Plasma Enhanced Chemical- and Physical- Vapor Depositions Using Hollow Cathodes

KASPARS SILINŠ
Abstract

Development of coating deposition technologies, in terms of performance and costs, is an ongoing process. A promising class of deposition technologies are based on hollow cathode discharges.

This thesis investigates performance of selected hollow cathode plasma sources developed at the Plasma group, at Uppsala University for coating deposition at moderate pressures. Amorphous carbon film deposition was investigated by Radio frequency (RF) Hollow Cathode Plasma Jet (RHCPJ) and Magnets-in-Motion (M-M) linear hollow cathode plasma sources. Titanium nitride (TiN) films were deposited by a magnetized Hollow Cathode Enhanced magnetron Target (HoCET). Aluminium nitride (AlN) deposition by RHCPJ was compared with High Power Impulse Magnetron Sputtering (HiPIMS).

Amorphous carbon films were prepared on glass substrates without an interlayer. The AlN and TiN films were deposited on Si substrates. Optical emission spectroscopy was used to analyze plasma composition. The coating structure was analyzed by X-ray diffraction and Raman spectroscopy. The thickness of films was measured by scanning electron microscopy and profilometry. The TiN hardness was analyzed by microhardness test method and confirmed by nanoindentation analysis.

Adherent amorphous carbon coating deposition process was transferred from RHCPJ to the M-M linear hollow cathode. Utilizing the latter plasma source, it was found that thick and adherent amorphous carbon coatings can be deposited in a range of 0.25% to 0.5% of C\textsubscript{2}H\textsubscript{2} in Ar at constant a deposition pressure of 0.3 Torr and 1200 W of RF power. Deposition rates of 0.2 μm/min and 0.375 μm/min respectively were reached. Self-delaminating, thick (50 μm) amorphous carbon films can be deposited at a deposition rate of 2.5 μm/min at 2% C\textsubscript{2}H\textsubscript{2}. A non-linear relation was observed between the deposition rate and the C\textsubscript{2}H\textsubscript{2} content.

Utilizing the HoCET arrangement, high deposition rates of stoichiometric, polycrystalline TiN films are obtained. A maximum of 0.125 μm/min is obtained at 2.4% N\textsubscript{2} in Ar, 1200 W RF power, 14 mTorr deposition pressure. TiN films deposited at 4 - 20% nitrogen contents displayed hardness values above 28 GPa reaching a maximum of 31.4 GPa at 5% N\textsubscript{2}.

For a (002) oriented AlN film deposition the RHCPJ offers deposition rates of up to 150 nm/min. Using the HiPIMS at comparable deposition conditions the AlN films were achieved at a rate of 24 nm/min.

Keywords: Hollow cathode, TiN, AlN, amorphous carbon, hybrid PVD/PE-CVD, ionized magnetron

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The more you know,
the more you know you don’t know.

Inspired by Aristotle
List of papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.


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Nomenclature

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<thead>
<tr>
<th>Symbol</th>
<th>Unit</th>
<th>Description</th>
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<tbody>
<tr>
<td>$\omega$</td>
<td>cm$^{-1}$</td>
<td>Raman shift value</td>
</tr>
<tr>
<td>$\omega_0$</td>
<td>cm$^{-1}$</td>
<td>position of the peak intensity maximum</td>
</tr>
<tr>
<td>$\omega_G$</td>
<td>cm$^{-1}$</td>
<td>position of the G peak</td>
</tr>
<tr>
<td>$I_\omega$</td>
<td>counts</td>
<td>intensity at the Raman shift value</td>
</tr>
<tr>
<td>$I_D$</td>
<td>counts</td>
<td>intensity of the D peak</td>
</tr>
<tr>
<td>$I_G$</td>
<td>counts</td>
<td>intensity of the G peak</td>
</tr>
<tr>
<td>$Q$</td>
<td>–</td>
<td>Fano factor</td>
</tr>
<tr>
<td>$FWHM_G$</td>
<td>cm$^{-1}$</td>
<td>full width at half maximum of the G peak</td>
</tr>
<tr>
<td>$FWHM_D$</td>
<td>cm$^{-1}$</td>
<td>full width at half maximum of the D peak</td>
</tr>
<tr>
<td>$H_{film}$</td>
<td>kgf/mm$^2$</td>
<td>coating hardness</td>
</tr>
<tr>
<td>$H_S$</td>
<td>kgf/mm$^2$</td>
<td>substrate hardness</td>
</tr>
<tr>
<td>$H_C$</td>
<td>kgf/mm$^2$</td>
<td>composite hardness</td>
</tr>
<tr>
<td>$t$</td>
<td>µm</td>
<td>thickness of the coating</td>
</tr>
<tr>
<td>$d$</td>
<td>µm</td>
<td>average length of indent diagonals</td>
</tr>
<tr>
<td>$H_\alpha$</td>
<td>counts</td>
<td>Optical emission intensity of H$\alpha$ line</td>
</tr>
<tr>
<td>$H_\beta$</td>
<td>counts</td>
<td>Optical emission intensity of H$\beta$ line</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>nm</td>
<td>X-ray wavelength of Cu K$\alpha$ radiation</td>
</tr>
<tr>
<td>$\theta$</td>
<td>degrees</td>
<td>X-ray scattering angle</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>AC</td>
<td>Alternating Current</td>
<td></td>
</tr>
<tr>
<td>airPLS</td>
<td>adaptive iteratively reweighted Penalized Least Squares</td>
<td></td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical Vapor Deposition</td>
<td></td>
</tr>
<tr>
<td>DC</td>
<td>Direct Current</td>
<td></td>
</tr>
<tr>
<td>DLC</td>
<td>Diamond-Like Carbon</td>
<td></td>
</tr>
<tr>
<td>ECR</td>
<td>Electron Cyclotron Resonance</td>
<td></td>
</tr>
<tr>
<td>ECWR</td>
<td>Electron Cyclotron Wave Resonance</td>
<td></td>
</tr>
<tr>
<td>EELS</td>
<td>Electron Energy Loss Spectroscopy</td>
<td></td>
</tr>
<tr>
<td>FCVA</td>
<td>Filtered Cathode Vacuum Arc</td>
<td></td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width at Half Maximum</td>
<td></td>
</tr>
<tr>
<td>GIXRD</td>
<td>Grazing Incidence X-ray Diffraction</td>
<td></td>
</tr>
<tr>
<td>HCA</td>
<td>Hollow Cathode Arc</td>
<td></td>
</tr>
<tr>
<td>HCD</td>
<td>Hollow Cathode Discharge</td>
<td></td>
</tr>
<tr>
<td>HCM</td>
<td>Hollow Cathode Activated magnetron</td>
<td></td>
</tr>
<tr>
<td>HiPIMS</td>
<td>High Power Impulse Magnetron Sputtering</td>
<td></td>
</tr>
<tr>
<td>HoCET</td>
<td>Hollow Cathode Enhanced Target</td>
<td></td>
</tr>
<tr>
<td>HPPMS</td>
<td>High Power Pulsed Magnetron Sputtering</td>
<td></td>
</tr>
<tr>
<td>HYP LP</td>
<td>Low Pressure Hybrid Plasma</td>
<td></td>
</tr>
<tr>
<td>ICP</td>
<td>Inductively Coupled Plasma</td>
<td></td>
</tr>
<tr>
<td>IGBT</td>
<td>Insulated-Gate Bipolar Transistor</td>
<td></td>
</tr>
<tr>
<td>IPVD</td>
<td>Ionized Physical Vapor Deposition</td>
<td></td>
</tr>
<tr>
<td>LAD</td>
<td>Linear Arc Discharge</td>
<td></td>
</tr>
<tr>
<td>LC</td>
<td>Critical Load</td>
<td></td>
</tr>
<tr>
<td>M-M</td>
<td>Magnets-in-Motion</td>
<td></td>
</tr>
<tr>
<td>MOS</td>
<td>Metal-Oxide-Semiconductor</td>
<td></td>
</tr>
<tr>
<td>MPP</td>
<td>Modulated Pulse Power</td>
<td></td>
</tr>
<tr>
<td>MSIB</td>
<td>Mass Selective Ion Beam</td>
<td></td>
</tr>
<tr>
<td>MW</td>
<td>Microwave</td>
<td></td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
<td></td>
</tr>
<tr>
<td>OES</td>
<td>Optical Emission Spectroscopy</td>
<td></td>
</tr>
<tr>
<td>PBS</td>
<td>Plasma Beam Deposition</td>
<td></td>
</tr>
<tr>
<td>PE-CVD</td>
<td>Plasma Enhanced Chemical Vapor Deposition</td>
<td></td>
</tr>
<tr>
<td>PET</td>
<td>Polyethylene Terephthalate</td>
<td></td>
</tr>
<tr>
<td>PLD</td>
<td>Pulsed Laser Deposition</td>
<td></td>
</tr>
<tr>
<td>PVD</td>
<td>Physical Vapor Deposition</td>
<td></td>
</tr>
<tr>
<td>RF</td>
<td>Radio Frequency</td>
<td></td>
</tr>
<tr>
<td>RHCPJ</td>
<td>Radio Frequency Hollow Cathode Plasma Jet</td>
<td></td>
</tr>
<tr>
<td>RPJ</td>
<td>Radio Frequency Plasma Jet</td>
<td></td>
</tr>
<tr>
<td>SAW</td>
<td>Surface Wave Acoustic</td>
<td></td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
<td></td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
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Over the years, with the development of coating deposition technologies, many areas of our lives have become more easy, comfortable and efficient. Despite the development of such technologies, improvements in the deposition processes, in terms of performance and costs, remain ongoing. One promising, though unconventional, class of deposition technologies is based on hollow cathode discharges.

The goal of the thesis is to analyze the performance of novel Hollow Cathode plasma sources developed at the Plasma group, at Uppsala University, for thin film deposition at moderate pressures. The performance is evaluated by the achieved deposition rate and quality of deposited amorphous carbon, titanium nitride (TiN) and aluminium nitride (AlN) coatings at various deposition conditions. The aim is to deposit adherent, high quality films at high deposition rates. The parameters used to control the deposition process were deposition pressure, supplied power and concentration of reactive gas in the deposition chamber. The depositions were performed in a reactive physical vapor and a hybrid physical vapor/plasma-enhanced chemical vapor deposition modes. The capability of hollow cathodes to deposit AlN films in comparison to high power impulse magnetron sputtering (another emerging approach) is addressed and discussed in more detail.

In this thesis, the principles of the deposition processes are first reviewed, followed by a brief overview of the deposited films: amorphous carbon, TiN and AlN. The experimental section provides a description of the employed deposition systems and analysis methods of the deposition processes and coatings. The research results are subsequently presented and discussed, and the conclusions drawn.

1.1 Deposition methods

The two types of processes that are used to form thin film coatings are Chemical Vapor deposition (CVD) and Physical Vapor Deposition (PVD). Both are vapor deposition processes where coatings are formed by atoms and molecules. In CVD the solid coatings are formed by chemical reactions of activated precursor gases (chemical compounds) while in the PVD process they are formed by condensation of evaporated/sputtered species of solid (or liquid) material. In the conventional CVD processes the activation of precursor gases is facilitated by a thermal energy supply. The process temperatures often reach,
or exceed, 600 °C, posing limitations on the deposition on temperature sensitive substrates [1]. One successful approach to offsetting this problem has been to replace thermal activation by plasma activation.

1.1.1 Plasma enhanced chemical vapor deposition (PE-CVD)

Plasma enhanced chemical vapor deposition (PE-CVD) (also can be termed PA-CVD where "PA" stands for plasma assisted or plasma activated) is a coating deposition method where the precursor species are activated and partially decomposed by non-thermal plasma. The non-thermal (or non-equilibrium) plasma is defined by a condition where ions have a considerably lower energy than electrons and the rest of neutral gas has a low enough temperature not to melt or damage substrates (usually <1000 °C). To generate the low temperature plasma, energy needs to be delivered selectively to the electrons of the process gases. The means of doing so is by generating a pulsed DC or an AC electric field within the deposition chamber. To generate the alternating electric field either radio frequency (RF) (most often 13.56 MHz) or microwave frequency (MW) (most often 2.45 GHz) power supplies are used. The use of either one changes the design of the deposition chambers. Typical setups of both RF and MW powered PE-CVD systems are shown in Figure 1.1.

Figure 1.1. PECVD: a) Radio Frequency PE-CVD, b) Microwave Frequency PE-CVD. Reprinted from [1] with permission from Elsevier.

In both setups the process gases (precursor and carrier) are introduced into the deposition chamber from above. In the RF PE-CVD the activation and decomposition of the gases takes place between the electrode and substrate. There the activated gaseous species take part in vapor phase chemical reactions near or on the substrate to form the coatings. The substrate temperature can
be controlled with heaters or coolers – depends on the material and desired properties. In the MW PE-CVD systems the process takes place around the substrate. The energy is delivered through a waveguide while in the RF PE-CVD systems the energy is delivered through electrodes. In this thesis a RF PE-CVD type of process was employed for thin film deposition.

It is common to place an auxiliary electrode on the back side of the substrate table to provide an additional bias voltage. This is done to increase the kinetic energy of generated ions and radicals and their flux arriving onto the substrate where the film is formed.

The main parameters used to control the deposition process are RF power, process gas composition and pressure, the substrate bias voltage and temperature. All these parameters influence the processes within the plasma volume and on the surface of the substrate. An important parameter to strive for is high plasma density \(10^{10} \text{ to } 10^{13} \text{ particles/cm}^3\) as it brings about high deposition rates. PE-CVD methods include Electron cyclotron resonance (ECR), Electron cyclotron wave resonance (ECWR), Inductively coupled plasma (ICP) and plasma beam source (PBS) deposition.

In PE-CVD deposition systems there are two major sources of impurities which can be found in the deposited coatings. The primary one is linked with purity of the process gases, the secondary one is sputtering of the electrode material and deposition chamber walls. The latter occurs due to the PVD processes.

