in the film but also to avoid loss of energy of particles deliberated from the solid source due to collisions and mainly to keep enough energy of bombarding particles in sputtering (ions) or in evaporation (electrons and/or ions). In PVD the film is formed when the evaporated or sputtered species condensate or sublimate on the substrate and all other colder surfaces in the vacuum chamber.

Unlike most of CVD techniques the PVD is considered to be a “cold” process in that meaning that the substrate is not heated unless it is not heated deliberately or exposed to intense bombardment by charged particles. If the substrate and the film itself can endure higher temperatures, an auxiliary additional heating can of course be used in PVD if needed to promote the film growth and to improve the adhesion and the film properties.

By introducing a reactive gas, oxygen, nitrogen, etc., in the chamber, compound material such as oxides and nitrides can be deposited. The possi-

bility of the process control and a big variety of possible film- and substrate materials are reasons for the wide spreading of PVD methods in thin film technology.

A disadvantage with most of the PVD methods is that the step coverage is not as good as in high pressure CVD methods. This disadvantage can however be partly improved by moving, e.g. rotating, the substrates during deposition.

3.2 Typical evaporation and sputtering based PVD methods

Evaporation can proceed when the film material source is heated to a liquid phase by resistive or inductive heating or by irradiation by electrons or ions in a very low pressure atmosphere (high vacuum). Materials with high melting point e.g. titanium cannot be evaporated by simple resistive or inductive heating. For such applications different heating methods must be used, e.g. electron beam evaporation (EBE). The electron beam is created by electrostatic optics focusing the electrons emitted from a resistive heated filament or from another type of electron source, for example a hollow cathode. The deposition rate from evaporation can be very high and this can be a considerable advantage. Among the disadvantages are the difficulties to deposit alloy films with a desired composition because metals with different melting points often results in alloy films with graded composition or in layered films.

Another type of evaporation method is (low voltage) cathodic arc evaporation [4] where an arc is created between two electrodes. In the cathodic arc evaporation a very high current density in localized spots at the cathode surface causes melting and evaporation of the cathode. Unlike most of the other PVD techniques the vapor in cathodic arc evaporation is highly ionized. This is a big advantage as it gives high deposition rates controlled by auxiliary electric fields and the vapor can provide lots of ions for an intense bombardment of the growing film. A major problem in the cathodic arc evaporation is the presence of droplets of molten film material, “macroparticles”, which can be incorporated into the film or be deposited on the surface of the film. These macroparticles can disturb the homogeneity of the film and give a rough film surface. To avoid this problem particle filters are often installed in the system that magnetically filter the particles out from the vicinity of the substrate [5]. This technique is often referred to as Filtered Arc Deposition (FAD) or Filtered Arc Evaporation.

On the contrary to evaporation the sputtering [6] is a kind of “cold” process where the film material is not heated enough to cause evaporation but atoms are knocked out from the target (cathode) by energetic ions from a

plasma. In the simplest form of a sputter deposition system, "diode", a DC voltage is applied between a cathode (made of the film material), the target, and an anode, the substrate. If the voltage is high enough so that an electrical breakdown occurs in a gas present in the system (e.g. argon) and a plasma is generated, positive ions from the plasma are accelerated by the electric field towards the target and can sputter it. With the DC voltage it is only possible to sputter conducting surfaces because a non-conductive material could be charged and no current could flow to the target. This problem can be overcome by using RF voltage instead of DC where the RF self-bias allows periodic neutralization of the charge and makes sputtering possible. However sputtering with a simple diode setup is not very efficient so virtually all sputtering systems nowadays are based on magnetrons [7], where the sputtering rate is at least one magnitude higher. In a magnetron a set of magnets placed behind the target confines the plasma close to the cathode (target) and enhances the ionization in the vicinity of the target surface for more efficient ion bombardment and sputtering. Magnetrons utilize an effect of the Lorentz force in crossed electric and magnetic fields that forces charged particles to move in a spiral path above the target allowing the electrons to cause multiple ionizations. The ions sputter the target material in a pattern that follows this ionization area leaving a "racetrack" erosion area on the target. The major disadvantage of magnetrons is an inefficient use of target material due to the formation of this local racetrack. Contrary to the evaporation techniques an advantage of sputtering is that alloys easily can be deposited either from an alloy target or by simultaneous sputtering of two or several metals.

In reactive sputtering [8] the target is sputtered in a reactive atmosphere, e.g. nitrogen, oxygen methane, etc, for deposition of nitride, oxide, and carbide films. Ions of the reactive gas are formed in the plasma. These ions can bombard both the substrate and the target and molecular ions can dissociate by the impact. The dissociated gas molecules can react with the target material and form the compound film. At low content of reactive gas the resulting film will not be fully reacted. To get stoichiometric compound films the gas flow rate must be sufficiently high. However, when the gas flow rate increases the compound is formed also on the target surface ("target poisoning") leading to a drastic drop in the deposition rate due to the slow sputtering of the compound. If the gas flow rate is decreased again there is a transition to higher deposition rate but this occurs at a lower flow rate than the transition to the lower flow rate. The different "transition flow rates" is a hysteresis phenomenon that makes the control of the process very complicated. This and the often low deposition rate are the major disadvantages of reactive sputtering.

A big advantage of sputtering is the versatility, almost all conceivable inorganic materials, even polymers, can be deposited onto almost any kind of substrate.

Two methods where a high degree of ion bombardment of the substrate and the growing film is involved are ion plating (IP) and ion assisted deposition (IAD). Ion plating [9] is a variant of evaporation where a plasma is introduced and such a high bias is applied to the substrate that the growing film is sputtered simultaneously with the deposition. This slows down the deposition rate but increase adhesion and quality of films. Ion plating can also be used in sputtering systems. In IAD [10] or IBAD (ion beam assisted deposition) a conventional sputter or evaporation system is equipped with an additional ion gun that bombards the substrate with gas ions.

3.3 Film growth

All thin film deposition processes consists of three steps:

1. production of the film forming species
2. transport of these species from the source to the substrate
3. condensation and stitching on the substrate

In PVD the first step is either evaporation or sputtering like it is described in the previous chapter, the second step implies line-of-sight transport if the process pressure is very low and there is a small probability for collisions or a flow transport if the pressure is high. The type of transport influences the actual growth of the film in the third step.

When an atom arrives at the substrate surface and is being adsorbed, it will diffuse on the surface until it is either desorbed or stuck to an energetic favorable site. This surface diffusion is dependent on what energy the atom has upon arrival to the surface and if the substrate is supplied by an additional energy, e.g. by heating or ion bombardment. The energy of the atom is dependent on the pressure in the deposition chamber, a high pressure decrease the energy due to energy losses in collisions. The ion bombardment of the surface is possible in plasma based methods and can be controlled by a negative bias voltage of the substrate with respect to the plasma.

If the atom sticks to another film atom at the surface, a low-mobility pair is created and this increases the probability for yet another atom to stick to them. At a critical number of atoms, or a critical nuclei-size, a nucleus is formed. These nuclei will grow to crystalline islands that will coalesce when meeting each other and finally form a continuous film. Depending on the process parameters the film growth will continue in different ways giving different microstructures. The film can grow layer-by-layer or in 3D-islands or in a combination of these two growth modes.

In PVD the film growth is often columnar, i.e. the crystallites grow in columns with more or less developed grain boundaries between them. The grain boundaries can contain voids and deteriorates most properties of the

film, but a real dense, columnar film can have for example excellent tribological properties. A complete dense microstructure in the film is often very desirable. As the dense microstructure is promoted by ion bombardment of the growing film, such films can often be deposited by PVD-methods in high-density plasmas.

Several film growth models for the influence of the deposition condition on the microstructure of the film have been developed. Commonly used are the empirical structure zone models where different growth modes (zones) are identified in a diagram for different temperature to melting temperature ratios (T/T_m). An extensive review of such models was published by John A. Thornton in 1977 [11] and here follows a short summary of this. Movchan and Demchishin made the following classification: Zone 1 appears when $T/T_m < 0.3$ and is characterized by high surface roughness and voided grain boundaries. Zone 2 appears when $0.3 < T/T_m < 0.5$ and is characterized by a mat, smooth surface and columnar grains with distinct, dense boundaries. Zone 3 appears when $0.5 < T/T_m < 1$ and are characterized by a bright surface and equiaxed grains. The structure and properties of this zone are close to bulk material. Thornton has proposed an extended model where the influence of the process gas pressure is added into a second axis in the diagram. In this diagram a fourth zone (zone T, transition) can be identified between zone 1 and zone 2. The zone T structure is dense and fibrous without voided grain boundaries.

3.4 Applications and materials for thin films

Widespread applications of thin films are found in the microelectronics, optics, sensors, food packaging, and machinery. The applications in microelectronics are based on deposition of dielectric films for electric insulation and passivation; deposition of polysilicon for gate electrodes in MOS processes; and metallization for interconnections, ohmic contacts, and rectifying metal-semiconductor contacts. These applications are mostly destined for integrated circuits but also for discrete components. Almost all optical components such as lenses for glasses and binoculars have today thin coatings for antireflection. Other thin films for optics are polarizing coatings and reflective coatings for mirrors. Sensors are a growing market where all kinds of sensors utilize thin film technologies. To preserve food from degradation packages are provided with diffusion and/or light barriers in the form of polymer or metal coatings. In machinery thin films are utilized for wear protection coatings for tools and mechanical components e.g. in automotive industry. There exist a large number of materials that can be used for these different protective applications [12, 13]. Common materials for hard coatings for cutting tools are nitrides, carbides, carbo-nitrides, and borides of Ti and Zr, Al_2O_3, and Si_3N_4. Hard coatings can be in the form of monolayers,

multilayers or nanostructured layers where the two latter forms can combine two or several different materials. Another very important application of thin films is in magnetic storage media, especially in hard disks where a large number of different layers give desired magnetic, mechanical, and tribological properties.

Different applications make different demands on film properties and hence on the deposition processes. In microelectronics a good control of film thickness, low temperatures, and possibilities for process integration are important factors. For the packaging industry the coating process must be continuous leading to dense films and upscaling of the deposition techniques is essential. Cutting tools like drills and mills can have very complicated shapes so the process must be able to give a uniform coating over the whole component. It is desired to control the film properties so that they fit the applications by controlling the deposition process. To be able to do this the film properties must be determined by different analysis methods, of which some will be described in the next chapter.

3.5 Methods of film analysis

3.5.1 Scanning electron microscopy

Scanning electron microscopy (SEM) is a technique where electrons from an electron gun are accelerated by a high voltage (5 – 50 kV) towards the sample surface where they cause emission of secondary electrons and scattering of electrons from the sample surface. These primary electrons can also be backscattered from the surface. The secondary electrons are collected by a detector and converted to an electrical signal that can be displayed on a monitor or be computerized. The electron beam is focused to a small spot and scanned over the sample so that an image of the surface geometry can be recorded. The resolution of a SEM reproduction is not only instrument dependent but also dependent on the sample material. The limit is set by how well the beam can be focused and by scattering processes in the sample surface. Typical values of this limit are 10 – 20 Å, implying that smaller features than that cannot be detected. The image contrast can arise from several different phenomena of which one is the topographical contrast that means that it is more probable to detect electrons scattered from sample surfaces near the detector than from more distant surfaces. This kind of contrast gives images that are easy to interpret. Sample preparation is uncomplicated, the samples should be clean and preferably electric conducting and non-magnetic. Insulating surfaces cause problem with saturated charges. This requires either lower acceleration voltage for the beam (with consequently lower sensitivity) or an auxiliary coating of the surface by a thin conductive film, e.g. a gold film. For thin film analysis the SEM is a suitable tool for

imaging morphology of film surfaces and microstructure of film cross sections.

3.5.2 Electron spectroscopy for chemical analysis

The electron spectroscopy for chemical analysis (ESCA), also known as X-ray photoelectron spectroscopy (XPS), is a surface sensitive tool for element analysis where the sample is irradiated by monochromatic X-ray photons. The photons cause emission of electrons with characteristic kinetic energy depending on different elements present in the sample surface. Detection of these energies can give a qualitative as well as a quantitative analysis of the elements in the sample. Also the chemical state of the sample atoms can be determined through the chemical shift, i.e. the change in binding energy of an electron when the atom is bound to another atom. With sputtering and analysis by turns depth profiles of the sample composition can be obtained.

