Pulsed-DC sputtered TIC/DLC nanocomposite coatings
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Chapter 2
DEPOSITION AND CHARACTERIZATION TECHNIQUES

2.1 Introduction

In this chapter, firstly, the PVD setup employed to deposit the nanocomposite coatings is described with a brief introduction to magnetron sputtering. Furthermore the characterization techniques viz. mass energy spectrometry (plasma characterization), Grazing incidence X-ray diffraction (nanostructure characterization), Atomic force microscopy (surface morphological characterization), Tribological testing (frictional and wear behavior), Confocal microscopy (characterization of wear and transfer film) and Raman microscopy (structural characterization) are briefly described. The microstructure of these coatings was scrutinized by high resolution scanning electron microscopy (SEM) and transmission electron microscopy (TEM). For description of SEM and TEM, the reader is referred to the previous PhD theses from our group.

2.2 PVD deposition setup

Physical vapor deposition and plasma enhanced chemical vapor deposition techniques were employed in this study to deposit the coatings. Magnetron sputtering has developed rapidly over the last decade to the point where it has become established as the process of choice for the deposition of a wide range of industrially important coatings.\(^1\),\(^2\) The driving force behind this development has been the increasing demand for high-quality functional coatings in many diverse market sectors.

In the basic sputtering process, a target (or cathode) plate is bombarded by energetic ions generated in a glow discharge plasma, situated in front of the target. The bombardment process causes the removal (i.e. sputtering) of target atoms, which may then condense on a substrate as a thin film.\(^2\) Secondary electrons are also emitted from the target surface as a result of the ion bombardment, and these electrons play an important role in maintaining the plasma. Magnetrons make use of the fact that a magnetic field can constrain secondary electron motion to the vicinity of the target.
Chapter 2

Figure 2.1 Effect of $\varepsilon$ and $B$ on electron motion. (a) Linear electron trajectory when $\varepsilon \parallel B$ ($\theta = 0$); (b) helical orbit of constant pitch when $B \neq 0$, $\varepsilon = 0$, ($\theta \neq 0$); (c) helical orbit of variable pitch when $\varepsilon \parallel B$ ($\theta \neq 0$) $^2$

When a magnetic field of strength $B$ is superimposed on the electric field $\varepsilon$ between the target and substrate, electrons within the dual field environment experience the well-known Lorentz force in addition to electric field force $^2$, i.e.,

$$F = \frac{mdv}{dt} = -q(\varepsilon + v \times B) \quad (2.1)$$

where $q$, $m$ and $v$ are the electron charge, mass, and velocity, respectively. In the case where $B$ and $\varepsilon$ are parallel as shown in Figure 2.1a. When electrons are emitted exactly normal to the target surface and parallel to both fields, then $v \times B$ vanishes; electrons are only influenced by the $\varepsilon$ field, which accelerates them toward the anode. Next consider the case where the $\varepsilon$ field is neglected but $B$ is still applied as shown in Figure 2.1b. If an electron is launched from the cathode with velocity $v$ at angle $\theta$ with respect to $B$, it experiences a force $qvB\sin\theta$ in a direction perpendicular to $B$. The electron now orbits in a circular motion with a radius $r$ that is determined by a balance of the centrifugal $(m(v\sin\theta)^2/r)$ and Lorentz forces involved, i.e., $r=m\nu\sin\theta/qB$. $^2$ The electron motion is helical; in corkscrew fashion and it spirals down the axis of the discharge with constant velocity $v\cos\theta$. If the magnetic field were not present, such off-axis electrons would tend to migrate out of the discharge and be lost at the walls. The case where electrons are launched at an angle to parallel, uniform $\varepsilon$ and $B$ fields is somewhat more complex. Corkscrew motion with constant radius occurs, but because of electron acceleration in the $\varepsilon$ field, the pitch of the helix lengthens with time $^2$ (Figure 2.1c). Time varying $\varepsilon$ fields complicate matters further and electron spirals of variable
radius can occur. Clearly, magnetic fields prolong the electron residence time in the plasma and thus enhance the probability of ion collisions. This leads to larger discharge currents and increased sputter deposition rates. Comparable discharges in a simple diode-sputtering configuration operate at higher currents and pressures, therefore, applied magnetic fields have the desirable effect of reducing electron bombardment of substrates and extending the operating vacuum range.