1.1.2 Physical vapor deposition

Physical vapor deposition (PVD) is a coating deposition method where material is "evaporated" from a solid target or a liquid source. If not by heat, the evaporation can be facilitated by ion bombardment (arc evaporation), high-energy electron bombardment or high-energy photon bombardment (pulsed laser deposition (PLD)). The prevailing method of choice in industry is PVD sputtering. A component of the PVD sputtering process was employed in this thesis work. Sputtering is ejection of atoms from a target surface by bombardment of energetic particles, mostly ions that are generated by plasma [2] (see the example on the left-hand side of Figure 1.2). In e.g. ion beam deposition, the atoms are ejected by exposing the target surface to a beam of high energy ions.

The produced species (mainly atoms) are transported to the substrate where they condense. The substrate is located in a line of sight of the target material. On the right hand side of Figure 1.2 a closed-field magnetron sputtering is displayed. It entails placing a magnet arrangement behind the target to trap the electrons at the surface of the target. The free electrons are trapped by the magnetic field lines increasing their path length in the discharge. The longer the path length, the higher the probability to ionise the gas atoms is. This
method can also be termed balanced magnetron sputtering. There are also unbalanced magnetrons. There the magnetic field lines are open allowing the hot electrons to be directed away from the target towards the substrate. This approach increases the incident ion/atom ratio at the substrate which improves the overall film properties [3]. It is common to utilise planar targets of either rectangular or circular shapes.

For PVD plasma generation similar principles to the PE-CVD are used. The target acts as a cathode which is connected to an RF or a DC power source. While in the PE-CVD chemical compound gases are used as process gases, in the case of PVD the chemically inert noble gases are used, with the most common being Ar, He and Ne. A single element or compound materials can be used as the target. An alternative to compound deposition from multi-element targets is reactive PVD. It is a technique where a reactive gas (oxygen, nitrogen, hydrocarbon, sulphide, etc.) is introduced together with the carrier noble gas. The reactive gas is activated in the plasma volume and reacts, chemically, with the sputtered species to form the compound on the substrate. A drawback is "target poisoning". Due to chemisorption and ion implantation processes a compound layer can form on the target as well. This is usually accompanied by hysteresis in discharge voltage and partial pressure of the reactive gas. The most apparent drawback of target poisoning is a drop in deposition rate of the desired coating.

In PVD sputtering systems the deposition rate can be increased by increasing the plasma density between the target and substrate. When the plasma density is increased the sputtered vapor contains significantly more ions than the neutral species (atoms and molecules) [4]. Additionally, having high ionisation at the substrate allows better control over the coating properties. This deposition is termed Ionized PVD (IPVD).
1.1.3 Ionized PVD and High power impulse magnetron sputtering (HiPIMS)

Conventional ionized physical vapor deposition (IPVD) systems are based on magnetron sputtering systems where a secondary discharge is generated. The sole purpose of the secondary discharge is ionization of the sputtered vapor heading towards the target. This approach was first demonstrated by Steve Rossnagel and Jeff Hopwood from IBM in 1993 [5], where an RF controlled inductively coupled plasma discharge was used to ionize the sputtered vapor. A water-cooled, two-turn inductive coil was placed in between the magnetron discharge and the substrate. Another approach has been demonstrated by Xu et al. where a microwave (MW) electron cyclotron resonance (ECR) magnetron sputtering apparatus was used [6]. There the volume between the target and substrate was ionized by twinned MW-ECR plasma source.

Another approach is to employ high power pulsed magnetron sputtering (HPPMS) techniques. A major advantage of HPPMS to other IPVD techniques is that it is compatible with the conventional magnetron sputtering equipment. The only requirement is to change the power supply. The deposition chamber requires no changes. In HPPMS a high power, pulsed DC voltage at a low frequency and low duty cycle is used to generate the discharge. Depending on the peak power density at the target and the duty cycle of the high power pulse, modulated pulse power (MPP) and high power impulse magnetron sputtering (HiPIMS) can be distinguished. For the MPP the peak power density is in between 0.05 kW/cm² and 0.5 kW/cm². In HiPIMS the cathode peak power density is higher – from 0.5 kW/cm² to 10 kW/cm². The HiPIMS duty cycle is in the range of 0.5% to 5%, the frequency is set in between 50 to 5000 Hz, the pulse width typically is 50 – 500 μs, voltage is in the range of 500 to 2000 V and the current densities can reach up to 3 – 4 A/cm² [7, 8].

The HiPIMS power sources can be used to power the so-called "Hollow Cathode Magnetrons" [9]. These magnetrons use negative targets – cathodes having shape of a hollow cylinder. An example of a well-known producer of such magnetrons is the American company ISOFLUX. In Hollow Cathode Magnetrons the magnetic field has a component parallel with the surface of cylindrical target to enhance the confinement of ions close to the target surface and to enhance sputtering. It is one of the major differences that separates the Hollow Cathode Magnetrons from the conventional Hollow Cathodes. The Hollow Cathodes are based on the "hollow cathode effect" – oscillating electrons (pendulum motion) between opposite walls inside the cathode (see more in the next section). Such motions are either reduced or impossible in the magnetic field used in the Hollow Cathode Magnetrons. The Hollow Cathodes can be used as an auxiliary tool to enhance the ionization in magnetron systems.

Hollow Cathode activated Magnetron (HCM) is another type of IPVD deposition systems. The HCM system has been developed and first patented by Cuomo et al. in 1986 [10]. There a Hollow Cathode served as a secondary
source of electrons to increase the ionization in the magnetron plasma. The following section focuses more on the hollow cathode effect and discharge.

1.2 Hollow cathode plasma sources

The Hollow Cathode is, in essence, an electrode that consists of two walls at the same potential. It can be in the form of a cylinder, a spiral wire or two parallel plates [11]. The Hollow Cathode discharge is based on the hollow cathode effect. It is observed when an avalanche multiplication of electrons and ions occur [12]. This is closely related to the pendulum motion of electrons in between the cathode walls whose negative glow regions coalesce. The pendulum motion is ensured by repelling potentials of space charge sheaths. A simple representation of the sheaths (in white) is given in Figure 1.3.

![Figure 1.3. Representation of hollow cathode sheath region (in white).](image)

It can be seen that the positive ions are attracted towards the cathode walls while the electrons are returned back to the centre of the hollow cathode. The average electric potential of the sheath decreases with distance away from the cathode wall [13, 14]. In the discharge the centre of Hollow Cathode acts as a virtual anode. Reflected high energy electrons pass through the coalescing negative glow plasma region. On the other side the electrons are reflected back by the increasing negative potential of the opposite cathode sheath. Due to the elongated pathway electrons travel, the ionisation probability of process gases is increased.

The main benefit of the hollow cathode discharge is high plasma density, which is 1 to 2 orders of magnitude higher than conventional planar electrode systems. The ionization of process gases occurs inside the hollow cathode. The species for deposition are carried through the outlet of the hollow cathode as the process gases pass through.

The hollow cathode systems can operate in the PE-CVD [15, 16], PVD or in a hybrid PVD/PE-CVD modes. In the PVD mode, the cathode walls serve as a target material which is sputtered by the positive ions of process gases. The substrate is located underneath the hollow cathode outlet at a certain distance.
Most of the gas phase reactions occur in between the hollow cathode outlet and the substrate.

In the hybrid deposition process the film forming particles (atoms, molecules, ions) are extracted from both, the cathode walls (ion bombardment, PVD process) and from plasma activation of the precursor gas (PE-CVD process). In the thesis hollow cathode discharge based thin film deposition systems operated in PVD and the hybrid PE-CVD/PVD modes have been used (see Chapter 2.1). The hollow cathode systems can be operated in the hollow cathode discharge as well as in hollow cathode arc regimes (HCA). Hollow cathode arc regime are characterised by high cathode wall temperature at the outlet, low discharge voltage, high current and a predominant thermionic emission form cathode wall [17]. In the HCA regime instead of sputtering the dominant particle generation mechanism is evaporation. The HCA deposition is outside of scope of this thesis.

In the Plasma group at Uppsala University many designs of hollow cathode plasma systems have been developed. A good overview of moderate pressure (mTorr, Torr range) and atmospheric pressure plasma processing systems can be found in [18]. Out of the described systems two hollow cathode plasma sources for thin film deposition at moderate pressures have been introduced. In this thesis work, the RF hollow cathode plasma jet (RHCPJ) (for a more detailed description refer to Chapter 2.1.1) and Magnets in motion (M-M) RF linear hollow cathode source (see Chapter 2.1.2) have been successfully used to deposit films at high deposition rates. A recently developed magnetized Hollow Cathode Enhanced Target (HoCET) arrangement previously has been used to deposit Ti films [19]. For the thesis work the system was used to deposit TiN films (see Chapter 2.1.3).

1.3 Characterisation of deposited films

The hollow cathode system performance in depositing amorphous carbon, Ti and TiN has been analysed in the thesis. A brief comparison of potential to deposit AlN films in with HiPIMS has been done. This section provides a description of the coating materials.

1.3.1 Amorphous carbon

Amorphous carbon films, polycrystalline films and diamond films are commonly used as tribological coatings in car engines [20], on sunglasses, bar code scanners and windows [21, 22] and razor blades [23]. In these applications the coating is used to reduce wear and friction in between moving surfaces. This considerably prolongs lifetime of the products. The coatings are also used in hard drives for data protection. The magnetic storage disks and their read heads are coated with ultrathin amorphous carbon films as a smooth
and chemically inert protection layer [24]. The amorphous carbon films can improve the lifetime of biological implants as well. Lots of attention is dedicated to biocompatibility and hemocompatibility studies of amorphous carbon films [25, 26]. The most common biological implants are for joints (e.g. hip joint) and cardiovascular system (stents). Other uses of the carbon coatings include microelectromechanical systems, field emission guns, and semiconductors [27, 28]. The amorphous carbon coatings have low gas permeability. That can be used to prevent decarbonisation of fizzy beverages by coating the inner surface of PET bottles as a gas membrane barrier [29, 30].

The atomic structure of carbon coatings is often closer to diamond than graphite. This results in properties similar to diamond – high hardness, low friction, high thermal conductivity and high band gap. Diamonds are fully crystalline (long range periodicity), while amorphous carbon films are amorphous (disordered structure with no periodicity). The bonding is a combination of $sp^2$ and $sp^3$ hybridised bonds. Figure 1.4 illustrates the different hybridisation states of simulated amorphous carbon structures [31].

![Figure 1.4. Atomic structures of amorphous carbons. a) 52% of $sp^3$ (red) and 48% of $sp^2$ (blue) bonded atoms, b) 81% of $sp^3$, c) 95% of $sp^3$. [31]](image)

In order to attain the properties of diamond, a high $sp^3$ fraction in the deposited amorphous carbon films is aimed for. To understand the physical meaning of the $sp^2$ and $sp^3$ hybridisation it helps to address the basic chemistry principles. There are two types of covalent bonds that can be formed – the stronger $\sigma$ and weaker $\pi$ bonds. A stronger bond means that more energy is required to break it, additionally the electrons forming the bond are less mobile than in $\pi$ bonds. If a single bond is formed, it is a $\sigma$ bond. If a double or triple bond is formed, then one is $\sigma$, and the rest are $\pi$ bonds. As the carbon has 4 valence electrons it can form up to four bonds in total. For example in an acetylene ($C_2H_2$) molecule, each carbon atom forms one $\sigma$ bond with hydrogen and a triple bond (one $\sigma$ and two $\pi$ bonds) with the other carbon atom. In methane and diamond the carbon atoms form four $\sigma$ bonds, in graphite the carbon atoms form three $\sigma$ and one $\pi$ bond. The $\pi$ bonds are responsible for high electric conductivity and $\sigma$ bonds – for thermal conductivity and strength of the material.
In the case of methane and diamond the bonding is denoted as $sp^3$ hybridised (all four of the bonds are $\sigma$ bonds). Pure diamond crystals are formed of 100% $sp^3$ hybrid bonded carbon atoms. When one of the formed four bonds is a $\pi$ bond, then the bonding is denoted as being $sp^2$ hybridised. Pure graphite crystals are formed of 100% $sp^2$ hybrid bonded C atoms. In the case of acetylene or any other case when carbon atoms form a triple bond, it is denoted as $sp^1$ hybridisation.

Hybridised orbital ($sp$) has a characteristic shape of both the spherical "s", and the "8" shaped "p" orbital. In the "p" orbital the nucleus is located at the intersection of the both loops. The electron configuration in carbon is the following $1s^22s^22p^2$. The first energy level is always occupied by a maximum of one electron pair with the distribution function of a sphere ($1s^2$). For e.g. carbon they do not participate in the bonding processes. The 2nd energy level can accommodate up to 8 electrons as it is in the case of Neon ($1s^22s^22p^6$) – one electron pair in the spherical 2s orbital ($2s^2$) and 3 electron pairs at the respective $2p_{x,y,z}$ orbitals. For carbon there are 4 electrons in the 2nd energy level – the outer shell. The outer shell electrons participate in the bonding processes. An electron pair has a spherical orbital and 2 electrons are confined to 90° mutually oriented "8" shaped orbitals. To form more than 2 bonds, the carbon atoms need to use electrons in the 2s orbital. In order to do that the orbitals adjust their shape to the hybridised $sp$ orbital transforming the electron distribution function.

The $sp^3$ bonds can be formed through different mechanisms from which the most accepted one is ion subplantation. It depends on the incoming ion energies where the optimum has been estimated to be around 100 eV [32]. This can be achieved with most of the available deposition methods.

Various measurement techniques can be used to estimate the $sp^3$ and $sp^2$ content. The common ones are Nuclear Magnetic Resonance (NMR), Electron Energy Loss Spectroscopy (EELS), Raman and Infrared spectroscopy. In this thesis Raman spectroscopy was used to estimate the atomic structure of the deposited coatings.

Deposition of amorphous carbon films was first reported by Aisenberg and Chabot in 1971 using ion beam deposition [33]. Since then, various physical vapor deposition (PVD) and plasma enhanced chemical vapor deposition (PE-CVD) methods have been used. Among the different PVD techniques magnetron sputtering, filtered cathode vacuum arc (FCVA), mass selective ion beam (MSIB) and pulsed laser deposition (PLD) are well known [34].