3.5.3 X-ray diffraction

X-ray diffraction (XRD) is a versatile material analysis technique for crystalline materials. Some examples of what XRD can be used for are: determination of lattice constants, identification of unknown substances, phase analysis and measurements of grain sizes and intrinsic stress.

The idea behind x-ray diffraction is that a crystal, with its regularly repeating structure, will diffract electromagnetic radiation with a wavelength of the same size as the crystal's inter-atomic distance, just like an optical grating will diffract visible light. One way to understand the x-ray diffraction is to regard the atom planes in the crystal as a stack of semi-transparent mirrors. The diffraction can now be treated like reflections in the atom planes where every plane reflects a part of the radiation so that there will be several reflections. These reflections will interfere constructively when they are in phase, i.e. the difference in path length equals an integer multiple of a wavelength. This occurs only when the angle of incidence satisfies Bragg's law: $2d \sin\theta = n\lambda$, where d is the distance between two adjacent atom planes, θ is the Bragg angle, n is an integer, and λ is the x-ray wavelength. For all other angles there will be a destructive interference and no reflection.

As there are several sets of atom planes with different spacing in a crystalline substance there will be strong reflections in several directions for a polycrystalline sample. Every strong reflection has two properties, diffraction angle and intensity, and this data can be compared with databases and an unknown substance and its crystal structure can be determined.

In the case of very thin films the intensity of the reflections from the film can be so weak that they will drown in the background radiation, e.g. from the substrate. This problem can be avoided by using a grazing incidence method, GI-XRD, which means that the incidence x-rays have a very small

angle with respect to the surface and this increases the intensity so that the technique becomes more surface sensitive.

By the use of a Goebel mirror parallel incidence x-rays are obtained that gives higher intensity and simplifies GI-XRD. For an ordinary XRD this also makes it possible to analyze non-flat samples.

3.5.4 The stylus profilometer

A stylus profilometer is used to measure the surface roughness and the film thickness. The principle is to move a stylus with a very small load over the surface and acoustically record the stylus vertical position as a function of the horizontal position.

To get a reliable measurement of the thickness of a thin film there must be a quite distinct step from the original substrate surface to the film. Otherwise the step cannot be distinguished from the surface roughness if this is too high. Such a step can be obtained by masking an area before the deposition or by etching afterwards. For a good profilometer a typical value of the vertical resolution is 5 Å, but this can limit the possibility to measure large vertical variations. Typical maximum measurable film thicknesses are about 15 μm for commercial profilometers.

3.5.5 Analysis of the mechanical properties of thin films

Among different mechanical properties of thin films, the hardness is one of the most important. The hardness is however not a property that can be unambiguously determined, especially not for thin films. First of all the hardness value is dependent on the measuring technique. All techniques include an indenter of a hard material (e.g. diamond) that is pressed into the tested material by a fixed load. The hardness value is then calculated from the load and area (real or projected) or the depth of the indent. The indenter can have different shapes (e.g. pyramids) and different load ranges that give results that not can be compared directly. For thin films the influence of the substrates complicates the hardness measurements and to decrease this influence, microhardness measurement techniques are employed, where very small loads (0.01 – 10 N) are used. Two of the most common microhardness techniques are micro Vickers and Knoop. Both techniques use pyramidal indenters but Knoop uses an elongated pyramid that gives shallower indentations than the Vickers indenter do. Despite the small loads the microhardness measurements give for thin films the hardness of the system film and substrate. To determine the hardness of the film only it can either be calculated from the hardness of the coated substrate and the hardness of the uncoated substrate using a model, e.g. the Jönsson-Hogmark model [14], or be obtained by a nanoindentation technique. In such techniques extremely small loads (a few mN) are used so that the sizes of the indentations become very

small because of the big contribution of elastic deformation. By nanoindentation the indents can be in the order of 100 nm and this is small enough to avoid influence of the substrates for μm thick films, but the indentations can not be measured optically like in a conventional microhardness tester. In a nanoindenter the relation between the load and the displacement (depth) of the indenter is recorded continuously during the whole load and unload cycle. From these load/unload curves not only the film hardness can be obtained but also the elastic (or Young's) modulus, i.e. the ability of a material to withstand elastic deformation. The values of these two properties can be calculated using a model by Oliver and Pharr [15].

3.6 Titanium nitride films

When sputtered or evaporated, titanium is a very reactive metal that easily form nitrides, oxides or carbides. Titanium nitride (TiN) has a NaCl structure that is stable over a broad composition interval allowing both under- and overstoichiometric phases. At low nitrogen content in an inert carrier (e.g. argon) also a Ti_2N phase is possible. Titanium nitride has a high hardness and a high resistance against corrosion and a low electrical resistivity somewhat lower than pure Ti. Furthermore thin TiN films can exhibit hardness much higher than and resistivity much lower than equilibrium bulk values. One of the most widespread applications of TiN films is in wear protection of cutting tools like drills and mills and of tool bits made from tool steel or high speed steel. On hard metal inserts for turning and milling TiN films often is the outermost layer in a multilayered coating. For this application CVD is the most utilized deposition method due to the possibility to coat very large batches at the same time. In the microelectronics TiN is used as a gate metal in MOS structures because of the low resistivity, but also as a diffusion barrier. The stoichiometric (Ti/N = 1) TiN highly resembles gold visually and this makes it popular for decorative coatings for watches and other objects. Titanium nitride is biocompatible material and this property has given rise to a large field of applications in medicine, e.g. surgical implants. Typical properties of a commercial, tribological TiN coating (Balinit® A) are a hardness of 2300 HV and a thermal stability up to 600 °C [16].

The big industrial interest and the wide variety of applications for TiN thin films have often made them popular research objects where many different PVD-methods have been tested and resulting film properties have been studied. Some common examples of frequently used PVD methods are electron beam evaporation, magnetron sputtering, and cathodic arc deposition.

A Taiwanese group has studied TiN deposition by a reactive hollow cathode discharge ion-plating (HCD-IP) technique [17-20]. In this method a RF hollow cathode is used as a high-current low-voltage electron gun for elec-

tron beam evaporation of a Ti-crucible and for simultaneous ionization of metal atoms and gas (Ar and N_2) molecules. Typical deposition conditions are an RF power of 6 kW, a working pressure of 0.29 Pa (2.2 mTorr) and an applied DC substrate bias of -40V. The preferred orientation of the obtained TiN films was (111) for most deposition conditions especially for films thicker than 1 µm. The hardness of the films increased with increasing TiN (111) texture coefficient and it was saturated at 28 GPa as the coefficient approached unity. The group has also studied the influence of ion bombardment on preferred orientation in crystalline TiN films by varying the bias voltage, the deposition power, and the nitrogen partial pressure. The ion bombardment was found to cause strain accumulation or lattice damage and the authors suggest that the preferred orientation at low deposition temperatures is determined by which of these phenomena that dominates. The (111) preferred orientation develops at strain accumulation and the (220) orientation at lattice damage. The thermodynamically favorable orientation (200) occurs when no ion bombardment is present. Further, the group investigated how the porosity of TiN films was influenced by the deposition temperature, deposition time, and ion bombardment. They conclude that long deposition times or high temperatures and a high degree of ion bombardment reduce porosity and that ion bombardment also affects grain size and preferred orientation. Dense films have either large grains or small grains with high (111) texture coefficients.

Commercial techniques for reactive magnetron sputtering have frequently been applied for deposition of TiN films. Guruvenket et al. [21] have studied the influence of ion bombardment and substrate orientation on properties of TiN films deposited on Si substrates in a DC planar magnetron system. Films deposited at a total pressure of 0.1 Pa with negative bias on (100) Si substrates had a preferred orientation of TiN (220) while it was TiN (111) for films deposited on (111) Si substrates. The grain size decreases when the bias is decreased from +20 V to negative values but then remains almost constant for bias down to -60 V. At negative bias the grains were smaller on (111) Si than on (100) Si. The influence of nitrogen partial pressure on the properties of reactive DC magnetron sputtered TiN films has been studied by Meng et al. [22] Films with preferred orientation (111) were deposited on unheated glass substrates at a total pressure of 0.8 Pa while the nitrogen partial pressure was varied from 0.08 to 0.3 Pa. The results were that the TiN (111) texture coefficient decreased with increasing nitrogen partial pressure while the grain size increased.

Other common methods for deposition of titanium nitride thin films are based on cathodic arc deposition. Two such methods were presented by Martin et al. [23]: filtered arc deposition (FAD) and ion assisted arc deposition (IAAD). FAD has been used for TiN deposition on heated and biased Si and steel substrates (350 °C) in a nitrogen atmosphere. In this setup the stress and hardness could be controlled by varying the bias. In the IAAD a nitrogen

ion source, that supplies N_2^+ ions with a fixed energy of 500 eV, is added to the FAD system. This setup allows deposition on unheated Si and carbon substrates with control over stoichiometry by the ion beam current. The deposition rates were 100 nm/min (6 µm/h) for both setups.

The influence of deposition conditions on crystal and microstructure has been studied quite extensively and several models have been presented. One of these models was presented by Zhao et al. [24] and called "Overall energy model". The model aims to explain the evolution of preferred orientation in TiN films deposited by a biased filtered arc deposition method and is focused on the ion bombardment of the film. It is based on the minimization of a total energy that is the sum of the surface energy, the strain energy, and a "stopping energy" that is defined as the density of the deposited energy of ions along a certain crystalline direction. At small film thickness the surface energy dominates over the strain energy and the preferred TiN orientation should be (200). At an increasing film thickness or an increasing bias the strain energy becomes dominating which leads to a preferred orientation of TiN (111). At a very high bias a resputtering occurs and the stopping energy becomes dominating and the TiN (220) orientation becomes the preferred one. Other researchers have applied the Thornton structural zone model [11] originally developed for sputtering of pure metal films also for TiN film deposition [25].

All these findings and approaches are very important in the understanding of properties of films deposited in non-conventional systems like that used in the present PhD work.

3.7 Chromium films

Hard chromium coatings have been around for a long time and can be used to increase wear and corrosion resistance of tools and machinery components, e.g. piston rings, hydraulic cylinders, and moulds. Very thin chromium films are often used for decorative purposes in car or furnishing industry. Another type of application of chromium is the chrome-on-glass masks for photolithography in the microelectronics industry. The traditional deposition method for Cr is chromium plating, a wet electrolytic method. However this method uses hexavalent chromium that is carcinogenic and it is therefore necessary to replace it by health and environmental friendly deposition methods, for instance a PVD method. Sputtered or cathodic arc evaporated Cr, CrN, and CrC, but also chromium free coatings like diamond-like carbon (DLC), are considered as possible substitutes for electroplated hard chromium coatings in the large scale industrial applications [26].

The sputtering of chromium is quite slow. In magnetron sputtered Cr/CrN and Cr/Cr_2N multilayer coatings the chromium layers was sputtered by a

∅150 mm magnetron at a rate of 10 µm/h (≈ 170 nm/min) onto -20V biased steel substrates at a target current of 4 A (≈ 23 mA/cm^2) [27].

The development of texture in RF sputtered Cr films is discussed in a work by Feng et al. where a model based on the minimization of the surface and interfacial energies is proposed [28]. The model was tested in Cr depositions on glass substrates at different conditions. The films always had Cr (110) texture when deposited on glass substrates at room temperature but when preheated to 250 °C the (110) or (002) texture was determined by the amount of deposited energy from Ar ions or Cr atoms. The Cr (110) preferred orientation was favored by bombardment of the glass substrate.

Control of the preferred orientation is important e.g. when the Cr films are used as an under-layer for cobalt-based magnetic films, where the Cr (200) texture is desirable [29].

3.8 Chromium nitride films

Chromium nitride films exhibit excellent corrosion and wear properties and a high thermal stability. It is possible to deposit thick (several 10 µm) CrN films thanks to the fine grained and a low stress structure [30]. This fact together with that CrN is less brittle than TiN, but still quite hard, makes CrN more suitable for surface protection at relatively soft substrates such as aluminum alloys and stainless steels [31]. The adhesion to steel is often good but it can be enhanced by an intermediate Cr-layer [30]. Stoichiometric or near-stoichiometric CrN coatings have cubic NaCl-structures. With low nitrogen content the harder hexagonal Cr_2N phases can appear. Chromium is a less reactive metal than titanium and this has a consequence for reactive PVD. The required nitrogen partial pressure to form stoichiometric CrN films is higher than for stoichiometric TiN. Typical properties of a commercial coating (Balinit® D) are a hardness of 1750 HV and a thermal stability up to 700 °C [16].