Figure 2.2 Applied fields and electron motion in a planar magnetron.2

In magnetrons, electrons ideally do not even reach the anode but are trapped near the target, enhancing the ionizing efficiency there. This is accomplished by employing a magnetic field oriented parallel to the target and perpendicular to the electric field, as shown schematically in Figure 2.2. Practically, this is achieved by placing bar or horseshoe magnets behind the target. Therefore, the magnetic field lines first emanate normal to the target, then bend with a component parallel to the target surface (this is the magnetron component) and finally return, completing the magnetic circuit. Electrons emitted from the cathode are initially accelerated toward the anode, executing a helical motion in the process; but when they encounter the region of the parallel magnetic field, they are bent in an orbit back to the target in very much the same way that electrons are deflected toward the hearth in an e-gun evaporator. By solving the coupled differential equations resulting from the three components of Eq. 2.1, we readily see that the parametric equations of motion are

\[
y = \frac{qE}{m\omega_c^2} (1 - \cos \omega_c t) \tag{2.2}
\]

\[
x = \frac{\alpha t}{B} \left(1 - \frac{\sin \omega_c t}{\omega_c t}\right) \tag{2.3}
\]

where \(y\) and \(x\) are the distances above and along the target, and \(\omega_c = qB/m\). These equations describe a cycloidal motion that the electrons execute within the cathode dark space where both fields are present. If, however, electrons stray into the negative glow
region where the $\varepsilon$ field is small, the electrons describe a circular motion before collisions may drive them back into the dark space or forward toward the anode. By suitable orientation of target magnets, a “race track” can be defined where the electrons hop around at high speed. Target erosion by sputtering occurs within this track because ionization of the working gas is most intense above it.

Magnetron sputtering is presently the most widely commercially practiced sputtering method. The chief reason for its success is the high deposition rates achieved. These are typically an order of magnitude higher than rates attained by conventional sputtering techniques. In an unbalanced magnetron the outer ring of magnets is strengthened relative to the central pole. In this case, not all the field lines are closed between the central and outer poles in the magnetron, but some are directed towards the substrate, and some secondary electrons are able to follow these field lines. Consequently, the plasma is no longer strongly confined to the target region, but is also allowed to flow out towards the substrate. Thus, high ion currents can be extracted from the plasma to the substrate. In a multiple magnetron system, as the one used in this study, the magnetic arrays in adjacent magnetrons can be configured with opposite magnetic polarities. In this case the configuration is described as closed field. In closed field configuration, the field lines are linked between the magnetrons. Losses of the secondary electrons to the chamber walls are low and the substrate lies in a high density plasma region.

In this research, a TEER UDP400/4 sputtering system (Figure 2.3) was used to deposit coatings. The vacuum chamber is made up of stainless steel, and is double-walled to allow water cooling. Its internal diameter and height are 400 mm.
The system consists of four magnetrons, in a closed field unbalanced configuration, coupled to four targets with the geometry shown in Figure 2.4. The size of all the targets was 200×100 mm². The magnetrons 2 and 4 are powered by a Pinnacle Plus 5/5 kW double channel p-DC power supply (Advanced Energy) and the magnetrons 1 and 3 are powered by a Pinnacle 6/6 kW double channel DC power supply. Magnetron 1 and 3 were coupled with Ti and Cr targets, respectively. Magnetron 2 and 4 were coupled with two graphite targets each, for the deposition of TiC/a-C nanocomposite coatings (Ar environment), whereas these magnetrons were coupled to two Ti-targets each for the deposition of TiC/a-C:H nanocomposite coatings (in Ar+C₂H₂ environment). All the power units for sputtering were operated in current-control mode. The substrates were biased by a Pinnacle Plus 5 kW single channel p-DC power supply (Advanced Energy). The pumping system consists of a oil-free turbomolecular pump backed by a rotary pump. The base pressure of the chamber before deposition was 3-4×10⁻⁶ mbar. The substrates were first ultrasonically cleaned in acetone followed by Ar plasma etching for 15 minutes at p-DC -400 V bias voltage at 250 kHz and 87.5 % duty cycle. The substrate holder was rotated by 3 rpm. No external heating was applied to the substrates.
A Hiden EQP 300 mass and energy analyzer was used to study the \( \text{Ar}^+ \) ion energy distribution function (IEDF) function at the substrate. The experimental setup includes a single unbalanced magnetron sputtering system, GENLAB (GENCOA Ltd), installed with a \( \varnothing 150 \text{ mm} \) circular magnetron, with the mass energy spectrometer attached. Figure 2.5 shows the schematic showing the relative positions of the target and the probe of the mass energy spectrometer. It had a typical unbalanced configuration of adjustable magnetic field strength, which was set to resemble the field strength of the magnetrons installed in the TEER UDP400/4 rig. The single magnetron was powered with a 5kW Pinnacle Plus unit and operated at comparable sputtering parameters used for coating deposition. The extractor head of the EQP300 instrument was pointed to the racetrack of the target and fixed directly behind a metallic substrate at 100 mm distance to the target, which had a large opening hole that was covered with a fine nickel grid and aligned with the entrance orifice (\( \varnothing 100 \text{ µm} \)) of the extractor. The instrument is commercially available, and has been described in detail elsewhere.\(^5\) The ion energies were effectively measured with reference to ground potential of the chamber wall. The counts of \( \text{Ar}^+ \) ions in each energy bin \( <E, E+dE> \), where \( dE = 0.1 \text{ eV} \) was the energy resolution of the instrument, were accumulated for 10 ms time period and one scan of the whole energy spectra took 20 seconds. Therefore, the ion counts of different energies were a direct measure of the ion flux and it can be confidently compared among the measurements, provided the instrument settings remained unchanged.