Hollow cathode use for amorphous carbon deposition has been previously reported [35–37]. In this thesis RHCPJ (Section 2.1.1; Paper I) and M-M linear hollow cathode (Section 2.1.2; Paper II) was used to deposit amorphous carbon coatings. The first results of diamond and glassy carbon film deposition by RHCPJ system has been presented in [38] and [39]. The films were deposited on a heated silicon substrate ($800 – 900 \, ^\circ C$). High deposition rates (higher than 16.6 $\mu m/min$) at depositing glassy carbon films were achieved.
at a 4 Torr deposition pressure and CH$_4$-to-H$_2$ gas ratio of 0.1. In this thesis work, deposition was performed without substrate heating.

1.3.2 Titanium nitride (TiN)

Titanium nitride films are commonly used as a diffusion barrier, on tools and decorative coatings [2]. TiN films have a metallic gold colour making it appealing for various decorative purposes (e.g. watches and jewellery). Due to titanium nitrides high hardness and high corrosion resistance it is a common coating on tool steels and alloys. Not only TiN serves as an alternative to hard amorphous carbon coatings due to high wear resistance, but also displays good biocompatibility properties [40]. Diamond-like carbon (DLC) and TiN are used to coat orthopaedic and dental implants, where high wear resistance is important. Due to low electrical resistivity, TiN can be used as gate metal in some metal-oxide-semiconductor (MOS) structures [41].

TiN coatings exhibit cubic face-centred crystalline structure that up to a certain degree holds at both under- and overstoichiometric phases. The Ti$_2$N has a hexagonal crystalline structure. X-ray diffraction (XRD) (see Section 2.3.2.2) is a very common technique to analyse the crystalline structure of crystalline solids. There the presence and orientation of crystallites is detected as peaks to which miller indices are assigned. For cubic TiN films the dominant XRD peaks are (111), (200) and (220) which lie in the range from $35^\circ$ to $65^\circ$ 2$\theta$. During the deposition process the thermodynamically preferred crystal growth mode is with the (200) crystalline plane being parallel to the coating surface. The (220) preferential growth can arise from lattice damage during the film growth by ions [42]. This occurs at high substrate bias settings. The (111) orientation is characteristic for when the growing TiN film surface is bombarded by energetic particles. This causes an increase in the film strain, which through total energy minimization mechanism, brings about (111) texturing. Although previously it has been reported [43] that high hardness values can be correlated to the (111) preferential growth mode (texturing) other research has shown [44, 45] that it is not really true. Hardness of the films more strongly relates to the grain size and grain boundary sliding and rotation mechanisms. The thicker the film is, the more dominant the grain sliding and rotation effects become decreasing the effect of texture. The hardness of industrial-grade TiN films can be in the range from 24 GPa up to 29 GPa [46, 47].

For the TiN deposition both PVD and CVD methods are very common. A major drawback with the CVD method is high toxicity and temperature of the process. For CVD TiN deposition a common precursor is TiCl$_4$ [48]. As the source of nitrogen either ammonia (NH$_3$) or nitrogen together hydrogen gases are used. The residual is the HCl which upon contact with moisture rapidly forms hydrochloric acid, which is extremely dangerous to humans. The CVD temperatures can reach high temperatures, which are above the tempe-
ring temperatures of tool steels. The result is softening of the substrate material during the deposition. The low temperature PVD sputtering techniques are more common. This can be avoided by using PE-CVD approach or similar, but it does not eliminate the toxicity factor that brings about extra costs on the additional safety expenses.

PVD deposition of TiN films is more cost efficient due to lower deposition temperatures considerably lower toxicity level. It has been demonstrated that reactive PVD of TiN films yields higher deposition rates and better control over the deposited film properties [49]. Thus the conventional approach is reactive magnetron sputtering of a pure Ti target in the presence of N₂ and an inert carrier gas. The deposition rate often can be controlled with deposition power and process gas partial pressures and flow rates. TiN can be deposited by other deposition systems as well e.g. filtered cathode arc and reactive hollow cathode discharge ion-plating.

In the Plasma group, at Uppsala University TiN (and Ti) films have previously been deposited by various hollow cathode based deposition systems. In the early 90’s, the first results on TiN deposition were reported [38, 50]. For the deposition a developed radio frequency plasma jet (RPJ) system was used to coat inner walls of tubes made of glass and metal. The hardness values of TiN reached about 19.6 GPa. The deposition rate of up to 50 nm/min was observed. The system could be operated at both, the Hollow Cathode Discharge (HCD) and Hollow Cathode Arc (HCA) modes. Further developments in the mid-90’s [51, 52] allowed TiN deposition at as high as 1 μm/min deposition rates at the HCA mode. In the late 90’s the system was renamed to radio frequency hollow cathode plasma jet (RHCPJ) and scaled up for large area processing [53]. In the newly developed Linear arc discharge system (LAD) it was possible to reach TiN deposition rates of 160 nm/min. In 2001 a new plasma source based on linear hollow cathode system was developed [54]. The newly developed magnets-in-motion (M-M) linear hollow cathode system yielded a maximum TiN deposition rate of 2 μm/min. With the system it was possible to deposit films with a microhardness of about 25.5 GPa.

With a Low Pressure Hybrid Plasma (HYP LP) source it was possible to deposit TiN films that reached hardness values of up to 30 GPa. The HYP LP was developed in 2004 [55]. The new plasma source utilizes a combination of ECR microwave plasma together with the M-M linear hollow cathode plasma. The TiN film deposition rates were estimated to be in a range between 130 nm/min and 160 nm/min [56].

Recently a new hybrid plasma source for thin film deposition has been developed – hollow cathode enhanced magnetron target (HoCET) [19]. The hybrid plasma source combines magnetron and a radio frequency hollow cathode plasmas. Paper V investigates performance of the system to deposit Ti and TiN coatings. The aim of the study was to test whether the HoCET arrangement exhibits similar effects in the reactive deposition of TiN coatings as the hollow
1.3.3 Aluminium nitride (AlN)

Aluminium nitride coatings have high chemical stability, good thermal conductivity, good piezoelectric and dielectric properties. The films have applications for surface passivation of semiconductors, thin film resonators, pH sensing devices, metal insulator semiconductor devices and integrated circuit packaging [57] as well as in microelectromechanical systems [58], optoelectronic devices (e.g. UV light emitting diodes [59]) and Surface Wave acoustic (SAW) devices [60] for their piezoelectric properties.

The AlN piezoelectric properties are determined by the electromechanical coupling coefficient. It is a numerical value that represents the materials capability to convert electrical into acoustic energy and vice versa. AlN films are of wurtzite hexagonal structure. The coupling coefficient is directly related to the grain orientation within the film. Every grain has its own dipole moment. To attain high coupling coefficients, the grains should be oriented in the same direction [61]. For AlN films, highest electromechanical coupling coefficient values are characteristic for films with (002) preferential growth (c-axis orientation).

Both, reactive PVD and CVD techniques can be used to deposit AlN films. As it was in the case of TiN, reactive plasma PVD sputtering is the method of choice due to low deposition temperature, lower process costs and considerably lower toxicity. In the reactive PVD AlN are prepared by sputtering an Al target in the presence of activated N2.

It has been shown that HiPIMS is a more efficient method to deposit AlN films with strong (002) preferred orientation [62] than pulsed-DC reactive magnetron sputtering. This is attributed to the higher plasma density which brings about a high flux of low energy Al and N ions. Nevertheless, pulsed-DC reactive sputtering offers higher deposition rates of up to 12.6 nm/min than the HiPIMS. Lower deposition rates at HiPIMS deposition is a known limitation and still a researched topic [63]. Similar observation for deposition rates has been recently made by Kohout et al. [64]. In their comparison of ionized PVD magnetron systems run by various DC power sources, deposition rates as high as 50 nm/min were reported. High deposition rate does not necessarily equate to strong (002) texture. Still a common approach to increase the crystalline quality of growing AlN films is heating of the substrate during the deposition see e.g. [65], although many solutions are sought after where the strong (002) texture can be achieved without any substrate heating.

Hollow cathodes have been previously used to deposit AlN coatings. AlN deposition by hollow cathode electron beam vapor deposition has been reported by Mu et al. [66]. Hollow cathode magnetron deposition has been de-
monstrated by Pessoa et al. [67]. At the Plasma group at Uppsala University the radio frequency plasma jet system has been used to deposit AlN at high deposition rates (up to 150 nm/min) [68].

In this thesis the deposition capabilities of (002) textured AlN films will be compared between the RHCPJ and in Paper IV reported HiPIMS process. This was the first time at the Institute of Biomaterials and Surface Engineering (Southwest Jiaotong University), when HiPIMS was used to deposit AlN films.
2. Experimental methods

This chapter first describes the employed hollow cathode discharge based or enhanced deposition systems for thin film deposition, followed by plasma composition and coating analysis methods. To gain an insight into the plasma chemical composition during the deposition processes, an optical emission spectroscopy (OES) was used. The deposited coatings were analysed using scanning electron microscopy, Raman spectroscopy, X-ray diffraction and scratch testing. This chapter provides a brief theoretical background of these methods and the conditions used for the analysis where necessary.

2.1 Hollow cathode discharge – based systems

The radio frequency hollow cathode plasma jet (RHCPJ) can be used in applications where targeted surface modification is required. The Magnets in Motion (M-M) radio frequency linear hollow cathode and a magnetron coupled with the Hollow Cathode Enhanced Target (HoCET) have been developed for large surface area processing.

2.1.1 Radio frequency hollow cathode plasma jet (RHCPJ)

In this thesis work the RHCPJ was used to deposit amorphous carbon films. Previously the system has been used to deposit AlN [68] and TiN films [17, 52]. The RHCPJ system comprises a hollow cylinder through which the process gases (Ar and C2H2) were introduced. Acetylene was chosen as the PE-CVD carbon source due to its low ionization potential value which is directly correlated to increased deposition rates [34]. The gas mixture was admitted into the deposition chamber pumped by a roots blower and a rotary pump. The outer diameter of the nozzle was 6 mm and the inner diameter was 2 mm. The nozzle was manufactured out of graphite, which served as a target for the PVD process. The hollow cathode was connected through an impedance matching box to an RF power supply (13.56 MHz). To increase the power density inside the nozzle, a coaxial space-charge shielding was used around the cathode (see Figure 2.1).

To bias the holder with substrate, a separate RF power source (13.56 MHz) was used, also connected through an impedance matching unit. First the films were grown on Si substrates to optimize the process and then on glass without an interlayer. The substrates were placed 15 mm below the outlet of the
nozzle. Prior the depositions the substrates were Ar sputter-cleaned. No other chemical processes were used. The amorphous carbon films were formed at a 1500 sccm Ar flow, 1.5 sccm of C$_2$H$_2$, at a pressure of 0.35 Torr (46.5 Pa) and an RF power of 100 W. The deposition was carried out for 20 minutes. The parameters where used for the process transfer to large area surface modification using the M-M RF linear hollow cathode system.

### 2.1.2 M-M linear hollow cathode

Amorphous carbon films were deposited using a patented Magnets in Motion (M-M) radio frequency linear hollow cathode plasma source [69]. Previously the M-M linear hollow cathode has been used for successful deposition of Ti, TiN and TiO$_2$ on various substrates [54, 70].

The cylindrical hollow cathode of the RHCPJ has been replaced with two parallel plates immersed in a static confining magnetic field – see the linear arc discharge source (LAD) in [53]. The M-M RF linear hollow cathode system is a new development of the LAD source where the static magnets are replaced by a rotary magnet system.

The deposition system (see Figure 2.2) comprises two cathode plates, two rotating NdFeB magnet assemblies placed at the outer side of each cathode plate, two RF power supplies connected through an impedance matching unit and a multiple nozzle system for Ar and C$_2$H$_2$ supply. The process gases are uniformly introduced from above, in between the cathode plates.
Figure 2.2. Magnets-in-Motion RF linear hollow cathode plasma source. (Paper I, Figure 1.)

The cathode plates serve as a target material for the PVD process. The plates were manufactured out of graphite and the substrate table was located 45 mm underneath the cathode plates.

The magnetic field within the hollow cathode facilitates the pendulum motion of the electrons thus increasing the plasma density. The rotary magnet assemblies are essential to ensure a uniform deposition rate along the hollow cathode slit. The rotating magnets create a time varying magnetic field. Due to this field a symmetrisation of plasma parameters occurs that brings about a uniform ion bombardment of the cathode plates.

One 13.56 MHz RF power source was used to generate the hollow cathode discharge and another one – to bias the substrate holder. To control the pressure in the deposition chamber a mechanical rotary pump and a roots blower were used. The coatings were deposited on a microscope glass slides (the substrate). No interlayer was used to facilitate the adhesion of the coatings. The substrates were Ar sputter-cleaned before each deposition.

The amorphous carbon films were deposited at a PVD and hybrid PVD/PE-CVD regimes. The coatings were grown at RF excitation powers of 1000 W and 1200 W. The substrate table was biased at a constant 500 W. The film deposition was performed in a total of three total chamber pressures (0.07 Torr, 0.3 Torr and 0.35 Torr). The pressure was set by partial flow rates of the process gases. The PVD deposition of amorphous carbon films was run at Ar gas flow rates of 315 sccm (0.07 Torr) and 1500 sccm (0.3 Torr). The hybrid PVD/PE-CVD deposition was performed at a total flow rates of the Ar+C$_2$H$_2$ gas mixture at 315 sccm (0.07 Torr), 1500 sccm (0.3 Torr) and 1888 sccm (0.35 Torr). In all trials the deposition was carried out for 20 minutes.

The deposition at 0.3 Torr pressure was carried out at different gas mixing ratios. The C$_2$H$_2$ content in Ar was varied in a range from 0% to 6%. When
the C2H2 content is 0% it means that the deposition system operates in the PVD regime.