The high thermal stability makes CrN-coatings very suitable for wear and corrosion protection in working processes at elevated temperatures, e.g. in die casting under pressure. Examples of the CrN-coated components are plastic moulds, extrusion dies, and tools for machining and cold forming of metals as Cu and Ti [30].

The common deposition methods for CrN films are the reactive magnetron sputtering and the arc evaporation. The DC magnetron sputtering was used in [32] to investigate an effect of preferred orientation on mechanical properties of the CrN coatings. Two coatings were produced at a total pressure of 0.27 Pa (2 mTorr), a target current of 2.5 A, OEM controlled N_2 flow, and at different DC bias voltages a) 70 V and b) 120 V. The deposition rate was ~18 and ~28 nm/min respectively. The resulting films were a) CrN with a preferred orientation of (200), columnar structure and a hardness of

2300 HV and b) Cr_2N with a preferred orientation of (111), dense structure and a somewhat higher hardness (2400 HV) but with a weaker adhesion to the steel (SKD11) substrates.

A high rate deposition of CrN_x by DC magnetron sputtering with a pulsed DC bias was studied by Nam et al. [33]. The films were sputtered with a target power density of 13 W/cm^2 at a constant argon pressure of 0.24 Pa (1.8 mTorr) and a nitrogen flow varied from 0 to 45 sccm and a varied bias voltage. This made it possible to control the microstructure and phase composition of the CrN_x films. The maximum deposition rate was 210 nm/min for Cr_2N (89% of the rate for pure Cr deposition) and the maximum hardness was 2250 kg/mm^2 (Knoop) for a mixed phase CrN+Cr. The same group has also made a study of properties of the CrN_x films deposited at different deposition rates [34]. In this study they used a constant bias voltage of -100V and a constant argon pressure of 0.2 Pa (1.5 mTorr) and used the target power densities 5, 10, and 13.2 W/cm^2 and the nitrogen flow was varied from 0 to 160 sccm. They concluded that the deposition rate of CrN increased linearly with the target power density (max 430 nm/min at 13.2 W/cm^2) and that the film stress was changed from tensile to compressive with increasing deposition rate. Further the highest hardness and best adhesion was found for the film deposited at highest target power density owing to a high compressive stress and high adatom mobility.

Carbide tools coated with Cr_xN_y films by RF magnetron sputtering have been tested in wood machining [35]. For structural and chemical analysis the films were deposited on Si substrates. Depositions were made at RF powers of 450 W and 650 W and a varied total pressure from 0.1 to 1 Pa. Deposition times were selected between 15 and 80 minutes with a maximum deposition rate of 4.4 μm/h (73 nm/min) for Cr_2N. The Cr_2N films had a columnar structure while the CrN films seemed to be featureless with a maximum hardness of 2100 HV. Cr_2N films were found to be harder but less adherent than the CrN films.

An RF magnetron sputtering was also used for a study of CrN_x films deposited within a wide nitrogen partial pressure range 0.005 – 30 Pa where the chemical and mechanical properties were analyzed [36]. The target power was kept constant at 300 W (the target power density was 6.8 W/cm^2) and the Ar partial pressure constant at 0.3 Pa. Stoichiometric Cr_2N was obtained for nitrogen partial pressures between 0.02 and 0.04 Pa and a stoichiometric CrN was obtained for 0.3 Pa, while for other pressures the CrN and Cr_2N phases were mixed. The conclusion was that the nitrogen content in CrN_x films can be controlled by changing the nitrogen partial pressure, but not independently of the deposition rate and the microstructure. The Cr_2N films were very hard (27.1 GPa) and stiff (E = 348 GPa), a single phase CrN was almost as hard as Cr_2N but more elastic (E = 300 GPa) and the deposition rate was lower.

The microstructure and mechanical properties of chromium nitride films deposited on high speed steel substrates by reactive arc evaporation were studied by Odén et al. [37] The 10 µm thick films were deposited for 220 min at a nitrogen partial pressure of 8 Pa and different negative substrate biases from 20 to 400 V. The microstructure of the films was dense and columnar, the preferred orientation was CrN (220) and the CrN (220) texture coefficient increased with an increasing negative bias up to 200V. A maximum nanohardness of 29 GPa was reached for a substrate bias of -100 V.

The CrN coatings for a dedicated application, cutting tools for machining of copper, were produced by a cathodic arc ion plating [38]. These films were deposited at nitrogen partial pressure of 4 Pa and different negative substrate biases, 0 – 200 V. The preferred orientation was CrN (111) and the micro structure was dense and columnar. The grain size decreased with an increasing bias and a maximum Vickers micro hardness was reached for a bias of 100 V as well as the maximum compressive residual stress. The cutting performance tests indicated that the film hardness and the residual stress could not be taken as a measure of the performance in the milling of copper.

4 Hollow cathode plasma sources for material processing

The films that have been studied in this work were deposited by the hollow cathode discharge based PVD systems of two types: a) the radio frequency hollow cathode plasma jet (RHCPJ) and b) the linear hollow cathode and electron cyclotron resonance microwave hybrid plasma (HYP). Before the systems are described more in detail some of the basic physical processes involved in the hollow cathode PVD of films should be described.

4.1 Hollow cathode PVD

The principle of the hollow cathode effect was introduced in an earlier chapter. In the hollow cathode discharge there are several processes involved that influence the film deposition. First of all there is the hollow cathode discharge itself as the origin of ions that can bombard the cathode surface. This bombardment causes secondary electron emission and heating of the cathode with thermal electron emission as a consequence. Also a high-energy photon radiation from the plasma can cause emission of secondary electrons from the cathode. All these emissions of electrons contribute to the total electron density and enhance the HCD. With a suitable oriented magnetic field that supports the hollow cathode effect a further enhancement can be obtained. If the energy of the bombarding ions is high enough sputtering and/or evaporation can occur and the cathode then acts as a source of material for the film deposition. At very high energy densities the HCD can undergo transition to a hollow cathode arc (HCA) [39] where the cathode walls acquire temperatures over 1000 ºC and very high evaporation rates of the cathode metal can be obtained.

When the hollow cathode is RF-powered the acceleration DC bias is formed across the RF sheaths and the electrons can oscillate like in the DC case. The oscillating electrons cause multiple ionizations thereby generating a very dense plasma. Just like it was described for the RF diode discharge a DC bias across the sheath at the RF electrode causes bombardment of the cathode by positive ions and the same effects as in the DC case occur. As the sheaths separate the plasma from the RF electrode, the “ordinary” RF discharge in this case will act like a virtual anode [2] for the HCD. An impor-

tant feature for thin film processing of the RF plasmas is that all surfaces in contact with the plasma are surrounded by space charge sheaths that cause ion bombardment (plasma is always more positive than the surface), i.e. the substrate and the growing film will be exposed to an ion bombardment during deposition, unless there is no auxiliary substrate bias applied.

The hollow cathode can favorably be used as an inlet for the working gas; inert gas for pure metal deposition or a gas mixture with a reactive gas for deposition of compound films. The gas flow forces the HCD out of the hollow cathode into the RF-discharge and forms an active plasma jet channel [40]. Another important purpose of the gas flow is to transport sputtered or evaporated material from the cathode to the substrate promoting a very high deposition rate.

4.2 The radio frequency hollow cathode plasma jet (RHCPJ)

The RHCPJ [39] consists of a cylindrical hollow cathode made from the metal that should be deposited directly or reactively. Typical dimensions of the cathode used in this work are an outer diameter of 6 mm, an inner diameter of 1 – 5 mm and a length of 50 mm. The cathode, serving as the gas nozzle, is connected to a 500 W RF (13.56 MHz) generator via an impedance matching network. This nozzle is used as the inlet for mixtures of argon with a reactive gas, e.g. with oxygen or nitrogen. The flow rates of the gases in the working gas mixture are controlled by mass flow controllers. The RHCJP source is mounted on a grounded vacuum vessel equipped with an adaptive pressure control system. Substrates are mounted on a thermally insulated and ohmically heatable substrate holder with a thermo couple for temperature measurements. The distance between the substrate and the outlet of the nozzle is adjustable. A sketch of this setup is shown in figure 1. Further is the system equipped with an IR-thermometer for the measurement of the cathode temperature and an optical multichannel analyzer (OMA) for spectral analysis of optical emissions from the plasma. A 100 MHz oscilloscope is connected to the cathode for measurements of the average DC voltage of the cathode and the peak-to-peak RF voltage. This RHCPJ plasma source can be operated both in the hollow cathode discharge (HCD) and the hollow cathode arc (HCA) regime. Under HCD conditions this system has been used for example in reactive deposition of AlN and TiO_2 [39]. In the present work the RHCPJ has been used for deposition of chromium and chromium nitride films.

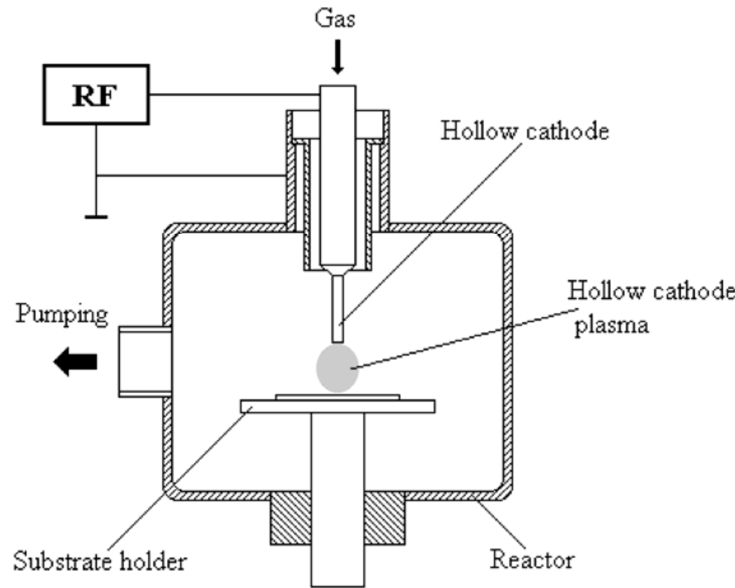

Figure 1. Sketch of the radio frequency hollow cathode plasma jet (RHCPJ).

4.3 The hybrid plasma (HYP) source

The hybrid plasma source combines a linear hollow cathode plasma with an ECR microwave plasma. A sketch of the source is shown in figure 2.
The microwave plasma is generated by 2.4 GHz power supply with a maximal power of 2 kW fed through a rectangular waveguide to a horn-type antenna integrated with the reactor. A pair of strong permanent magnets gives the magnetic induction of 0.09 T that is necessary for the ECR absorption of the microwave power and forming of the ECR plasma. This plasma provides a pre-ionization for the hollow cathode plasma and stabilizes it at low gas pressures. The linear hollow cathode is placed inside the antenna between the magnets so they can provide a focusing magnetic field for the hollow cathode plasma at the outlet slit. The pair of magnets is rotatable for operation of the hollow cathode in the magnets-in-motion (M-M) regime where the HCD is symmetrized and more uniform along the cathode plates [41]. A 13.56 MHz RF generator with a maximum power of 3 kW supplies the power to the cathode through an impedance matching network. The cathode consists of two 160 mm long parallel metal plates and the slit between them serves as the inlet for the processing gases. The flow of the gases is controlled by mass flow controllers. A background vacuum better than 10^{-4} Pa can be reached in the 50 cm diameter vacuum chamber that is pumped by a

1600 l/s oil diffusion pump backed by a 500 m^3/h blower and a 80 m^3/h rotary pump. The chamber is equipped with a 30×18 cm^2 sample table with an adjustable distance from the cathode outlet. Further a second substrate holder can be installed where substrates can be rotated. Both the table and the holder can be used for experiments with electrically biased, grounded, or floating substrates. To allow longer times of a high-power operation the cathode and the chamber are water cooled. In this work the titanium nitride films were reactively produced using cathode plates made from Ti with nitrogen as the reactive gas admixed in argon (90% Ar + 10% N_2 in most cases).