2.1.3 Magnetized Hollow Cathode Enhanced Target (HoCET)

Plasma processing apparatus consisting of a magnetron coupled with the magnetized hollow cathode has been developed in Plasma group at Uppsala University [71]. The hollow cathode is magnetized utilizing the magnetic field of the magnetron. The Hollow Cathode Enhanced Target (HoCET) comprises an ONYX-4MAGII\textsuperscript{TM} planar magnetron with a circular target as one of the hollow cathode plates and an additional hollow cathode plate positioned above the outer circumference (see Figure 2.3). The hollow cathode plate and the target were manufactured from Ti. The diameter of the magnetron target was 10.16 cm.

For the deposition a radio frequency (13.56 MHz) power source was used at a delivered power of 1200 W. The substrate bias was set to -10 V DC. The Ti and TiN films were grown on planar n-type 35x35 mm\textsuperscript{2} Si substrates. The substrate-target distance was 4.5 cm. They were fixed above the magnetron on a thermally insulated holder with a built-in thermocouple for temperature monitoring. All depositions were performed for 20 minutes. The total gas flow rate was kept constant at 60 sccm. Deposition of Ti and TiN films was investigated at 9 mTorr (1.2 Pa) and 14 mTorr (1.87 Pa) deposition pressures. Multiple gas inlets were arranged inside the hollow cathode slit distributing the gas between the cathode plates. As process gases Ar and N2 were used. At the 9 mTorr deposition pressure the N2 concentration in Ar+N2 gas mixture was varied from 0% (Ti film growth) to 4.1% (TiN film growth). At the 14 mTorr deposition pressure the N2 contents were varied from 0% to 100%. No additional heating was used during the deposition. The performance of HoCET at different deposition powers was previously investigated in [19].

![Figure 2.3. Schematic of the Hollow Cathode Enhanced Target (HoCET) with the magnetron target as one of the hollow cathode plates. (Paper V, Figure 1.)](image)
2.2 High Power Impulse Magnetron Sputtering (HiPIMS)

AlN films were deposited using High Power Impulse Magnetron Sputtering (HiPIMS) system in a reactive PVD mode. In Figure 2.4 a schematic sketch of the system is displayed. The system comprises a cylindrical-shaped vacuum chamber of 50 cm in height and 50 cm in diameter. The vacuum chamber accommodates a total of four rectangular planar magnetron targets equally spaced around the circumference of the chamber. The magnetic field is generated by an assembly of permanent magnets located behind each of the targets. More details on the target design can be found in [72]. A rotatable substrate holder is located at the centre of the deposition chamber. The distance from the target to the substrate is 60 mm.

The system uses two DC power sources: one to bias the substrate, one to supply power to the targets. The targets were powered by HPS-450D HiPIMS power source manufactured by Chengdu Pulsetech Electrical. An Insulated-Gate Bipolar Transistor (IGBT) was used to control a capacitor discharge, facilitating an unbalanced magnetron plasma discharge. The series resistor \( R_1 = 3 \, \Omega \) was used to limit the plasma current and protect the power source from arcing [73].

![Figure 2.4. Experimental setup of high power impulse magnetron sputtering (HiPIMS) system for AlN film deposition. Reprinted from [73] with a permission from Elsevier.](image)

In Paper IV, for deposition of AlN films, a target (135x170 mm²) manufactured from Al (99.95% purity) was used. The other three targets were inactive. The Al target was applied under a -800 V pulsed trigger voltage with a frequency of 200 Hz. The substrate DC bias was set to -50 V. The AlN coatings were deposited at an average powers of 200 W (50 µs pulse width) and 450 W (80 µs pulse width). At both pulse widths the reactive deposition was performed in an Ar environment with N\(_2\) content in the gas mixture of 11.1% (5 sccm) and 16.6% (8 sccm). The Ar flow was kept constant at 40 sccm. Ad-
ditionally the deposition at 200 W was carried out at a N₂ flow rate of 3 sccm (6.9%) and the deposition at 450 W was carried out at 21.6% N₂. These flow rates were used to better observe differences of film properties (growth rate and texture) at different deposition modes (transitional and compound). The temperature in the deposition chamber was kept below 50 °C. Prior the admittance of the process gases, the deposition chamber was pumped down to a base pressure of 10⁻³ Pa (7.5·10⁻³ mTorr) by a turbo molecular pump and a rotary pump as a backup. By varying the N₂ content in the gas mixture, the deposition pressure was varied from 0.42 Pa (3.15 mTorr) to 0.46 Pa (3.45 mTorr).

The films were deposited on Si (100) substrates. Prior the deposition, the target was Ar sputter-cleaned for 10 minutes and the substrate – for 15 minutes. The deposition time was kept at 30 minutes. No additional substrate heating was used during the film deposition.

2.3 Characterization of plasma composition and deposited films

2.3.1 Plasma composition by Optical emission spectroscopy

Optical emission spectroscopy (OES) detects the composition based upon the light emission from excited species inside the plasma. In the thesis OES was used for process control and identification of the emitting species. The OES can be used to determine the density of emitting species, electron temperature, vibrational and rotational temperature of the molecules as well.

The optical emission spectra consist of atomic lines and vibrational bands. When the excited species (an atom or a molecule) undergoes a transition to a lower state of energy a photon is emitted at a characteristic wavelength. In the case of energetic atoms – peaks are detected, in the case of molecules – a collection of peaks that are termed as vibrational bands are detected. The vibrational bands are a collection of photons of different wavelengths characterizing different vibrational and rotational transitions. The rotational transitions are visible in the OES spectra as fine structures on the vibrational bands.

In the case of atoms, the electrons transit between the different energy states (n = 1, 2, 3, 4, ..., 7). In the case of molecules it is more complex. Every molecule can transit between the different excitation states (energy levels) as well as vibrational and rotational states simultaneously. This is one of the reasons why the spectra of molecules exhibit bands of peaks instead of lines.

Common species observed in the acetylene plasmas are H, CH and C₂ (Paper I and Paper II). The detected CH and C₂ systems are transitions of the diatomic molecules between different energy levels of molecular states. The C₂ Swan system accounts for transition from the first excited state of the diatomic carbon molecule (A^3Π_g) back to its ground state (X^3Π_u). There the "A" and "X" denotes the energy state of the molecule and the "^3Π_g/u" denotes the
electronic state of the molecule i.e. molecular term symbol. This transition can occur between different vibrational states which are usually depicted in brackets behind the notation. For example a "C₂ Swan (0,0)" notation means that the C₂ molecule has returned from its vibrational ground state (v = 0) of the first molecular excitation state (A) to the vibrational ground state (v = 0) of its' ground state (X).

Similar principles applies for the CH system. For each transition between the energy levels of molecular electronic states there is a characteristic wavelength i.e. the 3900 Å and 4300 Å. In a way the CH (4300 Å) system is similar to the C₂ Swan system – it is the transition from the CH first excited molecular state of A₂Δ to the ground state of X₂Π. The CH (3900 Å) system is a higher energy transition. It accounts for the transition from the second molecular energy level B₂Σ⁻ to the ground state of X₂Π. The electronic state of the molecule can vary with the transition between the two energy levels due to a change in the rotational-vibrational behaviour of the molecule. For the analysis of plasma composition during the Ti and TiN growth optical emissions from Ti (3653.5 Å), Ti⁺ (3685.2 Å), Ar (4158.6 Å) and Ar⁺ (4103.9 Å) were used.

In Paper I, Paper II and Paper V the optical emission spectra were recorded using a PLASCALC-2000-UV-VIS-NIR Plasma Monitoring & Process Control System via an optical fibre probe. In Paper I and Paper II the spectra were recorded in the wavelength range of 350 nm (near Ultra violet) to 700 nm (near infrared).

2.3.2 Film structure

The atomic structure of the deposited coatings was analysed using Raman spectroscopy and X-ray diffraction techniques.

2.3.2.1 Raman spectroscopy

Raman spectroscopy is commonly used to analyze the atomic structure amorphous carbon films. The Raman spectra originate from excited vibrational modes of the bonded atoms in the coating. In the Raman spectroscopy a monochromatic beam is used to excite the vibrational modes of molecular structures. For this purpose the sample surface is exposed to a monochromatic laser beam. The Raman spectrum is formed by inelastically scattered photons of the beam. As the laser beam interacts with the sample surface, the majority of the beam is reflected and the minority is scattered in all directions from the sample. The beam is scattered both – elastically and inelastically.

The Raman spectrum consists of a measured intensity of photons plotted against the Raman shift. The Raman shift (ω) is expressed in cm⁻¹ as an inverse ratio of the wavelength difference between the incident and the inelastically scattered beam. The Rayleigh (elastically scattered light) beam is filtered out before it reaches the detector.
A typical Raman spectrum of amorphous carbon films contains two distinct peaks that are denoted as G (graphite) and D (disorder) peaks. Raman spectrum of pure graphite contains only the G peak. Once the graphite crystals have been distorted, the D peak starts to emerge [74]. Both peaks originate from sp² hybridized carbon-carbon bonds. The origin of the G peak is stretching of carbon atoms positioned in chains and six-fold rings. The D peak originates from a breathing vibrational mode of aromatic rings in small crystallites or at the boundaries of larger crystallites [74, 75].

For the analysis of amorphous carbon films a Renishaw inVia confocal Raman microscope was employed. The coatings were studied using an incident laser line of 532 nm. The microscope employs a patented SynchroScan™ technology which ensures a high spectral resolution of 0.5 cm⁻¹. The first order Raman spectrum (800 to 2000 cm⁻¹) was measured to identify the structure of the deposited carbon coatings.

For a more detailed structure evaluation the D and G peak positions, intensities and full width at half maxima (FWHM) values were used. Intensity ratio of the D and G peaks (I_D/I_G) was used to estimate the degree of order/disorder in the films. To acquire these parameters the peaks were fitted to a Lorentzian (to fit the D peak) and Breigt-Wigner-fano (to fit the G peak) functions [76]. The Breigt-Wigner-fano function is expressed as:

\[ I_{\omega} = \frac{I_G \cdot [1 + 2(\omega - \omega_0)/(Q \cdot FWHM_G)]^2}{1 + [2(\omega - \omega_0)/FWHM_G]^2} \]  

where \( I_G \) is intensity of the G peak, \( \omega_0 \) is the peak position, \( FWHM_G \) is full width at half maximum of the G peak and \( Q \) is Fano factor. The best fit for the G peak was achieved with a Fano factor value of \( Q = -8 \). The fitting was performed using a Matlab script developed by prof. T. O’Haver at the University of Maryland at College Park was used [77]. Due to the asymmetric character of the G peak, the position (\( \omega_G \)) was defined and reported as:

\[ \omega_G = \omega_0 + \frac{FWHM_G}{2Q} \]  

The background signal was accounted for using an airPLS (adaptive iteratively reweighted Penalized Least Squares) method [78]. The parameters used were the following: lambda (adjustable parameter) of 106, an order of the penalties difference of 2, a weight exception proportion at start and an end of the spectra of 0.1 and an asymmetry parameter for the start and end of 0.1. The method was chosen over a linear subtraction to account for slight shoulders at the start and end of the spectra.

2.3.2.2 X-ray diffraction (XRD)

X-ray diffraction (XRD) was used to determine the crystalline structure of the deposited films. For amorphous carbon films XRD was used to determine the
presence of crystallites and for TiN and AlN films XRD was used to analyse the crystalline structure and preferential growth mode.

XRD was run in two modes: Bragg Brentano (θ-2θ) and Grazing incidence XRD (GIXRD). Bragg Brentano geometry provides the information on which lattice planes are parallel to the coating surface – preferential growth. The X-ray source and the detector are coupled together and the 2θ angle is increased by moving both, the detector and the X-ray tube upwards. The drawback of the method is the high signal contribution from the substrate compared to the one of the coating. To increase the signal originating from the deposited coating, GIXRD was used.

Other authors can refer to GIXRD as a glancing angle XRD or an asymmetric scan. In GIXRD the sample surface is exposed to the X-ray beam at a fixed, low angle. This allows to ensure that the majority of the scattered signal originates from the coating material and not the substrate. The method provides information of the crystallites present in the coating regardless of their orientation to the surface.

In Papers I – III and Paper V the XRD equipment used for the experiments was a Siemens D5000 diffractometer. In Paper IV the texture of the deposited AlN films was analysed using a PANalytical X’pert diffractometer. The GIXRD was performed at a 2° incident angle. The X-ray beam was generated in an X-ray tube from a Cu anode. The Cu Kα radiation (λ = 0.15406 nm) was used. The contribution of the Kα2 was reduced in the post-processing of the acquired XRD spectra. The CuKβ line was filtered out by a Göbel mirror.

The Göbel mirror is a curved monochromator that converts the divergent beam coming from the X-ray tube into a parallel beam which is favoured for thin film analysis. To ensure more symmetric and narrow peaks the scattered beam from the sample to the detector a parallel plate collimator (Soller slits) was used. It is a system of parallel foils that reduces the divergence of the scattered beam. The X-rays were detected with a Siemens scintillation counter detector. It is based on a light emitting photocathode that emits light proportional to the X-ray intensity. The light intensity is measured in a photomultiplier tube.

2.3.3 Film thickness

Thickness of the deposited amorphous carbon films was measured using profilometry (Paper I) and Scanning Electron Microscopy (Paper II). The AlN film thickness was measured using profilometry (Paper IV). The thickness of Ti and TiN was measured using profilometry and SEM (Paper V).

2.3.3.1 Profilometry

Profilometry is an analytical method to measure the surface topography. There are contact and non-contact profilometers. In Papers I, II, IV and V a contact profilometer equipped with a mechanical probe (stylus) was used.
As the stylus is being drawn across the surface, the height variation in its path is registered. It is termed as a 2D measurement. The stylus is kept at a physical contact with the surface at a constant load – set point. As the profile height of the surface changes, the force feedback loop registers the difference from the set point and translates it to a height value.

The thickness in Papers I, II and Paper V was measured by stylus profiler Dektak 150. The stylus diameter was 12.5 μm. The load set-point was set to be 3 mg load. The lateral resolution was set to 0.333 μm. Two steps on each sample were formed by masking the substrate prior the deposition. The height of each step was measured and an average value used. Due to the high thickness of the deposited films (micrometer scale) profilometry proved to reproduce the results of SEM. In Paper IV the thickness was measured using a stylus profiler Ambios XP-2. The lateral resolution was set to a similar value.

2.3.3.2 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) is a microscopy method to view morphology of the coating surface or its cross-section. The electron microscopes are used not only in material science, but also in medicine and biology. The main advantage of the electron microscopy is the high resolution (about 0.1 nm compared to the 200 nm of the optical (light) microscope) and depth of field.

The SEM consists of three main parts – the illumination system, the sample stage and signal detectors. The illumination system comprises an electron gun and optics (condenser and objective lenses). The electron beam is formed in the electron gun where the electron energy can be controlled. The condenser lens gathers the electron beam into a fine spot onto the sample surface. The finer the spot size the higher the resolution of an image. The objective lens focuses the electron beam onto the sample surface. The secondary function of the objective lens is to control the scan over the sample surface. The electron detectors are located above the sample stage to attract and detect the scattered electrons. The secondary electron detector was used to measure the thickness. Secondary electrons are low energy electrons which have been extracted from the sample surface due to electron-electron collisions.

To measure the thickness, samples were fractured revealing the substrate-coating interface and the coating cross-section. In the thesis SEM was used to acquire precise measurements of the amorphous carbon, Ti and TiN coating thickness. For this purpose a Zeiss 1550 SEM was used.

2.3.4 Film mechanical properties

Mechanical properties are essential for coatings in tribological applications. In the thesis coating adhesion and hardness were evaluated. Thick amorphous carbon coatings often exhibit natural delamination. It is especially characteristic when the films are grown on amorphous substrates without an interlayer.
In this respect, the adhesion of the coatings was evaluated (Paper I and Paper II). In Paper V changes in the deposited Ti and TiN coating hardness were analyzed.

2.3.4.1 Adhesion

The adhesion shows how well the coating clings to the substrate. The adhesion of the amorphous carbon coatings was analyzed by scratch testing. The scratch tests were performed according to the procedure described in the ISO standard EN ISO 20502:2016. The scratch is made with a rigidly fastened stylus in the test equipment with a moving stage.

The stylus used in the experiments was a Rockwell C indenter. The tip is a 120° sphericonical diamond sphere. This type of indenter has been produced and calibrated to comply the EN ISO 6508-2:2015 standard and the clause A3.5 of the standard ASTM E18:2015. The scratch tests were performed at a progressive loading mode. There the normal force value was linearly increased from 0 N to 51 ± 0.05 N at a loading rate of 4.9 ± 0.11 N/mm.

The adhesion is characterized by 3 critical load (LC) levels: LC1, LC2 and LC3. Each load level is reported in Newton. The value of each critical load is defined as the normal force value at which the certain coating failure event starts, given that the events are clustered. Singular events are neglected. The three coating failure events are the following:

- LC1 – The coating starts to crack indicating a failure of the cohesive strength. It is an event where the cracks are observed at the sides of the scratch path left by the indenter;
- LC2 – The cracks reach the substrate indicating a failure of the cohesive and an adhesive strength. It is an event where coating delamination from the substrate can be observed at the sides of the scratch line;
- LC3 – The indenter tip reaches the substrate indicating a complete failure of the adhesive strength. It is an event where the coating delamination from the substrate can be observed at the centre of the scratch line.

To identify the critical load events, the scratches were viewed in an optical microscope Olympus AX70. Multiple photographs were made to capture the whole scratch length with a DeltaPix Infinity X21 CCD camera. The images were merged together and measurements performed. The normal force value was determined according to the scale bar and the measured distance across the scratch line to the failure event.

A total of 3 scratches were made per coating and the average LC1, LC2 and LC3 values were reported. The error estimation for the LC values and the loading rate has been estimated with a 95.4% confidence interval.
2.3.4.2 Hardness

Hardness shows how well a material can resist a compressive load. The hardness measurements are performed by pressing an indenter tip into the material at a fixed load. Microhardness tests are performed at loads up to 1 kgf (9.807 N).

Vickers hardness test was performed to determine the microhardness of the deposited coatings. The test was performed by making multiple indentations into the coating. The indenter tip is a right-angle, diamond pyramid with face angles of 136°. The hardness value is acquired by dividing the applied force with the surface area of the permanent impression made by the indenter. The surface area is determined from optically measured diagonals of the indentation. As the average diagonal lengths were higher than 1/10th of the coating thickness, contribution from the substrate hardness had to be accounted for.

To calculate the hardness value of the coating, the method developed by Jönsson and Hogmark was used (see equation 2.3),

\[
H_{film} = H_S + \frac{H_C - H_S}{[2sint(22) \cdot (7 \cdot t/d)] - [sinc^4(22) \cdot (7 \cdot t/d)^2]}
\]  

(2.3)

where \(H_{film}\) is the film hardness, \(H_S\) is the substrate hardness, \(H_C\) is composite hardness (substrate+film), \(t\) – coating thickness and \(d\) – (average) length of the indentation diagonals.

To measure the coating and substrate microhardness a Buehler Micromet 1600-6406 series microindenter was used. For ease of stage manipulation it was equipped with an Omnimet stage & focus controller. The substrate hardness and the \(H_C\) were acquired as an average value of 20 – 48 indents. The analysis was performed at exerted load levels of 50 gram-force (gf) (HV0.05), 10gf (HV0.01) and 5gf (HV0.005). The distance between the indents was not less than 50 \(\mu\)m (sufficient to follow the 4 diagonal lengths requirement specified in ASTM C1327). The indentations whose diagonal length difference is larger than 5% of the average value were neglected. Additionally the indentations corresponding to the "Unacceptable indentations" specified in ASTM C1327 standard where neglected as well. The microhardness measurements were confirmed by nanoindentation analysis. The measurements were performed by CSM UNHT ultra nanoindentation tester at a 100 nm indentation depth.
3. Results and Discussion

3.1 Amorphous carbon thin films prepared by RHCPJ and M-M linear hollow cathodes

The section is based on findings reported in Paper I, Paper II and Paper III. The aforementioned papers deal with deposition of amorphous carbon coatings on Si and glass substrates. First, the scale up of the radio frequency hollow cathode plasma jet (RHCPJ) system for large area processing is described. Then results on the performance of the magnets in motion (M-M) radio frequency linear hollow cathode system are presented and discussed.

3.1.1 Process transfer from RHCPJ to M-M linear hollow cathode

In Paper I deposition of amorphous carbon coatings was demonstrated by RHCPJ deposition system. The structure of amorphous carbon (prominent D and G peaks) and good adhesion on glass without an interlayer was achieved by depositing films in a hybrid PVD/PE-CVD deposition mode. The films were grown at 0.1% of C$_2$H$_2$ in the Ar+C$_2$H$_2$ gas mixture where the flow rate of Ar was 1500 sccm and the flow of C$_2$H$_2$ was 1.5 sccm. The process was carried out at a moderate pressure of 0.35 Torr (46.5 Pa) and an RF power of 100 W.

In Paper I and Paper III the deposition process transfer to the M-M linear hollow cathode system at the moderate deposition pressure was presented and discussed. To sustain the hollow cathode plasma discharge at a larger volume, the RF power and total gas flow had to be scaled up. The RF power was increased from 100 W to 1200 W and the total gas flow rate was increased from 1501.5 sccm to 1888 sccm Ar+C$_2$H$_2$. In such a way the acetylene content was increased from 0.1% to 1%. All these adjustments ensured deposition of thick and adherent coatings.

With the process transfer, changes in the structure of the amorphous carbon coatings were observed (see Figure 3.1). The changes have been discussed in Paper III.

Deconvolution of the spectra provided D and G peak positions, peak intensities and FWHM values. These values together with the $I_D/I_G$ ratios have been disclosed in Table 3.1.

In both deposition systems it was possible to deposit coatings of amorphous carbon structure where the majority of the atomic bonds are $sp^2$ hybridised.
From the respective G peak positions and $I_D/I_G$ ratios in accordance to the 3-stage model developed by Ferrari and Robertson [76, 79] it is evident that the fraction of $sp^3$ hybridised bonds is less than 20% in both deposition cases. From the high $FWHM_G$ values (higher than 50 cm$^{-1}$) for both spectra it is evident that the film crystallites are smaller than 10 Å [80]. To confirm this, XRD measurements were performed on the deposited carbon films. The acquired XRD spectra did not exhibit any crystalline carbon features.

From the change in $I_D/I_G$ ratio (from 0.35 $\pm$ 0.04 (RHCPJ) to 0.71 $\pm$ 0.06 (M-M)) it can be observed that the RHCPJ provides coatings with higher degree of graphitic disorder and degree of $sp^3$ bonding [76]. This difference can arise from the more polymer like structure of the coating [81] prepared by the M-M linear hollow cathode at the same pressure and the slightly higher C$_2$H$_2$ content. The higher acetylene content brings about an increased supply of hydrogen into the deposition chamber. In Figure 3.1 it can be observed that the M-M linear hollow cathode prepared coating displays a slope in the background signal. The slope originates from an increased hydrogen content within the film as it saturates a non-radiative recombination sites in the coating [82, 83].

With the process transfer it has been demonstrated that amorphous carbon films can be deposited across large areas on glass substrates without an interlayer using M-M linear hollow cathode system.
Table 3.1. Extracted D and G peak parameters of the fitted spectra. (Adapted from Paper III)

<table>
<thead>
<tr>
<th>Raman peak parameter</th>
<th>RHCPJ: 0.35 Torr, 0.1% C₂H₂</th>
<th>M-M: 0.35 Torr, 1% C₂H₂</th>
<th>M-M: 0.07 Torr, 4.8% C₂H₂</th>
<th>M-M: 0.07 Torr, 5.7% C₂H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>D peak pos. [cm⁻¹]</td>
<td>1358</td>
<td>1336</td>
<td>1338</td>
<td>1359</td>
</tr>
<tr>
<td>G peak pos. (ω₉) [cm⁻¹]</td>
<td>1557</td>
<td>1600</td>
<td>1604</td>
<td>1582</td>
</tr>
<tr>
<td>D peak int. [arb. u]</td>
<td>6829 ± 340</td>
<td>19070 ± 782</td>
<td>3571 ± 100</td>
<td>4365 ± 231</td>
</tr>
<tr>
<td>G peak int. [arb. u]</td>
<td>21462 ± 1068</td>
<td>26749 ± 1098</td>
<td>4506 ± 126</td>
<td>7281 ± 386</td>
</tr>
<tr>
<td>FWHM_D [cm⁻¹]</td>
<td>185 ± 9</td>
<td>115 ± 5</td>
<td>121 ± 3</td>
<td>154 ± 8</td>
</tr>
<tr>
<td>FWHM_G [cm⁻¹]</td>
<td>149 ± 7</td>
<td>54 ± 2</td>
<td>54 ± 1</td>
<td>91 ± 5</td>
</tr>
<tr>
<td>ID/IG</td>
<td>0.35 ± 0.04</td>
<td>0.71 ± 0.06</td>
<td>0.79 ± 0.04</td>
<td>0.60 ± 0.06</td>
</tr>
</tbody>
</table>

3.1.2 M-M linear hollow cathode: Deposition conditions and film properties

In the previous section a successful process transfer from RHCPJ to M-M linear hollow cathode plasma source was shown. Across large areas the amorphous carbon coatings on glass substrates without an interlayer were grown at 1200 W of RF power, 0.35 Torr deposition pressure and 1% C₂H₂ (18 sccm C₂H₂ flow and 1870 sccm of Ar) at a 500 W RF substrate bias. In Paper I it was demonstrated that films of a similar Raman structure can be deposited at the same flow of acetylene (18 sccm), but at a lower deposition pressure of 0.07 Torr. The results on the performance of M-M linear hollow cathode at 0.07 Torr for amorphous carbon film deposition have been reported in Paper I and Paper III. The deposition pressure was decreased by lowering the admittance of Ar into the deposition chamber. This gives an increase in the C₂H₂ content in the Ar+C₂H₂ gas mixture to 5.7% at the same 18 sccm of C₂H₂. In Paper III the changes in the Raman structure have been identified with a change in the acetylene content by 0.9% (4.8% vs 5.7%). Figure 3.2 displays the both Raman spectra.

In Figure 3.2 a slope difference of the spectra can be directly observed. The steeper slope points to higher hydrogen content in the film. The higher acetylene content yields more hydrogenated amorphous carbon films. From the analysis of parameters given in Table 3.1 it can be concluded that films grown at 5.7% C₂H₂ content exhibit higher degree of bond disorder and overall a more amorphous structure.
From a change in G peak position by 22.5 cm\(^{-1}\) it was found that the higher acetylene content yields increased carbon-carbon bond disorder (bond-angle and bond-bending) in the coatings. At the same time the \(I_D/I_G\) ratio decreases by 0.19 indicating a higher \(sp^3\) hybridized bond fraction. A change in the D position by 20 cm\(^{-1}\) indicates an increasing presence of smaller graphitic crystallites (aromatic clusters). An increased D peak intensity (by 22\%) further shows the increased number of such crystallites [76]. The FWHM of the D and G peaks increases by 38.6 cm\(^{-1}\) and 38 cm\(^{-1}\) respectively. Both increases reflect the increased graphitic disorder within the films [74, 79, 80].