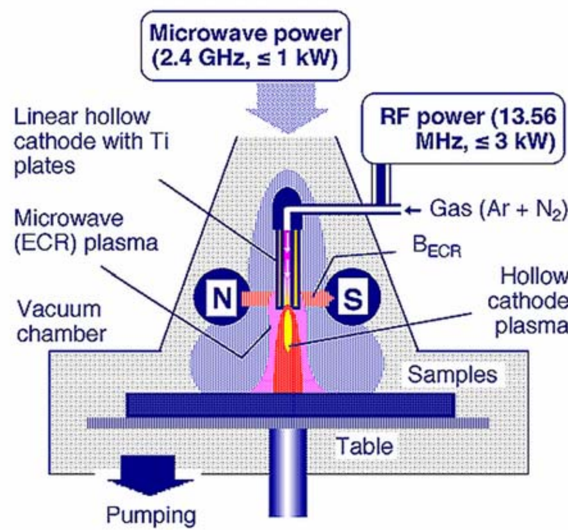

Figure 2. Schematic sketch of the hybrid plasma source (HYP LP).

A photograph of the hybrid system is shown in figure 3. In the upper left corner of the picture the microwave generator (magnetron) can be seen with a control unit below. The rectangular wave guide in the upper part ends in the conical microwave power launcher antenna mounted on top of the cylindrical vacuum reactor.

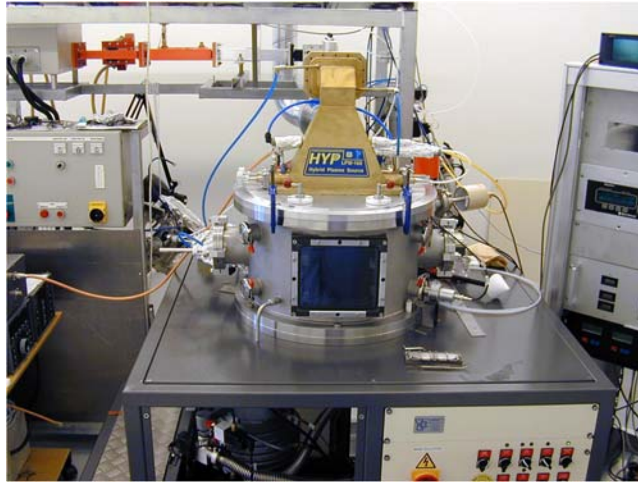

Figure 3. Photograph of the hybrid plasma source system.

4.4 The special thermoprobe for temperature and current-voltage measurements

For the temperature and current-voltage measurement of the plasma in the hybrid system a special substrate holder was developed. It consists of a cylindrical steel disc ∅30x3 mm^2 made from either steel (ferromagnetic), SS-2172, austenitic stainless steel (non-ferromagnetic), AISI 304, or copper. In the centre of this disc a ∅1.5 mm hole is drilled for the stainless steel cartridge of a thermocouple (type K). The thermocouple is thermally and electrically shielded by the cartridge which is inserted in the reactor through an electrically insulated vacuum feedthrough. Inside the reactor the thermocouple is protected from deposition by addition of alumina insulators. Because the thin stainless steel cartridge is the only direct thermal conductor and is the only support for the probe the system with the thermocouple provides a good thermal insulation for the probe. The cartridge serves as an electrical conductor for connection of a bias to the probe. Outside the reactor the electrical shielding is made in a coaxial arrangement with an additional electrically grounded outer conductor. The complete probe system can be seen in figure 4.

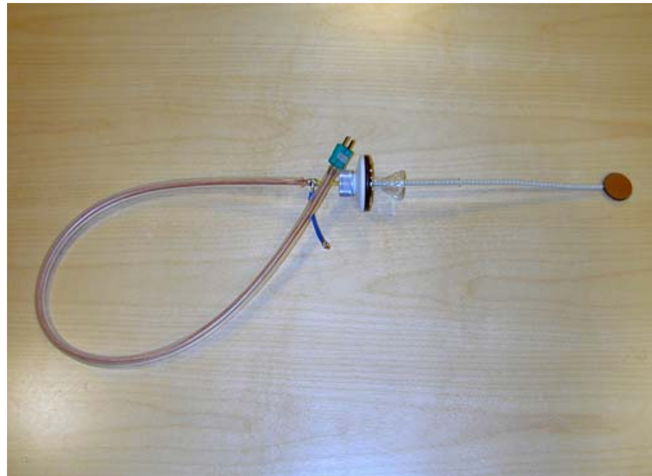

Figure 4. Photograph of the special probe/substrate holder system.

On this the 35x35 mm^2 substrates made from steel or silicon were mounted (one on each side of the probe/holder) and fixed with four stainless steel clamps, see figure 5.

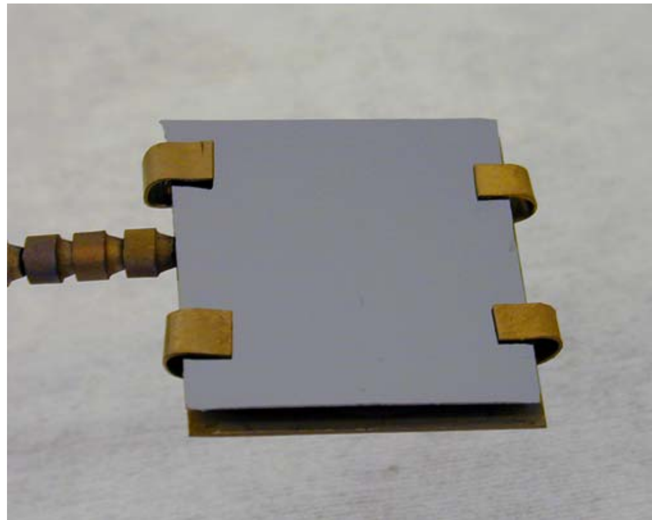

Figure 5. Close-up photograph of the probe with mounted Si substrates.

The temperature can be measured simultaneously with the voltage (bias) applied between the probe and the grounded reactor chamber and with measurements of the current through it. Using an LC-filter a DC voltage can be applied to the substrates without an RF influence through this probe so that the temperature can be measured under biased substrate conditions. For plasma diagnostics (I-V measurements) the probe can be considered as a large-area Langmuir probe.

5 Summary of papers

5.1 Summary of Paper I

This paper presents new microwave and hollow cathode hybrid plasma sources developed for both low pressure and atmospheric pressure. The results from the experiments with the low-pressure hybrid plasma source (HYP LP) were within the scope of this thesis. The performance of this source was studied with the deposition of TiN thin films. The properties of films produced by the source were characterized by different methods.

The radial profile of the ion plasma density and the electron temperature were measured by a double Langmuir probe 15 cm below the outlet of the hollow cathode both in N_2 and Ar atmosphere. In this measurement the pressure was 0.8 Pa (6 mTorr) and the gas flow was 70 sccm, the applied RF power was 1 kW and the incident microwave power was 1 kW. The profiles were flat and the ion density reached 4×10^{11} cm^{-3} and 9×10^{10} cm^{-3} for argon and nitrogen, respectively. This makes the hybrid source suitable for uniform thin film depositions. At an increased RF power of 2.5 kW the ion density was raised to 6×10^{11} cm^{-3} in Ar corresponding to an ionization degree of 0.3% classifying the source as a high-density source.

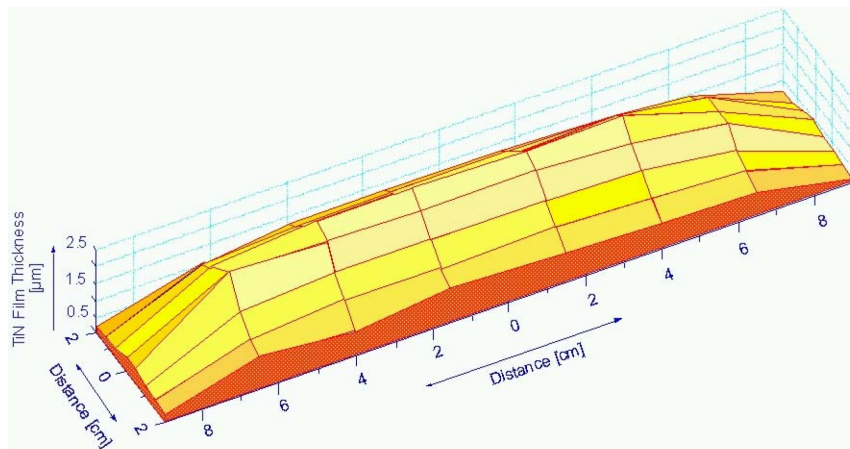

Figure 6. Distribution of the film thickness of TiN film deposited on 18×4 cm^2 Si substrate.

Titanium nitride films were deposited on large area (18×4 cm^2) silicon substrates at 3 kW RF power, 1 kW microwave power, 0.8 Pa (6 mTorr), 10% N_2 in Ar flowing at 70 sccm for 20 min. A typical thickness profile of this film is shown in figure 6. This profile was measured “point-by-point” by breaking the substrate and studying the cross sections in SEM. The film thickness (1.5 µm) is very uniform right under and along the cathode and this is consistent with the uniform plasma density found in the probe measurements.

The TiN films were deposited also on high speed steel (HSS) substrates. As the films on Si substrates, the TiN films on HSS substrates had very dense microstructures, as can be seen in the SEM cross section images. Studies of the crystalline structure of the films by x-ray diffraction showed a high degree of TiN (111) preferred orientation, exemplified by figure 7. The TiN films with this orientation usually exhibit a very high hardness [19]. An ESCA depth profile confirmed pure and stoichiometric TiN through the entire thickness of the films. This result is another proof of the high quality of the TiN films deposited in the hybrid system.

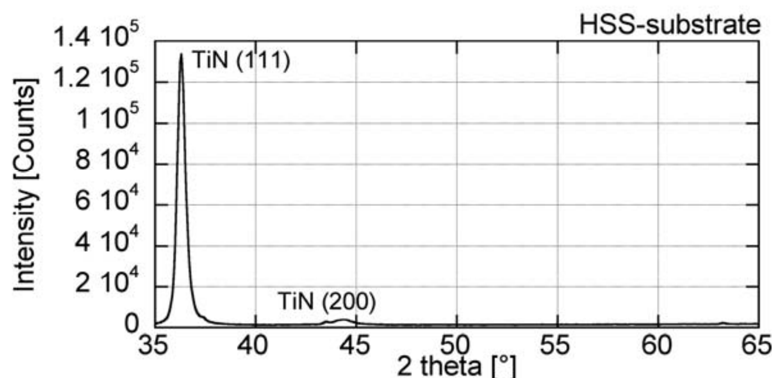

Figure 7. An example of an X-ray diffractogram for a TiN film deposited on HSS substrate.

5.2 Summary of Paper II

The aim of this paper was to compare some properties of titanium nitride films deposited by the LP HYP source with films deposited by selected conventional methods. The influence of the microwave power absorption on the growth conditions and formation of film defects were also discussed and confirmed by the temperature measurements.

Titanium nitride films were deposited by the LP HYP source and analyzed regarding their crystallinity and microstructure by XRD and SEM, and their mechanical properties by nanoindentation. The films were deposited on

3” Si wafers and on 40×20×2 mm^3 high speed steel (HSS), ASP 2030, respectively. For comparison the same analyses were performed on TiN films deposited by an electron beam evaporation (EBE) system at the material science division at The Ångström Laboratory and on commercial TiN films (Balinit® A, provided by Balzers Sandvik Coating AB) on identical substrates. The deposition conditions for the HYP deposited TiN films were an RF power of 3 kW and the absorbed microwave power in the reactor was approximately 200 W. The total gas (Ar + N_2) pressure was 0.8 Pa and the total gas flow rate was 70 sccm while two different Ar to N_2 flow rate ratios were tested. The substrates were unbiased and unheated and the cathode – substrate distance was 3 cm. Prior to the deposition the substrates were plasma cleaned for 5 min in pure argon microwave plasma. After this cleaning step a thin Ti-layer (~ 100 nm) was grown for 2 min in pure argon hybrid plasma to promote adhesion.

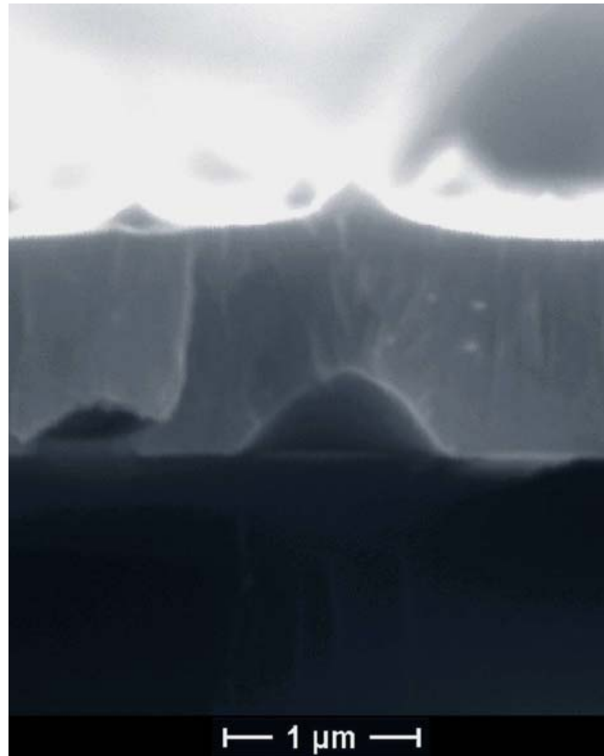

Figure 8.SEM micrograph: cross-section of a TiN film deposited on Si substrate showing interface “bubbles”.

The film surfaces were found to contain µm-sized macroparticles that can affect the performance of the films in tribological applications. These macroparticles are similar to those produced by low-voltage arcs, but more knowledge is needed to confirm the origin of such particles and other defects

in the hybrid plasma. It was confirmed by ESCA that these particles contain only Ti or TiN.

The film thickness measured on the SEM cross-section images was 1.3 μm for both types of substrates (Si and steel). With a deposition time of 10 min this gives an average deposition rate of 130 nm/min and this is 3.5 times faster than the electron beam evaporated film on Si and 2 times faster than the electron beam evaporated film on HSS. The study of the film cross-sections by SEM revealed that films deposited on Si by the HYP source have interfacial defects of a type that are not present in films deposited on HSS. This kind of defects is “bubble-like” as can be seen in figure 8.

The TiN films deposited in pure hollow cathode PVD do not have this kind of defects either and it can be suspected that the origin of these defects is connected to the deposition conditions, possibly with the substrate – microwave power interactions. This was confirmed by the probe temperature measurements. The copper probe was used with $35\times35\times0.5$ mm^3 Si and stainless steel substrates. The substrates were first exposed to the microwave plasma for 15 min (phase 1) and then to the hybrid plasma for another 15 min (phase 2). The conditions were the same as for the TiN film depositions. It was found that the temperature after the first phase was much higher for the Si substrate than for the steel substrate. This can be attributed to a higher absorption of the microwave power in Si than in steel. After the second phase the temperature is nearly the same for both Si and steel substrates. Also the XRD measurements provided an evidence of higher growth temperatures for Si substrates by the more pronounced appearance of the TiN (200) peak in the spectra of the films.

The mechanical properties of the TiN films were evaluated by nanoindentation measurements and the HYP deposited films were found to have very high nanohardness (30 GPa) similar to the best commercial TiN films.

5.3 Summary of Paper III

The ferromagnetic character of steel substrates has been found to have a considerable influence on the properties of TiN films deposited in magnetized plasma source PVD systems. The titanium nitride films were grown in the hybrid system on cylindrical substrates of ∅8 mm diameter made from two different steels, a non-ferromagnetic austenite stainless steel (AISI 304) and a ferromagnetic martensite steel (Swedish SS 2142). The depositions were made both on electrically grounded and insulated (floating) substrates under identical conditions. The individual samples showed quite different TiN surfaces, as can be seen in figure 9.

Figure 9. Photographs of Ø8 mm cylindrical sample made from martensite (ferromagnetic) and austenite (non-ferromagnetic) steels coated with TiN in hybrid plasma with both electrically grounded and insulated substrates.

The films on the ferromagnetic substrates seem rougher than those on non-ferromagnetic substrates and films on grounded substrates seem rougher than those on floating substrates. Differences can be explained by different particle bombardment on different substrates. Ferromagnetic substrates can affect the geometry of the magnetic field in the PVD system and thereby attract more charged particles. To further examine this assumption measurements with the special thermoprobe were performed. The probe was made from two steels: a) non-ferromagnetic austenite stainless steel (AISI 304) and b) ferromagnetic martensite steel (Swedish SS 2172). Austenite steel sheets (35×35×0.66 mm^3) and silicon slices (35×35×0.38 mm^3) served as substrates. The temperature measurements for grounded and floating steel substrates confirmed the observations for the ∅8 mm substrates; the highest temperature after 15 min of hybrid plasma exposure was reached for the grounded ferromagnetic sample, which indicates the most intense ion bombardment (the surface is negative with respect to the plasma). This is proved by the current measurements on the grounded probes; the current flowing

through the probe is higher for the ferromagnetic than for the non-ferromagnetic probe.

Depositions on the Si substrates were made in pure hollow cathode plasma to avoid microwave heating of the silicon as observed in Paper II. Four 0.7 µm thick films deposited on Si with grounded/floating, martensite/austenite probes were analyzed by XRD. The X-ray diffractograms in figure 10 show that the probe material also influences the texture of the TiN films. Films produced on the grounded probes have increased (200) peaks what is an indication of an increased deposition temperature.

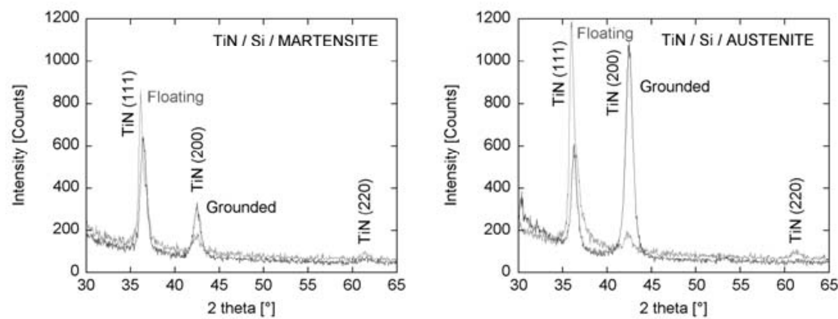

Figure 10. X-ray diffractograms of TiN films deposited on Si substrates using both the martensite and austenite substrate holders at both grounded and floating conditions.

For the temperature measurements on Si with different bias voltage the martensite probe was used and the final temperature was found to steadily increase as the bias was changed in the following sequence: +40 V, floating (corresponding to +30 V), 0 V (grounded), -80 V. From this it can be concluded that bombardment by positive ions gives a substantial contribution to the temperature rise.

5.4 Summary of Paper IV

Hard coatings for steel substrates are often deposited in PVD systems with magnetically confined or magnetically enhanced plasmas. In Paper III the ferromagnetic steel substrates have been found to be able to deform the magnetic field in the deposition system and thereby increase the ion bombardment of the substrate and the film. The TiN films were grown by the HYP PVD system on rectangular 35×35 mm^2 stainless steel sheets and Si substrates using the special thermoprobe/substrate holder made from either a non-magnetic austenite steel or a ferromagnetic steel. During the deposition process the temperature was recorded. After 15 min deposition the film

thickness had reached 1 µm. The film surfaces were studied by SEM and the crystalline structure by XRD.

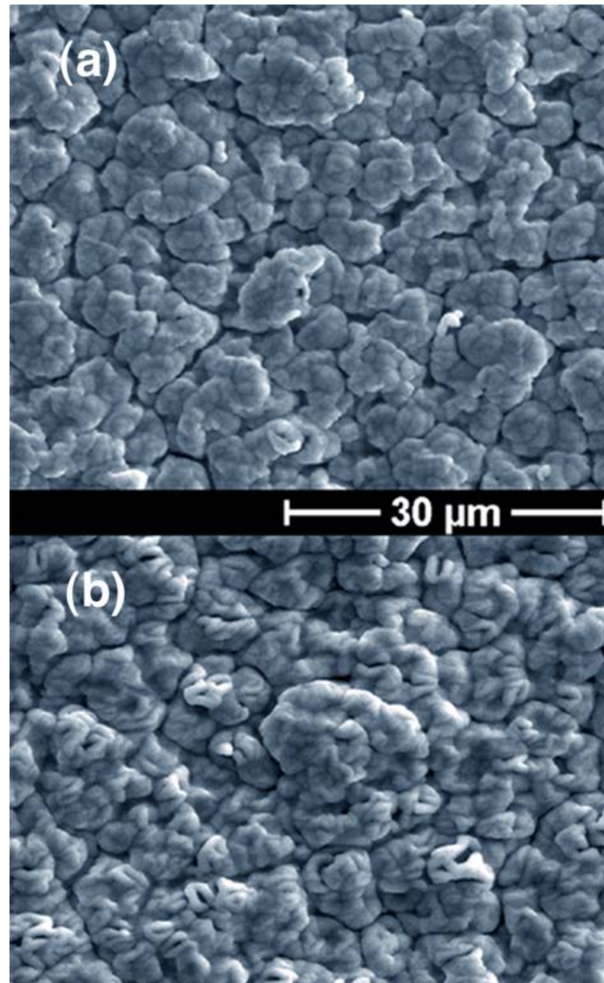

Figure 11. SEM micrograph: TiN film on stainless steel substrate mounted on austenite steel holder (a) and martensite steel holder (b).

The surface of the film deposited on a grounded, stainless steel substrate using the ferromagnetic holder is rougher than the corresponding film using the non-magnetic holder. This can be seen on the SEM images in figure 11 and the higher roughness is ascribed to more intense ion bombardment because of a disturbed magnetic field. At the floating substrates the ion bombardment can be expected to be reduced due to charge saturation effects and consequently the roughness of a film deposited under such conditions is lower than the films grown on the grounded probe.

To confirm the results obtained in the hybrid plasma system the influence of ferromagnetic substrates was tested also in a conventional magnetron sput-

tering system. The titanium films of 1 µm thickness were sputtered onto austenite and martensite steel substrates under identical deposition conditions. The ∅2" Ti target was sputtered by a DC power of 87 W at a pressure of 0.4 Pa (3 mTorr) and the substrate – target distance was 45 mm. The deposition time of 5 hours resulted in a deposition rate of 0.35 nm/min. The surfaces of these films shown in the SEM images in figure 12 have the same characteristics as the HYP deposited TiN films, i.e. the roughness is higher on the ferromagnetic (martensite) steel than on the non-magnetic (austenite) steel.

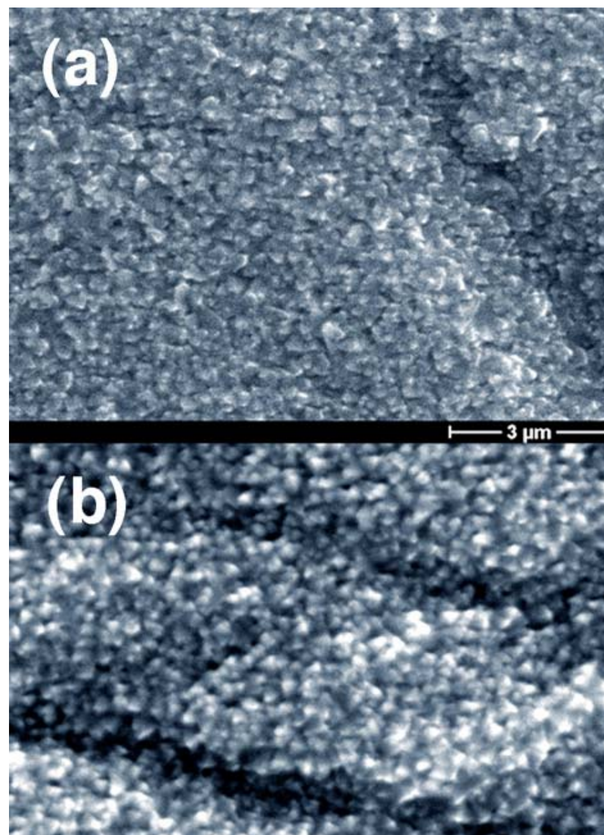

Figure 12. SEM micrograph: Ti film sputtered on austenite steel substrate (a) and martensite steel substrate (b).