### 3.1.2.1 Effect of RF power and deposition pressure on film deposition

The goal with the deposition process design is to form amorphous carbon films at high deposition rates with good adhesion. In Paper I it was confirmed that the deposition rate can be controlled with the RF power as well as the deposition pressure. At the deposition pressure of 0.07 Torr, an increase of the RF power by 200 W yields an increase in the deposition rate by 0.05 \(\mu m/min\) (0.075 \(\mu m/min\) to 0.125 \(\mu m/min\)). This can be explained by increased density of reactive species in the plasma volume, which participate in the coating growth. This change in the plasma density can be indirectly observed through OES by analyzing H\(_\beta\) and H\(_\alpha\) line intensities. A ratio of both \((H_\beta/H_\alpha)\) represents a measure of electron energy which directly relates to the plasma density through increased ionisation probability. In Figure 3.3 a rise in \(H_\beta/H_\alpha\) ratio with the increased RF power at the 0.07 Torr pressure is visible.
Figure 3.3. Deposition rate and OES \( H_\beta/H_\alpha \) ratio for amorphous carbon films deposited at RF powers of 0.07 Torr and 0.35 Torr and RF powers of 1000 W and 1200 W at the same C\(_2\)H\(_2\) flow of 18 sccm. (Adapted from Paper I)

If the deposition pressure is increased up to 0.35 Torr, the deposition rate increases considerably. In Paper I it was demonstrated that at the deposition pressure of 0.35 Torr the deposition rate reaches 0.800 \( \mu \)m/min. Together with the increase in the deposition rate, an increase in the \( H_\beta/H_\alpha \) ratio was observed. The adhesion scratch test showed that a failure of the adhesive strength occurs at low loads (not higher than 4 N) indicating rather low adhesion of the coatings. More results on the adhesion of M-M linear hollow cathode prepared amorphous carbon coatings are presented in Section 3.1.2.2. As it has been outlined here and in Paper I, the plasma discharge characteristics and especially the \( H_\beta/H_\alpha \) ratio can be used to predict changes in the deposition rate.

If the deposition pressure is slightly decreased down to 0.3 Torr, the deposition rate remains the same (0.800 \( \mu \)m/min) yielding the same 16 \( \mu \)m thick coatings. No changes in the OES spectra were observed.

Paper II reports results of M-M linear hollow cathode performance at varying acetylene contents at 0.3 Torr deposition pressure and 1200 W of RF power. Both the PVD and hybrid PVD/PE-CVD deposition modes were examined. The effects on the deposition rate and adhesion have been analyzed and discussed in the next section of the thesis.

3.1.2.2 Effect of acetylene content on film deposition
There are considerable plasma composition differences between the PVD (0\% of C\(_2\)H\(_2\) ) and hybrid PVD/PE-CVD deposition modes. In Paper I, by com-
paring the OES spectra of plasma discharges of both deposition modes at 0.07 Torr pressure, it was observed that in the PVD regime there are fewer species present than in the hybrid deposition mode (compare a) and b) in Figure 3.4). Figure 3.4 depicts a side by side comparison of OES spectra of discharges at 0% and 5.7% of C$_2$H$_2$ content in the Ar+C$_2$H$_2$ gas mixture. It can be observed that only Ar and Ar$^+$ lines together with some stronger C$_2$ Swan system bands are present during the PVD deposition.

![Figure 3.4. Optical emission spectra of depositions at 0.07 Torr and 1200 W. a) PVD deposition regime, b) PVD/PE-CVD deposition regime (5.7% of C$_2$H$_2$). (Paper I, Figure 3.)](image)

In Figure 3.4 it can be observed that in the hybrid deposition mode, the Ar and Ar$^+$ lines are weaker than in the PVD mode. As the RF power is kept constant, part of the electron energy is absorbed by the C$_2$H$_2$ rather than the Ar, leaving less energy for excitation of the Ar species.

In the hybrid PVD/PE-CVD deposition mode, the CH (0,0) band from the 3900 Å system, the CH (0,0) band from the 4300 Å system appears together with the H lines from the Balmer series (H$_\alpha$, H$_\beta$). The CH species in the plasma volume can originate from the PVD part in the hybrid process. Once the sputtered carbon reaches the growing film a chemical etching can occur. The hydrogen reacts with the carbon removing it from the surface in the form of CH. In turn this leaves the growing film surface with dangling bonds that can serve as a further attachment sites for the incoming carbon species from the plasma volume. It is possible that the dangling bonds are terminated by H species, yielding hydrogenated amorphous carbon films. The chemical etching and the bond termination are two competing processes.

In addition to the (0,0) band from the C$_2$ Swan system which was observed in the PVD discharge, a (1,1) band and weaker bands from (1,0), (2,1),
(3,2), (4,3) transitions in the Swan system become visible. Presence of the C$_2$ Swan bands are characteristic to acetylene plasmas due to the strong carbon-carbon triple bond in C$_2$H$_2$ molecules. The same has been observed from mass spectroscopy measurements, where species with an even number of carbon atoms are detected [84].

A successful plasma dissociation of C$_2$H$_2$ into C$_2$ and H$_2$ species is indicated by the presence of H$_2$ bands that are visible in the 550 – 565 nm region. The hydrogen molecules originate from the gas phase reactions. During the hollow cathode discharge an atomic hydrogen is released when the carbon-hydrogen $\sigma$ bonds in C$_2$H$_2$ are broken by collisions with the energetic species.

If the deposition pressure is increased to 0.3 Torr, and the acetylene content lowered down to 0.5%, the discharge characteristics are similar in terms of the detected species. In Figure 3.5 presence of the same species as in Figure 3.4 can be observed, but there are considerable changes in the intensities. What can be directly observed is weaker intensity of the CH 3900 Å band and H$\alpha$, H$\beta$ lines.

![Figure 3.5. Optical emission spectrum from the M-M linear hollow cathode discharge at 0.5% of C$_2$H$_2$ in Ar+C$_2$H$_2$ gas mixture. Total gas flow of 1500 sccm. (Paper II, Figure 1.)](image)
Primarily this can be explained with the change in deposition pressure. It brings about shorter particle residence times in the plasma volume as well as lower amount of supplied energy per particle. The higher the deposition pressure, the higher the gas flow rate is. At higher gas flow rates inside the deposition chamber, the particle residence time is lower, thus it is subjected to energy exchange processes for a lesser time period. Higher intensities of C₂ Swan system bands are observed which indicates higher dissociation efficiency of acetylene.

The following section presents and discusses effects of acetylene content on deposition rate, thickness and coating adhesion.

*Deposition rate and film thickness*

The amorphous carbon coatings were prepared at the following acetylene contents: 0%, 0.25%, 0.5%, 1.0%, 1.5%, 2.0%, 2.5% and 3%. When the acetylene content is 0% the deposition system works in a PVD mode. The deposition pressure was kept constant at 0.3 Torr, the RF power was 1200 W and the substrate bias voltage was set to 500 W. Previously multiple authors have demonstrated that higher acetylene content in the gas mixture yields steady increase in the deposition rates [85–87]. In the M-M linear hollow cathode when rising the acetylene content from 0% to 3% a non-linear relation in the deposition rate and film thickness was observed. The results are shown in Figure 3.6.

![Figure 3.6](image-url)

*Figure 3.6.* Elevation of deposition rate and film thickness with C₂H₂ content in Ar+C₂H₂ mixture. Total gas flow of 1500 sccm; 1200 W power; 40 Pa (0.3 Torr) pressure. (Paper II, Figure 2.)

A steady increase in the deposition rate can be observed from 0 % up to 2% C₂H₂. The deposition rate at 2% C₂H₂ was 2.5 μm/min which is slightly more than 3 times higher than at 1% of C₂H₂ (0.8 μm/min). Higher deposition rates
have previously been reported by [88] on PET substrates using a microwave plasma reactor. Using an acetylene gas, a 100 nm thin films were grown at a rate of 3.6 μm/min. Good adhesion is achieved by an interface layer which is formed through plasma etching of the PET substrate. Formation of the interface layer in the surface of Si and glass substrates is more difficult to accomplish, compared to PET, due to higher bond strength.

In the M-M linear hollow cathode plasma source, once the acetylene content is higher than 2% the deposition rate starts to decrease down to 2 μm/min at 2.5% C2H2 and 1.4 μm/min at 3% C2H2.

A similar relation of the deposition rate versus acetylene content has been observed by Capote G. et al. [89], however, at a much higher acetylene contents (above 30%) and lower deposition rates (0.04 to 0.58 μm/min). The steady increase of the deposition rate comes about from an increased carbon and hydrogen supply to the deposition process. At C2H2 concentrations higher than 2% an etching by atomic hydrogen becomes the predominant process [34]. The growth of the carbon films is an event of two competing processes – the deposition of carbon constituents and the etching of the film, mostly by Ar and H particles.

In the PVD deposition mode, when the C2H2 content in Ar+C2H2 mixture is 0%, the deposition rate is the lowest, just 0.075 μm/min producing a 1.5 μm thick coating. At the same time, higher acetylene contents yield coatings of thicknesses of up to 50 μm (at 2% C2H2). It is evident that most of the deposited material is supplied from the C2H2 PE-CVD process. Nevertheless, the use of the graphite hollow cathode plates ensures that no unintentional doping appears in the carbon coatings. Unwanted doping in this case directly relates to inclusion of impurities, it can occur when hollow cathode plates have been manufactured from other materials and low purity process gases are employed as well.

In Figure 3.6 it can be seen that the thickness of the coatings can reach up to 50 μm over a course of the 20 minute deposition at 2% C2H2. At higher C2H2 concentrations the thickness of the films decreases down to 40 μm (at 2.5%) and 27 μm (at 3%). Often thick films develop cracks and experience delamination due to residual stresses. These issues are common when the films are deposited on non-metallic substrates. The next section is dedicated for the adhesion results of the grown amorphous carbon films on glass substrates.

**Adhesion**

In Paper I and Paper II it has been reported that several amorphous carbon coatings grown on microscope slides in the M-M linear hollow cathode exhibit good adhesion. The adhesion test results are shown in Figure 3.7.

According to Paper II most of the films (deposited at 0%, 1.5%, 2.0%, 2.5% and 3.0% C2H2) were naturally delaminating. For these coatings the adhesion failure was evident right after the deposition. Out of these films, the thickest
was the one deposited at 2.0% C$_2$H$_2$ reaching 50 μm over the course of 20 min deposition. Very good adhesion of 50 μm thick amorphous carbon films recently has been demonstrated by Liu et al. [90] where an LC3 value of 73 N is reported. The good adhesion on high speed steel substrates was accomplished by the use of carbide forming interlayer system (Cr/CrC$_x$/CrC) at an average deposition rate (0.08 μm/min), for amorphous carbon coatings.

In this thesis the adhesion scratch tests were performed on the coatings deposited at 0.25%, 0.5% and 1% of C$_2$H$_2$ in the Ar+C$_2$H$_2$ mixture. Among the films grown at 0.3 Torr pressure, the lowest cohesive strength (characterized by LC1 value) was observed for the coating deposited at 1% C$_2$H$_2$ (LC1 = 1.43 ± 0.06 N). The highest first critical load (LC1) value was observed for the film deposited at 0.25% C$_2$H$_2$ (LC1 = 2.32 ± 0.10 N). The difference between the two is rather small, just by 1 N. It can be observed that higher acetylene contents gradually decrease the cohesive strength of the coatings. The films grown at the lower pressure (0.07 Torr), but at higher C$_2$H$_2$ content (4.8%) displays slightly lower LC1 value of 1.22 ± 0.01 N.

Among the films grown at 0.3 Torr pressure, the lowest second critical load was observed for coatings deposited at 1% C$_2$H$_2$ (LC2 = 1.91 ± 0.09 N). The highest second critical load (LC2) value was observed for the films deposited at 0.5% C$_2$H$_2$ (LC2 = 16.95 ± 0.75 N). The coating started to delaminate at the sides of the scratch at a much higher load (LC2 = 38.83 ± 0.88 N) when the deposition was carried out at the higher acetylene content and lower
deposition pressure. The better result can be explained with higher energy per particle that promotes the adhesion.

The amorphous carbon coatings deposited at 0.25% and 0.5% C₂H₂ were not delaminating at the centre of the scratch even at 51 ± 0.05 N pressure force. The lowest third critical load (LC3 = 2.04 ± 0.09 N) was observed for the coatings deposited at 1% C₂H₂. The coatings grown at 0.07 Torr were delaminating at the centre soon after cracks developed around the scratch path (LC3 = 39.45 ± 0.9 N).

As the LC3 was not reached, the best adhesion is characteristic for the coatings deposited at 0.25% and 0.5% C₂H₂ contents. The coating prepared at 1% acetylene content shows very low adhesion as all three critical load values were reached at low pressure force values. From an optical microscope observation of the sample surface, the coating appears more brittle than other films. Flaking/chipping off could be observed quite early, for the film grown at 1% of C₂H₂, during the scratch test. For the coatings deposited at deposition rates higher than 0.8 μm/min the natural delamination most likely is caused by the high film thickness, and internal stress. Since adhesion is influenced by film thickness, an evaluation for the set of coatings at varied deposition rates, but having identical thicknesses, is planned for the future experiments.

For the amorphous carbon coatings prepared by M-M linear hollow cathode system there is still room for improvement as the LC1 values could be higher. An acceptably good LC1 value should be 10 N or above values reported from industrial and academic research [91–94]. Adhesion can be improved with a use of a Si interlayer [34] or by increasing the ion energy [21, 22]. There it was demonstrated that during ion beam deposition a transfer layer is formed on the glass surface due to an ion implantation and mixing processes.

3.2 TiN and AlN films prepared by reactive PVD

3.2.1 TiN films prepared by HoCET

In Paper V the effects of nitrogen content in a mixture with argon on deposition rate, crystalline structure and hardness were investigated. First the changes in the deposition rate were analyzed as the deposition mode was transferred from a non-reactive to the reactive mode. These experiments were performed at two deposition pressures of 9 mTorr and 14 mTorr. Then changes in the microstructure and hardness were analyzed and discussed.

At the 9 mTorr deposition pressure the non-reactive deposition yielded 1 μm thick Ti films. Transition to the reactive deposition mode resulted in a rapid increase in the deposition rate. The highest TiN film thickness (1.22 μm) was observed when deposited at 1.1% of N₂ content in the Ar+N₂ gas mixture. This results in about 120% increase in the deposition rate of TiN over the non-reactive deposition rate of Ti films.
Figure 3.8. Film thickness and temperature at the substrate versus nitrogen content in the mixture with argon. Deposition pressure of 9 mTorr; 60 sccm total flow rate; 1200 W power. (Paper V, Figure 4.)