5.5 Summary of Paper V

The deposition of TiN by the hybrid hollow cathode and microwave ECR plasma system have been found to be influenced by the substrate material. In paper III differences in the substrate temperatures were reported for different

substrate holder materials and under floating/grounded conditions but also for some tests with different biased substrates. In this paper different bias voltages were used for temperature measurements and current-voltage measurements during TiN depositions on silicon and stainless steel substrates. Considerable differences in the substrate temperature for the Si and steel substrates were found after 15 min exposure to pure microwave ECR plasma. This can be explained by a more efficient absorption of the microwave power in Si than in steel. The time rises of the temperatures of DC-biased (-60V – +50V) Si substrates mounted on the ferromagnetic probe exposed to pure HC plasma for 30 min can be seen in figure 13. At zero bias the lowest temperature is reached and at biases of about ± 50 V the temperature is about 100 ºC higher.

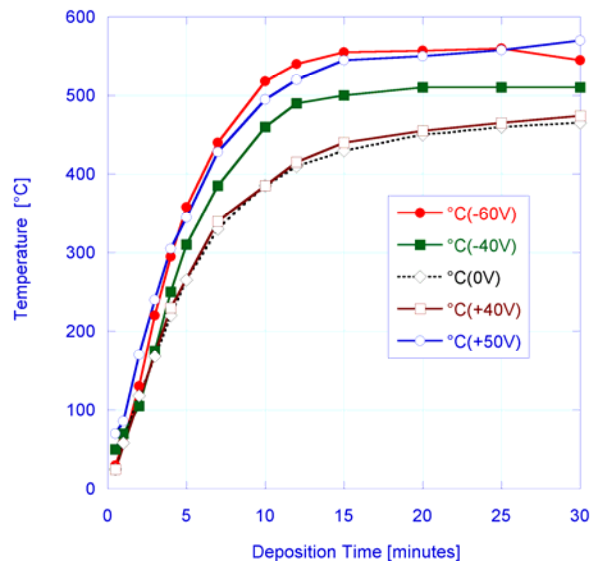

Figure 13. Time rises of the temperature of the DC-biased ferromagnetic thermoprobe with Si substrates in the HC plasma.

Current – voltage measurements on stainless-steel substrates with probes made from steels of two different kinds, martensite and austenite, were performed during TiN film deposition in hybrid and HC plasma, respectively. From these measurements it was found that for the same bias the martensite steel probe (ferromagnetic) exhibited higher electron current than the austenite steel probe (non-ferromagnetic) as expected and that the currents were higher in hybrid plasma than in pure HC plasma. This confirms that the bias has a substantially larger effect on the flow of charged particles than the

substrate material itself. The floating potential, i.e. when the electron and the ion currents are equivalent, was found to be about +30 V for both the martensite and the austenite probe. This somewhat surprising result (a positive floating potential) is believed to be due to the specific geometry of the hollow cathode and the magnetic field around the probe.

Ion bombardment during deposition can promote densification and structural quality of thin films. This has been examined by the reactive hollow cathode deposition of TiN on biased Si substrates using the ferromagnetic steel probe. The films were deposited for 30 minutes at different biases in the interval -80 V - +50 V. As can be seen in figure 14 most films exhibited a very dense columnar structure with small differences between the films.

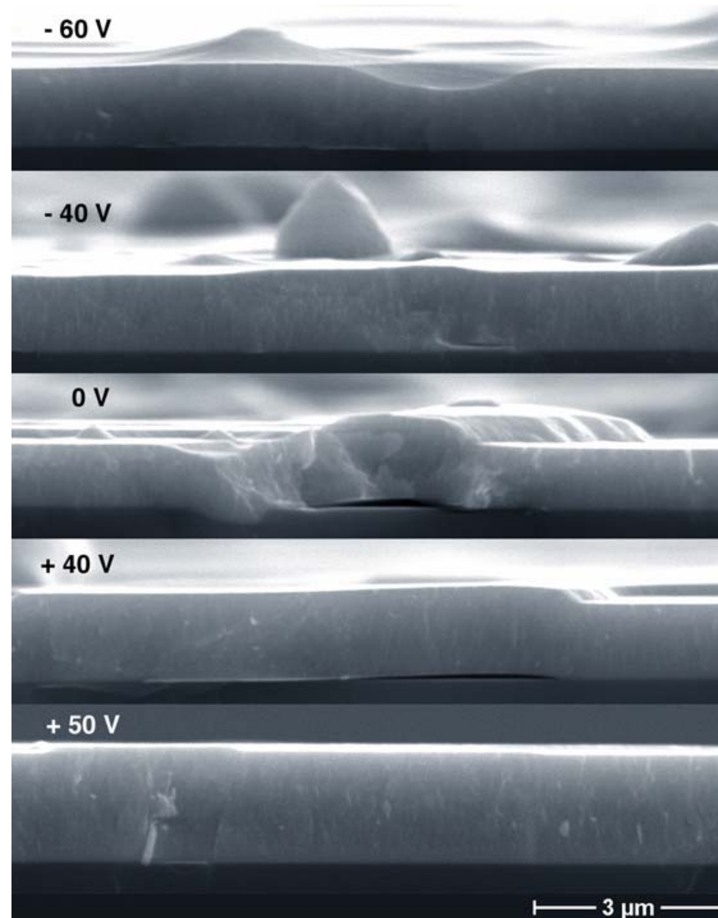

Figure 14. SEM micrographs: Cross sections of TiN films deposited on Si substrates at different DC-bias voltages.

The best films with very dense structures are always obtained at negative biases in the interval -40 – -60 V but when the bias is increased to -80 V the films are destroyed by the intense ion bombardment. X-ray diffraction meas-

urements of these films showed that all (except the damaged film deposited at -80 V) exhibits a preferred orientation of (111). As all films have about the same thickness, around 1.5 µm, the intensities of the different XRD-peaks can be directly compared for the films. The intensities for the (111), (200), and (220) peaks as function of the bias are plotted in figure 15 together with the final (saturated) probe temperature after 30 minutes of deposition. The minimum temperature is obtained near the floating potential (+30 V) where the lowest charged particle bombardment is expected. The (111) texture coefficient increases with increasing negative bias and this promises dense and hard films for a bias of -60 V. At positive biases higher than the floating potential the intensity of the (200) peak increases and this can be explained by increasing surface energy due to electron bombardment.

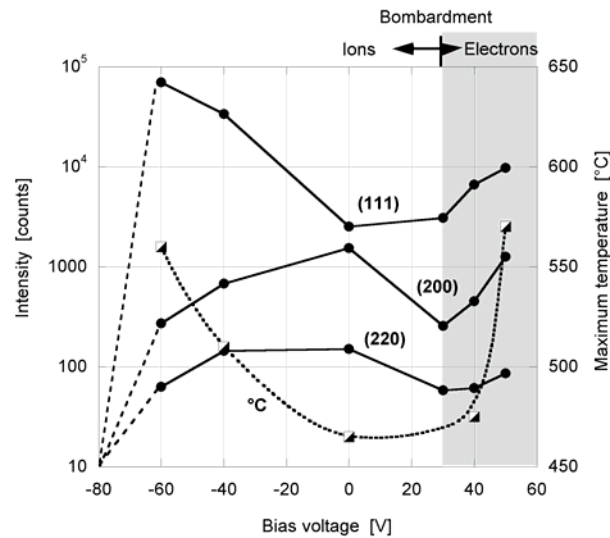

Figure 15. Peak intensities of the TiN textures in films deposited on Si substrates at different dc-bias voltages. Corresponding temperatures of the thermoprobe is also shown.

5.6 Summary of Paper VI

Due to the hazardous character with influence on health and environment, alternatives to the wet electroplating of chromium coatings must be developed. This is possible either by new methods for chromium film deposition or through a replacement of materials, such as CrN or CrC, instead of the Cr. Both possibilities can be realized by PVD methods. Especially the reactively deposited CrN is an interesting alternative to hard chromium coatings for tribological applications. In this paper the deposition of chromium and chro-

mium nitride films by the RHCPJ operated in the diffuse arc regime has been studied. The Cr and CrN films were deposited on unheated Si and high speed steel substrates by the RHCPJ system at a power of 150 – 300 W and a gas pressure of 67 Pa. The working gas flowing at 100 sccm through the Cr nozzle was pure Ar for Cr depositions and pure N_2 for CrN depositions. The maximum CrN film thickness measured by a stylus profiler after 20 min of deposition at a power of 250 W was 45 µm corresponding to a very high deposition rate of approximately 2.3 µm/min. For a Cr film deposited under the same conditions the deposition rate was 275 nm/min. The hardness of these very hard (23 GPa) CrN films was measured by a nanoindentation method. A study of the film cross sections by the SEM revealed that the Cr films had a dense structure while the CrN films had a columnar or fibrous structure.

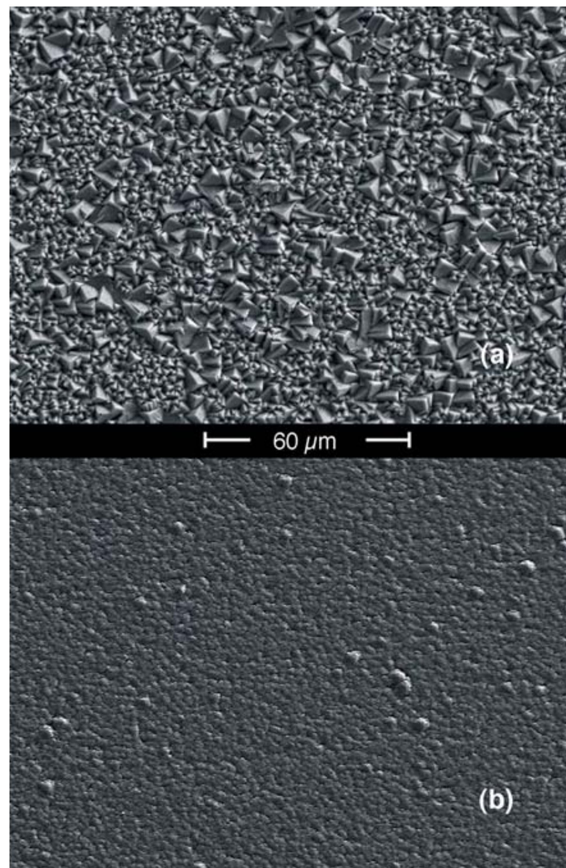

Figure 16. SEM micrographs: 40-µm-thick CrN films on (a) Si and (b) steel.

The surfaces of CrN films deposited on Si and steel have quite different appearances as can be seen in the SEM images in figure 16. While the surface of the film on Si consists of prism like grains the surfaces of the film on

steel are smoother with grains that are rounded off. This is also visible in cross section images for the same two films in figure 17, where it is evident that the films on steel are denser as well. Further to this it is clear that the grain size increases with an increasing film thickness and the thinner films (< 10 µm) were indeed more fine-grained and smoother than thicker ones. Some of the thicker films on Si substrates had a tendency to delaminate, possibly by an effect of stress accumulation on the non-cleaned substrates.

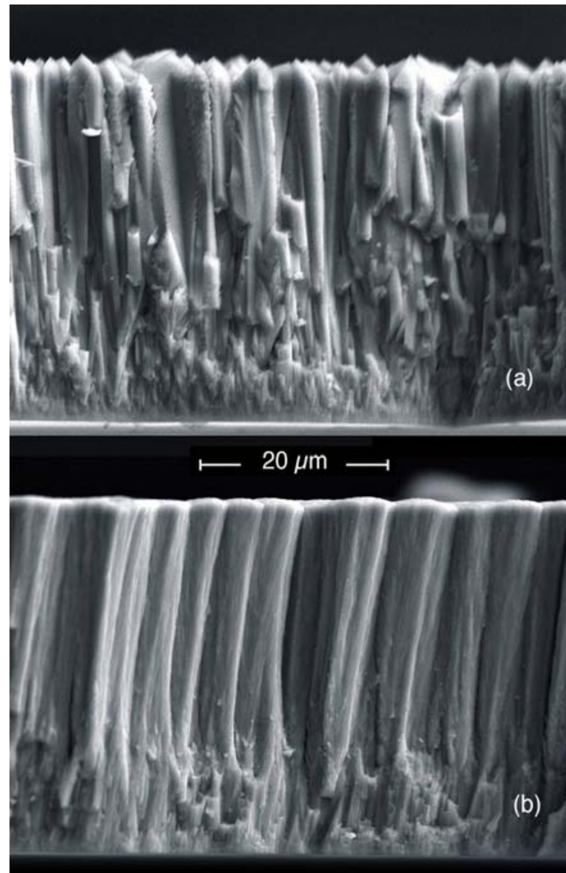

Figure 17. SEM micrographs: cross-sections of 40-µm-thick CrN films on (a) Si and (b) steel.