The data of the monitored temperature at the substrate has been plotted in Figure 3.8 together with the thickness of the deposited coatings. A direct fit can be observed between the substrate temperature and the coating thickness curves. By OES analysis in Paper V, it was shown that the temperature at the substrate can be interpreted as a measure of ion bombardment. The maximum film thickness, substrate temperature and the maximum OES signal from Ti and Ti\(^{+}\) were observed at the identical N\(_2\) content of 1.1\%. It was concluded that the emission from Ti and Ti\(^{+}\) is directly related to the metal flux towards the substrate i.e to the deposition rate of the film. An enhanced excitation/production of Ti and Ti\(^{+}\) was observed in a range of up to 3\% of nitrogen in the process gas mixture.

At the 14 mTorr deposition pressure the non-reactive deposition yielded thicker (1.75 \(\mu\)m) Ti films. The transition to reactive deposition mode resulted in a similar increase in the deposition rate (see Figure 3.9). The highest TiN film thickness (2.5 \(\mu\)m) was observed when deposited at 2.4\% of N\(_2\) content in the Ar+N\(_2\) gas mixture. This results in about 140\% increase in the deposition rate of TiN over the non-reactive deposition rate of Ti films. The maxima of the substrate temperature and the total Ti and Ti\(^{+}\) emission were observed at the same nitrogen content (2.4\%). The effects displayed in Figure 3.8, Figure 3.9 and the OES data reported in Paper V resemble similar trends observed for
hollow cathodes [95]. There Ti and TiN coatings were deposited by the hollow cathode Radio frequency Plasma Jet (RPJ). These effects are not typical to the conventional reactive magnetron sputtering, where the growth of Ti films is usually 2 times faster than the reactive sputtering of TiN films [96–98].

In the experiments performed at both deposition pressures a coupling between the deposition pressure and N2 content where the maximum ionisation, deposition rate and ion bombardment occurs can be observed. The higher deposition pressure shifts the optimum gas composition to slightly higher nitrogen contents (from 1.1% to 2.4% N2). Deposition of TiN films at lower rates is possible by pure N2 sputtering. The process is facilitated by the increased target self-bias at the higher nitrogen concentrations. The target self bias increases on the account of nitrogen due to a drop in the secondary electron emission coefficient of the process gas mixture.

Properties of TiN films

The XRD analysis showed that non-stoichiometric films are deposited at lower N2 contents. Stoichiometric TiN films can be deposited at higher nitrogen concentrations. Only at N2 concentrations below 1% dissolved Ti phases were observed. Deposition by HoCET arrangement at N2 contents in a range of 1.1% to 2.4% resulted in non-stoichiometric films. In this range strong XRD
reflections corresponding to Ti$_2$N (200) and (311) as well as TiN (220) were detected. Figure 3.10 displays normalized intensities of individual reflections from the XRD diagrams.

At nitrogen concentrations higher than 4% the stoichiometric, polycrystalline TiN films were deposited. A distinct feature in Figure 3.10 is intensity evolution of TiN (111) and (200) reflections. With nitrogen content between 4-6% a texture transition from (200) to (111) occurs. Both intensities exhibit saturation up to 100% of N$_2$. Besides the two reflections, the TiN (220), (311) and (222) are present.

Titanium nitride films prepared at 9 mTorr deposition pressure exhibited similar XRD patterns. A similar coupling between the deposition pressures and nitrogen contents was observed as well. The higher deposition pressure shifts the observed effects to higher N$_2$ concentrations. For films deposited at 9 mTorr pressure, the TiN (111), (311) and (222) reflections were present at 2.4% N$_2$.

The TiN films deposited at 14 mTorr pressure exhibit high microhardness values (28 GPa up to 31.4 GPa) in the interval of nitrogen contents of 4 – 20%. Hardness dependence on the nitrogen content has been plotted in Figure 3.11. The maximum value of 31.4 GPa was observed at 5% of nitrogen in the gas
mixture. At nitrogen contents lower than 4% titanium nitride films displayed lower hardness values. At N₂ contents higher than 20% a steady decrease in the microhardness was observed with the rising nitrogen concentration.

![Graph showing microhardness vs. N₂ content](image)

**Figure 3.11.** Microhardness of TiN deposited at different nitrogen contents in the mixture with argon. Deposition pressure of 14 mTorr; 60 sccm total flow rate; 1200 W power. (Paper V, Figure 9.)

The deposition rate achieved in present experiments with the HoCET arrangement was 0.125 μm/min. In Section 1.3.2 higher deposition rates by hollow cathodes were reported for arc evaporation regimes. Nevertheless HoCET displays very competitive deposition rates with the conventional magnetron sputtering systems and possibility to obtain higher rates in the reactive TiN deposition than those in non-reactive Ti depositions. For example, polycrystalline TiN films have recently been deposited by reactive DC magnetron sputtering on steel substrates at a rate of 0.06 μm/min [99]. A similar deposition rate (to the DC magnetron) has been observed for films deposited by HiPIMS [100].

Due to the possibility to reach high deposition rates and high TiN hardness values, the conventional magnetron equipped with HoCET arrangement is very promising for practical applications and commercial use.
3.2.2 Comparison of AlN films prepared by HiPIMS and RHCPJ

AlN films were prepared by High Power Impulse Magnetron Sputtering (HiPIMS) of a planar magnetron target (Paper IV). The deposition rate and crystalline structure were analysed in relation to N\textsubscript{2} content in Ar+N\textsubscript{2} gas mixture and the deposition power. A higher deposition rate was reached when a deposition power of 450 W (80 \(\mu\text{s}\) pulse width) was employed. The highest deposition rate, 24 nm/min, was reached at 11.1% N\textsubscript{2} content. The AlN films grown under these conditions displayed a high degree of (002) crystalline orientation. With an increase in the N\textsubscript{2} content, the (002) texture became weaker until (100) oriented grains started to emerge at 21.6% N\textsubscript{2} content.

A similar trend in the deposition rate was observed for films grown at 250 W deposition power. The maximum growth rate of 14.5 nm/min was reached at 6.9% N\textsubscript{2}. At higher N\textsubscript{2} contents the deposition rate was lower. At 16.6% N\textsubscript{2} the growth rate dropped to approximately 8 nm/min. Regardless of the tested nitrogen content, films with the (002) preferred crystal orientation were not observed at lower powers. This can be explained with the lower ionization fraction (OES observations) and plasma density that results from reduced power supplied to the ionization process.

These effects are directly related to the observed increase in the target peak current values, in Paper IV. The nitrogen contents used for AlN film depositions bring about two deposition modes: transitional and compound. The deposition rate is higher at the transitional mode than in the compound mode. In the compound mode, the target is covered by a layer of AlN that decreases the Al release rate from the target. This effect is termed target poisoning.

In [101] and [102] it has been reported that hollow cathode systems (RHCPJ and linear hollow cathode) do not exhibit any target poisoning. In fact, an inverse relation of the growth rate with the increased N\textsubscript{2} admixture has been observed for AlN films deposited on silicon [68] and glass [70] substrates by RHCPJ plasma source. In PVD deposition mode (100% Ar, 0% N\textsubscript{2}) a growth rate of 40 nm/min has been observed [68]. When N\textsubscript{2} was used as the only process gas (0% Ar, 100% N\textsubscript{2}) the deposition rate of AlN increased up to 150 nm/min. The increase in deposition rate was accompanied by an identical increase of the optical emission intensity of molecular N\textsubscript{2}\textsuperscript{+} ions.

Compared with the results reported in Paper IV, the AlN deposition rate by the RHPCJ system, at the same N\textsubscript{2} content, is higher. At 11.1% N\textsubscript{2} the deposition rate is about 48 nm/min, which is 2 times higher than the examined HiPIMS process. In HiPIMS it was observed that the deposition rate decreased down to 13 nm/s at 21.6% N\textsubscript{2}. At a comparable N\textsubscript{2} content in RHCPJ a deposition rate of 55 nm/min was observed. It should be noted that the deposition with RHCPJ system was performed at a much lower deposition power than in Paper IV (70 W for RHCPJ and 450 W for HiPIMS). It also should be noted that in the HiPIMS system the lower deposition power yielded lower film growth rates.
At the lower nitrogen contents higher (002) preferred orientation was observed for AlN films deposited by HiPIMS. When deposited by RHCPJ the highest degree of (002) orientation was observed for films deposited at higher N₂ contents [68]. The strongest (002) XRD peak was observed for films deposited at 100% N₂. AlN coatings grown by RHCPJ at nitrogen contents less than 10% were a-axis oriented (dominant (100) crystalline orientation) and no c-axis orientation was observed ((002) XRD peak not detected). From OES examination it was observed that the growth of high quality AlN films in RHCPJ is facilitated by the increased concentration of molecular nitrogen gas ions at higher N₂ admixture degrees. At the same time an increase in Al metal release was not observed. This means an increased utilization efficiency of sputtered Al particles in the RF hollow cathode plasma jet system. It should be noted that in neither Paper IV, nor [68], additional substrate heating was employed.

Deposition by HiPIMS was performed at 250 W and 450 W, at 0.42 Pa (3.15 mTorr) to 0.46 Pa (3.45 mTorr) while the RHCPJ had been performed at 70 W, 0.67 Pa (5.03 mTorr). AlN deposition at a lower power level, in HiPIMS, has been performed by Aissa et al. [103]. Deposition of (002) oriented AlN films on silicon substrates was performed at a deposition power of 150 W and a slightly higher deposition pressure range of 0.4 – 1.6 Pa (3.00 – 12.00 mTorr). The N₂ content in Ar+N₂ mixture was 53.8% and no additional substrate heating was done. At such conditions, a maximum deposition rate of just 17 nm/min was reached. Considering the lower supplied pulse-modulated DC power level, the higher deposition rate can be explained by the difference in the deposition system design, i.e. the target-substrate distance is 30 mm instead of the 60 mm (Paper IV). This means that the activated species need to travel shorter distances to reach the substrate, which decreases the probability of neutralization through gas-phase collisions. In the RHCPJ system the deposition rate of 50% N₂ was reported to be higher (80 nm/min) [68], outlining the high potential of hollow cathode discharge based systems for AlN film deposition.
4. Conclusions

The goal of this thesis was to analyze the performance of selected deposition systems employing hollow cathodes for amorphous carbon, TiN and AlN deposition at moderate pressures. Amorphous carbon coatings were deposited by Radio frequency Hollow Cathode Plasma Jet (RHCPJ) and Magnets-in-Motion (M-M) linear hollow cathode plasma sources. TiN films were deposited by magnetron equipped with the Hollow Cathode Enhanced Target. The AlN film deposition by RHCPJ has been compared with a HiPIMS deposition system.

Amorphous carbon films

- Using the RHCPJ and M-M linear hollow cathode deposition systems it is possible to deposit hydrogenated amorphous carbon coatings with an $sp^3$ fraction of less than 20%.
- In the RHCPJ system adherent amorphous carbon coatings can be deposited at 0.35 Torr, 100 W and 0.1% of C$_2$H$_2$ content in Ar.
- The deposition process was successfully transferred to the M-M linear hollow cathode for large surface area modification. It is possible to deposit thick (up to 50 $\mu$m) films directly on glass substrates without an interlayer at 0.3 Torr, 1200 W and 2% C$_2$H$_2$.
- The possibility to control both the deposition rate and the coating adhesion using the C$_2$H$_2$ content in Ar+C$_2$H$_2$ mixture was demonstrated. Although very high deposition rates (2.5 $\mu$m/min) can be reached, films deposited at rates higher than 0.8 $\mu$m/min were self-delaminating. The deposited coatings were adherent up to 16 $\mu$m of thickness.
- The best adhesion was observed for films deposited at 0.25% and 0.5% C$_2$H$_2$ contents in Ar+C$_2$H$_2$ gas mixture where 4 $\mu$m and 7.5 $\mu$m thick films were grown respectively.
- Deposition process carried out at a PVD mode (Ar sputtering of cathode walls) showed low deposition rate (0.075 $\mu$m/min) and poor adhesion of the coating.

TiN films

Magnetron equipped with magnetized radio frequency HoCET exhibits similar effects, in the reactive deposition of TiN, to hollow cathodes. The HoCET provides approximately 140% increase in the reactive deposition rate of TiN over the non-reactive deposition rate of Ti films. High deposition rates
of TiN films are obtained at small nitrogen contents in Ar+N₂ gas mixture. Stoichiometric, polycrystalline TiN films can be deposited at rates of up to 0.125 μm/min (2.4% N₂ in Ar+N₂, 1200 W supplied RF power and 14 mTorr deposition pressure).

By employing the HoCET arrangement the coatings can be grown by pure nitrogen sputtering. At 100% of N₂ deposition rates are about 2.8x slower than the fastest rate. The microhardness of such coatings was 17 GPa. The TiN films deposited at smaller contents of nitrogen exhibit very high microhardness values. Coatings deposited in the interval of nitrogen contents of 4 – 20% exhibited hardness values above 28 GPa, reaching a maximum of 31.4 GPa at 5% of nitrogen in the gas mixture.

AlN films

For a (002) oriented AlN deposition the RHCPJ system offers very high deposition rates (up to 150 nm/min) as compared to the HiPIMS system, where a deposition rate of 24 nm/min was observed at comparable conditions. In both systems the N₂ can be used to control the deposition rate. Due to the absence of target poisoning in RHCPJ plasma source, higher deposition rates can be reached. The hollow cathode discharge based deposition systems can be a valid alternative to the HiPIMS deposition systems which require rather complicated pulsed power generators and deliver relatively low deposition rates.
5. Future work

**M-M linear hollow cathodes for amorphous carbon film deposition**

Adherent, thick amorphous carbon coatings have been deposited on glass substrates without an interlayer. Since adhesion is influenced by film thickness, an evaluation for the set of coatings deposited in Paper II, having identical thicknesses, should be carried out. This would allow a more reliable comparison of adhesion that neglects the influence of thickness.

For future work a more in-depth analysis of the films’ tribological properties could be carried out. Additional properties, such as surface roughness, nanohardness, stress, coefficient of friction, elastic modulus, wear resistance and $sp^3/sp^2$ ratio. The latter should be measured with such methods as EELS (Electron Energy Loss Spectroscopy) and/or NMR (nuclear magnetic resonance) as they are more reliable than the visible Raman spectra where the $sp^3$ sites are invisible. The band gap, contact angle and biocompatibility studies are also important characteristics that should be determined for other applications.

An exploration of how the properties change with varying deposition pressure, acetylene content, RF power or bias voltage would help to identify the commercial areas where the M-M system would be the most appropriate, offering high deposition rates and good adhesion primarily. The system could be scaled up, with e.g. larger deposition chamber, electrodes and a moving substrate holder to coat larger surface areas.

The research can be also steered in a more basic direction, to understand the plasma and coating surface growth. The first steps would be to use the Mass spectrometry and laser ablation spectroscopy for the plasma analysis. That would enable a further discussion on the plasma chemical reactions and the amorphous carbon film growth modes.

**HoCET for reactive deposition**

Hollow cathode discharge systems display very high deposition rates for crystalline TiN and AlN film deposition. The drawback of such systems is relatively small deposition area which often requires movement of large substrates. One reason why the High Power Impulse Magnetron Sputtering (HiPIMS) systems are gaining popularity is direct possibility to use well-known magnetron arrangements. To employ HiPIMS deposition the power source has to be replaced by rather expensive high pulsed power generator. As has been demonstrated in this thesis, a magnetron equipped with a magnetized Hollow
Cathode Enhanced Target (HoCET) is a very promising alternative for thin film coating deposition and commercial use. The HoCET arrangement would entail relatively low investment costs.

Further development and research of HoCET for thin film reactive deposition should be done in the future. Further investigation of deposited TiN film properties would indicate how effective the deposition system is. The physical properties, such as grain size, surface roughness, residual stress as well as abrasive wear and corrosion resistance, could also be investigated on the prepared samples. For commercial applications it would be useful to deposit films on other substrates, e.g. high speed steel and Al, Cu or Mg alloys. To test the versatility of the HoCET arrangement attempts to deposit other coatings like amorphous carbon, AlN, CrN, TiO₂, Al₂O should be investigated. This would require a change in the hollow cathode plate and target material and replacement of the nitrogen gas with another gas, e.g. oxygen for TiO₂ and Al₂O, or hydrocarbon gas for DLC deposition.
6. Summary of papers

Paper I

Paper I discloses a scale up of radio frequency hollow cathode plasma jet (RHCPJ) system for amorphous carbon deposition on glass substrates. The process was transferred from the cylindrical hollow cathode to a Magnets in motion (M-M) linear hollow cathode plasma source. The depositions were carried out at moderate pressures using argon, neon and acetylene gas mixtures. The effect of deposition pressure (0.07 Torr to 0.35 Torr), RF power (1000 W to 1200 W), and gas mixture has been analyzed. The use of optical emission spectroscopy (OES) for process control has been evaluated.

Thick and adherent amorphous carbon films were grown on microscope glass slides without an interlayer. Deposition rate of 800 nm/min was observed for 1200 W and 0.35 Torr depositions. Better adhesion is observed for films deposited at 0.07 Torr deposition pressure. It was demonstrated that OES hydrogen line $H_\beta/H_\alpha$ ratio can be successfully employed for process control.

The author has contributed to writing the Introduction and Experimental parts of the paper. The author has performed the XRD and adhesion analysis.

Paper II

Paper II further investigates the performance of M-M radio frequency linear hollow cathode plasma source to deposit amorphous carbon films on glass substrates without an interlayer. The depositions were carried out at deposition pressure of 0.3 Torr, 1200 W RF power using argon and acetylene gas mixture. The effect of acetylene gas content in the gas mixture on the deposition rate, film thickness and adhesion was evaluated.

It was possible to reach deposition rates of up to 2.5 $\mu$m/min yielding 50 $\mu$m thick, yet non-adherent films. The deposition rate increases with the acetylene content reaching the maximum at 2% C$_2$H$_2$. At higher acetylene contents lower deposition rates were observed. Adhesion analysis showed that several $\mu$m thick films with good adhesion can be deposited at C$_2$H$_2$ contents in a range of 0.25% to 0.5%.

The author has written the majority of the paper. The author carried out the XRD and adhesion analysis.
Paper III

Paper III investigates changes in microstructure of deposited amorphous carbon coatings on glass substrates at constant deposition pressures. The structure changes have been evaluated for the process transfer from the RHCPJ to the M-M linear hollow cathode deposition system. The structure changes have been evaluated for films deposited by M-M linear hollow cathode at varying acetylene contents. Structural changes were evaluated using Raman analysis.

The results reveal that for all deposited coatings the sp³ fraction is less than 20%. With the process transfer the film structure has changed considerably. The coatings deposited using the M-M linear hollow cathode plasma source are more hydrogenated and less amorphous. In the M-M linear hollow cathode a higher acetylene content brings about higher graphitic disorder in the film structure.

The author is the main author of the paper. The author did the Raman analysis.

Paper IV

Paper IV investigates deposition of AlN coatings by High Power Impulse magnetron sputtering (HiPIMS) at different deposition modes. The deposition modes were controlled by changing the N₂ content in Ar+N₂ gas mixture. The depositions were performed at moderate pressures (0.42 to 0.46 Pa), at 50 μs and 80 μs DC pulse widths. The results show that (002) textured AlN films with low surface roughness and residual stress can be deposited rather at transitional mode, rather than compound mode. Deposition at higher pulse modulated DC power yields higher deposition rates with lower residual stress values.

The author contributed to writing all parts of the paper. The author participated in the discussions on the deposition process, thickness evaluation and XRD analysis.

Paper V

Paper V investigates performance of magnetized hollow cathode enhanced target magnetron to deposit Ti and TiN coatings. The aim of the study was to test whether the deposition system exhibits rapid increase in the reactive deposition of TiN coatings as hollow cathodes. It was found that the effects are similar. The effects of nitrogen content in a mixture with argon on deposition rate, crystalline structure and hardness were investigated.

The Ti and TiN films were prepared at 9 mTorr and 14 mTorr deposition pressures with a supplied 1200 W RF power. By controlling N₂ content in
a gas mixture with argon reactive and non-reactive deposition modes were compared. At the 9 mTorr deposition pressure the N\textsubscript{2} content was varied from 0% (non-reactive mode) to 4.1% (reactive mode). At the 14 mTorr deposition pressure the N\textsubscript{2} contents were varied from 0% to 100%.

With a transition from the non-reactive to reactive deposition mode a rapid jump in the deposition rate can be observed at small N\textsubscript{2} concentrations. Higher deposition pressure shifts the optimum composition to higher nitrogen content. TiN films deposited at 14 mTorr pressure exhibit high hardness values (above 28 GPa and up to 31.4 GPa) in the interval of nitrogen content of 4 – 20%.

The author conducted the microhardness and XRD analysis. The author contributed to writing the Experimental section.
7. Sammanfattning på Svenska


Vidhäftande amorft-kol-deponering överfördes framgångsrikt från RHCPJ till den M-M linjära ihålig-katod plasma-källan. Filmer deponerades vid olika deponeringstryck, radiovägseffekt och $C_2H_2$ innehåll i Ar+$C_2H_2$ blandningen. Tjocka och vidhäftande amorft-kol-filmer kan deponeras i ett intervallet 0.25% till 0.5% $C_2H_2$, ett deponeringstryck på 0.3 Torr och radiovägseffekt på 1200 W som gav deponeringshastigheterna 0.2 $\mu$m/min respektive 0.375 $\mu$m/min. Självdelaminerande, tjocka (50 $\mu$m) amorft-kol-filmer kan deponeras vid deponeringshastighet 2.5 $\mu$m/min vid 2% $C_2H_2$. En icke-linjär relation observerades mellan deponeringshastighet och $C_2H_2$ innehåll. En anledning till detta kan vara den dominerande kemiska etsningen av atomärt väte
vid högre än 2% C₂H₂-innehåll. Sputtring med Fysisk förångningsdeposition ger icke-vidhäftande amorft-kol-filmer med låg deponeringshastighet.

Genom att använda en magnetron utrustad med HoCET är det möjligt att deponera stökiometriska, polykristallina TiN-filmer vid höga deponeringshastigheter. Den högsta deponeringshastigheten, 0.125 μm/min, uppnåddes vid 2.4% N₂, 1200 W RF-effekt och 14 m Torr-deponeringstryck. TiN-filmer deponerade i intervallet 4 – 20% N₂ uppvisade microhårdhet över 28 GPa och nådde ett högsta värde av 31.4 GPa vid 5% N₂. Det är möjligt att deponera TiN-filmer genom sputtring med bara kväve.

Deponering av (002)-orienterande AlN-filmer med RHCPJ utfördes vid hastigheter på upp till 150 nm/min. Genom att använda HiPIMS systemet vid jämföbara deponeringsförutsättningar kunde AlN-filmer produceras vid endast 24 nm/min.

Ihålig katod plasma-källor visar bra potential för framtida användning. Det kan hantera utmanande substrat, deponering över relativt stora ytor, och producerar tjocka, vidhäftande ytbeläggningar.
Līdz ar plāno kārtīnu uzklāšanas tehnoloģiju attīstību ir novērojams augsts tehnoloģiskais progress daudzās mūsu dzīves jomās (elektronika, optika, transports, medicīniskie implantāti). Neskatoties uz to, darbs pie pārklājumu uzneses procesu efektivitātes celšanas un kopējo izmaksu samazināšanas ir aktuāls un turpinās. Nākotnē perspektīvas pārklājumu uznešanas tehnoloģijas ir tās, kas balsītas uz dobo katodu plazmas izlādi.

Promocijas darbā pētīts izvēlētu dobo katodu plazmas izlādes avotu, kas ir izstrādāta Upsalas Universitātes Plazmas grupā, sniegums plāno kārtīnu uznešanā. Amorfa oglekļa plāno kārtīnu uznešanas pētniecība tika veikta ar radiofrekvences dobā katoda plazmas kūla (Radio frequency Hollow Cathode Plasma Jet (RHCPJ)) un rotējošo magnētu (Magnets-in-motion (M-M)) lineāro dobo katodu plazmas izlādes avotiem. Titāna nitrida (TiN) pārklājumu uznešana tika veikta izmantojot magnetronu, kas aprikojots ar magnetizētā dobā katoda uzlaboto mērķi (Hollow Cathode Enhanced Target (HoCET)). Aluminija nitrida (AlN) pārklājumu ieguve RHCPJ plazmas izlādes avotā tika salīdzināta ar ieguvi augstas jaudas impulsu magnetronās uznešanas (HiPIMS) iekārtā.


Ar RHPCJ iekārtu uzklātie amorfa oglekla pārklājumi izrādīja labu adhēziju. Lielāku virsmu apstrādei, pārklājumu ieguvšo process tika aprobēts M-M linārā dobā katoda plazmas izlādes avotā un tā darbība – pētīta. Pārklājumu ieguve tika veikta pie dažādiem uzneses spiedieniem, uzstādītās RF jaudas un C2H2 gāzes koncentrācijām Ar+C2H2 gāzu maisījumā. Nobīdes spriegums uz substrāta tika turēts nemainīgs – 500 W. Tika noskaidrota, ka biezi amorfa oglekļa pārklājumi, ar labu adhēziju iegustami pie 0.3 Torr spiediena, pie 1200 W RF jaudas un pie 0.25% līdz 0.5% C2H2 koncentrācijām kopējā gāzu maisījumā.
Acetilēna koncentrācijām atbilstošie uznešanas ātrumi bija 0.2 $\mu$m/min un 0.375 $\mu$m/min. Zems adhēzijas līmenis, bet ļoti augsts uznešanas ātrums (2.5 $\mu$m/min) raksturīgs pie 2% C$_2$H$_2$ koncentrācijas. Nelineāra kopsakarība tika novērota starp uznešanas ātrumu un C$_2$H$_2$ koncentrāciju. Pie augstākas acetilēna gāzes koncentrācijas tika novērota uznešanas ātruma samazinājums. Fizikālā tvaika izputināšanas režīmā pārklājumu ieguve noteik lēni, turklāt pārklājumiem tika novērota zema adhēzija.

Izmantojot mangetronu, kas aprīkots ar HoCET, iespējams iegūt stohiometriskus, polikristāliskus TiN pārklājumus pie augstiem uznešanas ātrumiem. Augstākais ātrums (0.125 $\mu$m/min) tika novērots pie 2.4% N$_2$ satura Ar+N$_2$ gāzu maisījumā, izmantotās 1200 W RF jaudas un 14 mTorr spiediena. TiN pārklājumi, kas tika uznesti 4 - 20% N$_2$ satura intervālā, izrādīja mikrocietību, kas pārsniedza 28 GPa. Viscietākie TiN pārklājumi, 31.4 GPa cieti, tika iegūti pie 5% N$_2$ satura gāzu maisījumā. Pārklājumus iespējams iegūt tīra slāpekla putināšanas apstāklos.

Iepriekš ticis noskaidrots, ka izmantojot RHCPJ plazmas izlādes avotu ir iespējams iegūt AlN pārklājumus ar (002) orientāciju pie uznešanas ātrumiem līdz 150 nm/min. Ar disertācijas ietvaros izmantoto HiPIMS iekārtu, salīdzināmos uzneses procesa apstāklos, (002) orientēti AlN pārklājumi bija iegūtami pie 24 nm/min uzneses ātruma.

Dobo katodu plazmas izlādes avotiem ir liels potenciāls plāno kārtinu uzneses procesos. Ar pētītājiem plazmas avotiem iespējams apstrādāt lielus virsmu laukumus un ir raksturīgi lieli pārklājumu uzneses ātrumi labas kvalitātes pārklājumu ieguvei.
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References


3875, 2006.


[73] F. Jing, T. Yin, K. Yukimura, H. Sun, Y. Leng, and N. Huang, “Titanium film deposition by high-power impulse magnetron sputtering: Influence of pulse


[88] N. Boutroy, Y. Pernel, J. Rius, F. Auger, H. Bardeleben, J. Cantin, F. Abel,


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