From the XRD it was found that both Cr and CrN films on Si substrates were highly textured in Cr (110) and CrN (111) orientations respectively. This is not the case for the CrN film deposited on steel where a prominent CrN (200) and a smaller CrN (220) are present in the diffractogram besides the CrN (111) peak. It is believed that this difference can be attributed to a lower temperature during growth on steel than on Si. However, it can not be excluded that the difference is influenced by variances in the ion bombard-

ment, due to a higher electrical conductivity of steel substrates and less charge saturation effects than on Si substrates.

5.7 Summary of Paper VII

The performance of the RHCPJ during deposition of Cr films in an argon atmosphere and CrN films in a nitrogen atmosphere were studied. At the pressure of 67 Pa (0.5 Torr) and a flow of 100 sccm the RF power dependence of the cathode self-bias voltage and the cathode temperature was measured in the power interval 100 – 320 W. The self-bias voltage at the cathode was about 10 times higher in N_2 than in Ar for all powers and this can be explained by the higher secondary electron emission coefficient in argon than in nitrogen. The temperature of the cathode outlet was higher in the N_2 atmosphere than in the Ar atmosphere except at powers below 125 W. These two results are consistent in that way that the higher electric field in nitrogen probably causes a more effective bombardment leading to a higher substrate surface temperature. The maximum cathode (Cr nozzle) temperature reached nearly 1400 ºC and at this temperature the hollow cathode operated in the diffuse arc regime, i.e. an arc with the hot thermionic cathode.

Slices of Si and steel were used as substrates and the temperature of the unheated substrates did not exceed 400 ºC during the deposition. The deposition rate as a function of the RF power for both Cr and CrN depositions can be seen in figure 18. At high powers the rate reached 1 µm/min for Cr and 2.8 µm/min for CrN film deposition, respectively. Both these values exceeded substantially the growth rates reported in the literature.

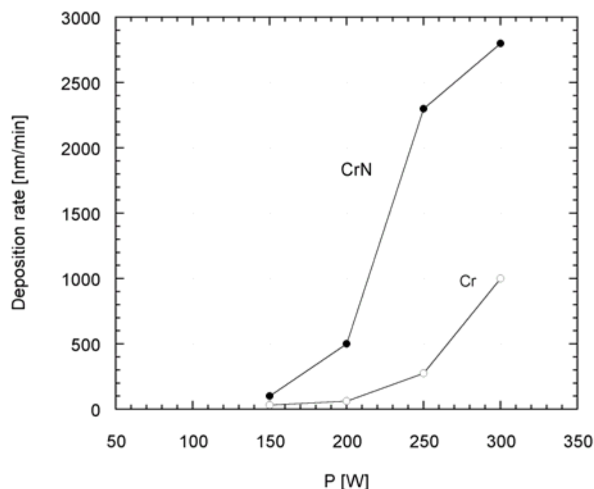

Figure 18. Dependence of Cr and CrN deposition rates on RF power.

The characterization of the films revealed that the chromium films were dense and had a preferred crystalline orientation of (110) and that the CrN films were very hard and had a columnar/fibrous structure and a strong (111) texture when deposited on Si. The CrN films deposited at a low power were however not strongly textured but they had considerable (200) and (220) reflections.

6 Conclusions

By the general characterization the HYP LP source can be classified as a high density plasma source. This is based on that the ion density of the source reached 6×10^{11} cm^{-3} in Ar and 1.5×10^{11} cm^{-3} in N_2 for a RF power of 2.5 kW and a microwave power of 0.3 kW dissipated in the plasma. The flat density profile of the plasma makes it suitable for uniform deposition of films. The plasma density exceeds 2×10^{11} cm^{-3} along a diameter of more than 40 cm, which implies that this source can be utilized in large-area processing. Properties of TiN films deposited under such conditions confirmed high hardness related to the stoichiometry and crystallinity of these films.

From the characterization of titanium nitride films deposited on Si and HSS substrates with the HYP LP source it was found that the gold-colored TiN films were dense and highly textured with a preferred orientation of (111). These results imagine an arc ion plating character of the PVD regimes. The HYP LP sources can be a powerful tool in industrial applications for material processing because it can be incorporated, together with or instead of conventional sputtering or evaporation sources, into new PVD and/or PE CVD systems for new types of coatings.

In a comparative study the dense, hard TiN films were deposited by the HYP LP source at rates considerably exceeding the rates of conventional methods with mechanical properties comparable or better than the best commercial coatings. The high hardness could be attributed to the dense microstructure and the high TiN (111) preferred orientation.

It has been concluded that the film growth can be influenced by interaction between microwave power and the substrate itself. As to our knowledge this effect has not been studied in the PVD systems before. Temperature measurements on Si and steel substrates have demonstrated that the interaction of the microwave power with Si substrates strongly affects the Si substrate temperature. This finding is of more general importance not only for the PVD of films.

An original finding related to this work is the effect of ferromagnetic substrates on the growth of films in magnetized plasmas. An effect of the ferromagnetic substrates as an enhanced ion bombardment was clearly evidenced. The ion bombardment increases the growth temperature and affects the texture and morphology of the growing films. As the ferromagnetic substrates can affect the geometry of magnetic power lines it is suggested that ferromagnetic steel inserts can be used instead of permanent magnets to affect the

film growth conditions. The high Curie temperature (> 1000 ºC) of ferromagnetic steel enables such an application in almost arbitrary conditions without auxiliary cooling. The effect of ferromagnetic substrates has also been observed in conventional magnetron sputtering systems and it has therefore a broad practical importance.

It has also been found that a DC bias can substantially change the properties of the TiN films and control the effects of the ferromagnetic substrates. Highly textured (111) TiN films deposited on biased Si substrates have a very dense columnar structure, especially at a negative bias between -40 and -60V. At higher negative bias than this the ion bombardment can cause damage on the growing film. Both ion and electron bombardment increase the substrate temperature.

The depositions of chromium and chromium nitride films by the RHCPJ confirmed that the reactive PVD of CrN film in the hollow cathode plasma exhibit a very good stability and reaches extremely high static deposition rates. The process can be tuned and optimized with respect to the resulting properties of coatings, e.g. crystalline structure, grain size, and roughness. Further, the transition from the hollow cathode glow discharge regime to the hollow cathode arc regime is well controllable. At high RF powers accompanied by a high contribution of thermionic emission from the cathode, highly oriented crystalline CrN films can be grown at static deposition rates as high as 2.5 μm/min and even up to 4 μm/min. It should also be noted that the deposition rates of CrN are considerably higher than those of Cr, which is not observed in conventional arc and sputtering systems.

The performance of the reactive diffuse arc process and the properties of the CrN films indicate that the transfer of the process from small cylindrical cathodes to linear magnetized hollow cathodes with the magnets-in-motion (M-M) arrangement is feasible. It can be expected that the deposition rates comparable to the rates in the small cylindrical device can be reached in the linear hollow cathode, but the films can be deposited over considerable larger areas. This makes hollow cathodes very promising for CrN coating in industrial applications in the near future.

It should be noted that both the microwave plasma source and the RF hollow cathode can produce chemically active plasmas for PA CVD. This opens up for combined PA CVD regimes and PVD regimes in a common regime for the HYP LP. This new regime can also become a new route to new nanocrystalline materials for the future.

7 Sammanfattning

Tunna filmer av metaller och föreningar används i väldigt många tillämpningar idag. De används för mikroelektronik, optik, verktyg, livsmedelsförpackningar, osv. och syftet med dem är att förändra egenskaperna hos de belagda komponenterna, till exempel genom att ge dem en skyddande yta. Det finns en stor variation av metoder för att tillverka dessa filmer. Under 1900-talet utvecklades ett flertal så kallade atomistiska deponeringsmetoder, där filmerna byggs upp från enskilda atomer/joner eller molekyler. Dessa metoder brukar indelas i två huvudgrupper: kemisk ångfasdeponering (CVD) och fysikalisk vakuumytbeläggning (PVD), men det finns även metoder som kombinerar dessa två typer. Många av de olika deponeringsmetoderna utnyttjar plasma för att understödja filmtillväxten, t.ex. genom att tillföra energi och öka reaktiviteten. Detta kan öka produktiviteten och sänka kostnaderna samt tillåter nya kombinationer av film och substratmaterial. Högdensitetsplasman är väldigt reaktiva och tillåter att deponeringsförhållandena varieras inom stora intervall vilket medför att egenskaperna hos filmerna kan styras. Denna avhandling omfattar studier av filmdeponering med PVD-metoder med högdensitetsplasmakällor baserade på hålkatoder och syftar till att öka förståelsen för deponeringsprocessen och dess inverkan på filmegenskaperna.

En typ av filmer som studerats är filmer av titannitrid (TiN) som är ett mycket hårt material som dessutom har god elektrisk ledningsförmåga. Användningsområdena sträcker sig från slitstarka skikt på verktyg via elektrodmaterial i MOS-strukturer till biomedicinska komponenter. Tack vare det guldliknande utseendet hos stökiometrisk (Ti/N = 1) TiN kan sådana filmer användas för dekorativa ändamål.

Andra typer av filmer som studerats är krom- och kromnitridfilmer. Kromfilmer används för att öka nötnings- och korrosionsmotståndet på verktyg och maskindelar, men även för att ge föremål ett mer attraktivt utseende. Traditionellt görs detta med kromplätering, en våt elektrolytisk metod. Då denna metod använder sexvärt krom, som är cancerogent, är det nödvändigt att byta ut denna mot hälso- och miljövänliga metoder, förslagsvis en PVD-metod. Kromnitridfilmer har delvis samma användningsområden som kromfilmer och används därför som ersättare till dessa.

De plasmakällor som använts vid deponeringarna för detta arbete är av två typer: radiofrekvent hålkatodsplasmajet (RHCPJ) och radiofrekvent, linjär hålkatod för lågtryck och elektroncyklotronresonans (ECR) mikrovågshybridplasma (HYP LP). Hålkatodplasmakällor utnyttjar hålkatodeffek-

ten som leder till plasman med hög densitet och hög kemisk aktivitet. RCHPJ-källan består av en cylindrisk hålkatod driven av en RF-generator och har använts för deponering av Cr- och CrN-filmerna i detta arbete. HYP LP-källan består av en RF-driven, linjär hålkatod och en mikrovågsantenn samt är utrustad med ett par starka, roterbara permanentmagneter med dubbel funktion. Dels ska de ge den magnetfältstyrka som är nödvändig för genereringen av ett ECR-plasma och dels ska de fokusera och utjämna plasmat längs med katodplattorna.

Titannitridfilmer deponerade på kisel- och snabbstålssubstrat med hybridplasmakällan (HYP LP) hade kompakt struktur och hög (111) textur vilket leder till hög hårdhet. Nanohårdhetsmätningar visade att filmerna hade hårdheter på upp till 30 GPa. Dessa filmer kunde deponeras vid en betydligt högre hastighet än konventionellt deponerade TiN-filmer.

Denna avhandling visar att substratet kan inverka på deponeringsprocessen och därigenom påverka filmegenskaperna. Detta är något som inte har uppmärksammats tidigare. Vid deponering av TiN filmer på kisel- och stålsubstrat med hybridkällan uppnåddes en avsevärt högre temperatur på kisel än på stål. Orsaken till detta är att mikrovågseffekten absorberas effektivare i kisel än i stål. Vidare har inverkan av ferromagnetiska substrat på deponeringsprocessen i magnetiserade plasmasystem påvisats. Denna inverkan visar sig genom ökat jonbombardemang på sådana substrat jämfört med icke-ferromagnetiska. Effekten uppkommer genom att ferromagnetiska substrat ändrar geometrin hos magnetfältet i deponeringssystemet. Jonbombardemanget ökar temperaturen och påverkar strukturen hos den växande filmen. Denna effekt har även observerats i konventionella magnetronsputtersystem och har därför en mer generell praktisk betydelse. Även inverkan av applicering av en likspänning på substratet har undersökts. Egenskaperna hos TiN-filmerna kan ändras avsevärt på detta sätt och effekten av ferromagnetiska substrat kan kompenseras med hjälp av en sådan spänning.

Med RHCPJ-källan har krom- och kromnitridfilmer deponerats. Vid den reaktiva deponeringen av CrN-filmerna uppnåddes extremt höga deponeringshastigheter och processen hade god stabilitet. Om RHCPJ-källan drivs med hög effekt arbetar den i en ”ljusbågsregim” och högtexturerade CrN-filmer kan deponeras vid så höga hastigheter som 2,5 μm/min och till och med upp till 4 μm/min. Uppförandet av den reaktiva diffusa ljusbågsprocessen och CrN-filmegenskaperna är en indikation på att processen kan överföras från små cylindriska hålkatoder till linjära, magnetiserade hålkatoder vilket tillåter deponering på betydligt större ytor. Detta är en viktig aspekt för industriella tillämpningar.

Både RF-hålkatoder och mikrovågsplasmakällor kan generera kemiskt aktiva plasman för plasmaaktiverad CVD (PA CVD) och detta gör det möjligt att utveckla kombinerade PA CVD och PVD regimer till en gemensam regim för HYP LP-källan. Denna nya regim kan bli ett verktyg för framställning nya nanokristallina material i framtiden.

Acknowledgements

There are number of persons who have been of direct or indirect assistance to me during the work behind this thesis. I feel a great gratitude to them and they all deserve to be acknowledged.

First of all I would like to give my sincere thanks to my supervisors, Ladislav Bárdoš and Hana Baránková, for all aid, support and guidance.

Then I must thank the rest of the Plasma Group, Daniel Söderström, for the proofreading and the discussions on everything and nothing.

I thank Björn Hagman who "lured" me to the Solid State Electronics Division and been a friend since I started my undergraduate education in Uppsala.

Many thanks go to (in no specific order):

- Some people from other divisions and departments for providing reference coatings and help with analyses. Members and former members of the Materials Science Division (Urban W., Daniel N., Nils S., Malin S.) and Ola W. at the Department of Materials Chemistry.
- Balzers Sandvik Coating AB for providing reference coatings.
- Friends, colleagues, and former colleagues at SSE for making Ångström a pleasant place to work.
- The administrative and technical personnel at the Department of Engineering Science for “ground service”. A special thank goes to Marianne who keep SSE running.
- Those nice people who show up in our lunchroom at Friday afternoons for some “afterwork” and keep the tradition alive.

Finally, I send my deepest thanks to my family, who mean a lot to me.

References

[1] H. Conrads and M. Schmidt, “Plasma generation and plasma sources” *Plasma Sources Science and Technology*, vol. 9, 2000, pp. 441-454.

[2] L. Bárdoš, “Radio frequency hollow cathodes for the plasma processing technology” *Surface and Coatings Technology*, vol. 86-87, 1996, pp. 648-656.

[3] J.R. Roth, “*Industrial plasma engineering – Volume 1: Principles*”, USA: IoP Publishing, 1995, pp. 501.

[4] I.G. Brown, “Cathodic arc deposition of films” *Annual Review of Materials Science*, vol. 28, 1998, pp. 243-269.

[5] A. Anders, “Approaches to rid cathodic arc plasmas of macro- and nanoparticles: a review” *Surface and Coatings Technology*, vol. 120-121, 1999, pp. 319-330.

[6] K. Wasa, M. Kitabatake, and H. Adachi. *Thin Film Materials Technology - Sputtering of Compound Materials*. USA: William Andrew Publishing/Noyes, 2004, pp. 100.

[7] S.M. Rossnagel, “Magnetron plasma deposition processes” in *Handbook of plasma processing technology*. USA: Noyes Publications, 1990, pp. 160.

[8] J. Musil, P. Baroch, J. Vlček, K.H. Nam and J.G. Han “Reactive magnetron sputtering of thin films: Present status and trends” *Thin Solid Films*, vol. 475, n. 1-2 SPEC. ISS., Mar 22, 2005, pp. 208-218

[9] D.M. Mattox, “Ion plating” in *Handbook of plasma processing technology*. USA: Noyes Publications, 1990, pp. 338.

[10] J.J. McNally, “Ion assisted deposition” in *Handbook of plasma processing technology*. USA: Noyes Publications, 1990, pp. 466.

[11] J.A. Thornton, “High rate thick film growth” *Annual Review of Materials Science*, vol. 7, 1977, pp. 239-260.

[12] R.F. Bunshah and C.V. Deshpandey, “Hard coatings”, *Vacuum*, vol. 39, 1989, pp. 955-965.

[13] H. Holleck, “Material selection for hard coatings” *Journal of Vacuum Science and Technology A*, vol. 4, 1986, pp. 2661-2669.

[14] B. Jönsson and S. Hogmark, "Hardness measurements of thin films" *Thin Solid Films* vol. 114,1984, pp. 257-269.

[15] W.C. Oliver and G.M.Pharr, "An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments" *Journal of Materials Research*, vol. 7, 1992, pp. 1564-1583.

[16] www.balinit.dk

[17] W.J. Chou, G.P.Yu, and J.H. Huang, "Deposition of TiN thin films on Si(100) by HCD ion plating" *Surface and Coatings Technology*, vol. 140, 2001, pp. 206-214.

[18] Y.M. Chen, G.P. Yu, and J.H. Huang, "Role of process parameters in the texture evolution of TiN films deposited by hollow cathode discharge ion plating", *Surface and Coatings Technology*, vol. 141, 2001, pp. 156-163.

[19] W.J. Chou, G.P. Yu, and J.H. Huang, "Mechanical properties of TiN film coatings on 304 stainless steel substrates" *Surface and Coatings Technology*, vol. 149, 2002, pp. 7-13.

[20] Y.M. Chen, G.P. Yu, and J.H. Huang, "On the porosity of TiN films deposited by HCD ion plating" *Surface and Coatings Technology*, vol. 155, 2002, pp. 239-244.

[21] S. Guruvenket and G. Mohan Rao, "Effect of ion bombardment and substrate orientation on structure and properties of titanium nitride films deposited by unbalanced magnetron sputtering" *Journal of Vacuum Science and Technology A*, vol. 20, 2002, pp. 678-682.

[22] L.J. Meng and M.P. dos Santos, "Characterization of titanium nitride films prepared by d.c. reactive magnetron sputtering at different nitrogen pressures" *Surface and Coatings Technology*, vol. 90, 1996, pp. 64-70.

[23] P.J. Martin, A. Bendavid, and T.J. Kinder, "The deposition of TiN thin films by filtered cathodic arc techniques" *IEEE Transactions on Plasma Science*, vol. 25, 1997, pp. 675-679.

[24] J.P. Zhao, X. Wang, Z.Y. Chen, S.Q. Yang, T.S. Shi, and X.H. Liu, "Overall energy model for preferred growth of TiN films during filtered arc deposition" *Journal of Physics D: Applied Physics*, vol. 30, 1997, pp. 5-12.

[25] J. Musil, V. Poulek, V. Valvoda, R. Kuzel, Jr., H.A. Jehn, and M.E. Baumgaertner, "Relation of deposition conditions of Ti-N films prepared by d.c. magnetron sputtering to their microstructure and macrostress" *Surface and Coatings Technology*, vol. 60, 1993, pp. 484-488.

[26] B. Navinšek, P. Panjan, and I. Milošev, "PVD coatings as an environmentally clean alternative to electroplating and electroless processes", *Surface and Coatings Technology*, vol. 116-119, 1999, pp. 476-487.

[27] M.L. Kuruppu, G. Negrea, P. Ivanov, and S.L. Rohde, “Monolithic and multilayer Cr/CrN, Cr/Cr_2N, and Cr_2N/CrN coatings on hard and soft substrates” *Journal of Vacuum Science and Technology A*, vol. 16, 1998, pp. 1949-1955.

[28] Y.C. Feng, D.E. Laughlin, and D.N. Lambeth, “Formation of crystallographic texture in rf sputter-deposited Cr thin films” *Journal of Applied Physics*, vol. 76, 1994, pp. 7311-7316.

[29] R. Balu, A.R. Raju, V. Lakshminarayanan, and S. Mohan, “Investigations on the influence of process parameters on the structural evolution of ion beam sputter deposited chromium thin films” *Material Science and Engineering B*, vol. 123, 2005, pp. 7-12.

[30] B. Navinšek, P. Panjan, and I. Milošev, “Industrial applications of CrN (PVD) coatings, deposited at high and low temperatures” *Surface and Coatings Technology*, vol. 97, 1997, pp. 182-191.

[31] E.J. Bienk, H. Reitz, and N.J. Mikkelsen, “Wear and friction of hard PVD coatings” *Surface and Coatings Technology*, vol. 76-77, 1995, pp. 475-480.

[32] S. Han, J.H. Lin, G.H. Wang, and H.C. Shih, “The effect of preferred orientation on the mechanical properties of chromium nitride coatings deposited on SKD11 by unbalanced magnetron sputtering” *Materials Letters*, vol. 57, 2003, pp. 1202-1209.

[33] K.H. Nam, M.J. Jung, and J.G. Han, “A study on the high rate deposition of CrN_x films with controlled microstructure by magnetron sputtering” *Surface and Coatings Technology*, vol. 131, 2000, pp. 222-227.

[34] K.H. Nam, Y.M. Jung, and J.G. Han, “A comparative study of microstructure and mechanical properties for CrN_x films with various deposition rates by magnetron sputtering” *Surface and Coatings Technology*, vol. 142-144, 2001, pp. 1012-1016.

[35] C. Nouveau, M.A. Djouadi, C. Deces-Petit, P. Beer, and M. Lambertin, “Influence of CR_xN_y coatings deposited by magnetron sputtering on tool service life in wood processing” *Surface and Coatings Technology*, vol. 142-144, 2001, pp. 94-101.

[36] Z. Han, J. Tian, Q. Lai, X. Yu, and G. Li, “Effect of N_2 partial pressure on the microstructure and mechanical properties of magnetron sputtered CrN_x films” *Surface and Coatings Technology*, vol. 162, 2003, pp. 189-193.

[37] M. Odén, C. Ericsson, G. Håkansson, and H. Ljungcrantz, “Microstructure and mechanical behaviour of arc-evaporated Cr-N coatings” *Surface and Coatings Technology*, vol. 114, 1999, pp. 39-51.

[38] A. Kondo, T. Oogami, K. Sato, and Y. Tanaka, “Structure and properties of cathodic arc ion plated CrN coatings for copper machining cutting tools” *Surface and Coatings Technology*, vol. 177-178, 2004, pp. 238-244.

[39] H. Baránková and L. Bárdoš, "Effect of gas and cathode material on the r.f. hollow cathode reactive PVD" *Surface and Coatings Technology*, vol. 120-121, 1999, pp. 704-708.

[40] L. Bárdoš and S. Berg, "Low pressure r.f. plasma jet – a new tool for surface processing" *Surface and Coatings Technology*, vol. 54-55, 1992, pp. 91-95.

[41] H. Baránková and L. Bárdoš, "New Magnets-in-Motion (M-M) Plasma Sources" in *Proceedings of the 42nd Annual Technical Conference of the Society of Vacuum Coaters*, 1999, pp. 136-137.

Acta Universitatis Upsaliensis

Digital Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology 194

Editor: The Dean of the Faculty of Science and Technology

A doctoral dissertation from the Faculty of Science and Technology, Uppsala University, is usually a summary of a number of papers. A few copies of the complete dissertation are kept at major Swedish research libraries, while the summary alone is distributed internationally through the series Digital Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology. (Prior to January, 2005, the series was published under the title "Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology".)

ACTA
UNIVERSITATIS
UPSALIENSIS
UPPSALA
2006

Distribution: publications.uu.se
urn:nbn:se:uu:diva-6925