![Figure 2.6 Waveforms of 1.25A p-DC sputtering graphite target at 200 kHz and different duty cycles: (a) voltage and (b) current.](image)

The mass energy spectrometry results presented here are based on Ref. 7. Figure 2.6 presents the \( p-\text{DC} \) voltage and current waveforms applied to the graphite target at 1.25A of sputtering current. The voltage waveform of the asymmetric bipolar pulsed DC exhibited three characteristic periods: the pulse on period A of negative voltage, the transition period B and the pulse off or reverse period C (see Figure 2.6a), which are well documented in literature.\(^5\)
The duty cycle of DC pulses was defined as the percentage of the pulse-on period to the whole pulse cycle. The significant features of the asymmetric bipolar $p$-DC power supplies used in this research include the overshoot peak of high positive voltage (around 500 V in this case) in the transition period B and the adjacent oscillating peaks as well as the small positive voltage remaining during the reverse period C. During this transition and onset of the reverse period, correspondingly, the current waveform possessed several current peaks of amplitude strongly depending on the duty cycles used (Figure 2.6b). For instance, the current peaks at 50% duty cycle were of 13 A, 6.5 A, 4 A, 1.5 A, etc., and the strongest peak was one order of magnitude as high as the nominal current (1.25 A).

Figure 2.7 Energy distribution of impinging $Ar^+$ ions incident on the growing coatings during sputtering graphite target with DC or pulsed DC at different frequencies (a) and at 200 kHz of different duty cycles (b); (c) flux of impinging $Ar^+$ ions in three energy ranges as well as the sum at different $p$-DC frequencies of 50% duty cycle (substrate grounded). The hatched part of the columns is the missed flux due to the cutoff of the energy spectrometer beyond 195 eV, estimated according to the fraction of the reversing period in a pulse for different frequencies.

The time averaged energy distribution and the flux of the impinging $Ar^+$ ions during sputtering graphite are shown in Figure 2.7. The IED curves of the impinging $Ar^+$ ions under $p$-DC magnetron sputtering showed three distinct populations of the ions that reflect the target voltage waveforms. That is to say, impingements of $Ar^+$ ions of low
energy (< 20 eV, peak A in Figure 2.7a) occurred during the pulse-on period, supported by the fact that DC magnetron sputtering produced only the low energy ions of the same category. The ions of intermediate energy (20-50 eV, peak C in Figure 2.7a) were generated during the reverse period, which was evident because the population of this category ions diminished with decreasing reverse period (i.e. increasing the duty cycle at a chosen p-DC frequency), as shown in Figure 2.7b. Those ions of high energy extending over 200 eV were created during the transition period, accelerated by the high potential fall (positive voltage peaks) towards the grounded substrate. Because of the detection limit of the energy spectrometer, the energy distribution function curves at a p-DC frequency above 200 kHz were partly cut off beyond 195 eV. As shown in Figure 2.7c, the flux of the total impinging Ar+ ions at p-DC sputtering mode of low frequencies (e.g. 100 kHz) was comparable with that of DC magnetron sputtering. However, the total ion flux dramatically increased with increasing the frequency beyond 100 kHz. The flux of total impinging ions differed by one order of magnitude between DC sputtering and p-DC sputtering at high frequencies. It is clear that the energy distribution function of the impinging Ar+ ions was governed by the sputtering mode: p-DC frequency and the duty cycle.

In comparison with sputtering of graphite target, the voltage in the pulse on period was lower, with about 500 V in sputtering Ti versus 900 V in sputtering C. Especially, the overshoot peaks of voltage and current measured during sputtering titanium were much lower (see Figure 2.8a), only about one third of the amplitudes of those peaks observed in the former case. As a result, the energy spread of the high energy Ar+ ions was reduced (Figure 2.9a). This led to a lower ion flux at each p-DC frequency (Figure 2.9b), even though the sputtering current of 2.5 A is doubled on Ti target of the same size. Similar results of impinging Ar+ ion energy distribution as a function of p-DC frequency were observed during sputtering Ti target, as shown in Figure 2.9.

Figure 2.8 Waveforms of 2.5A p-DC sputtering titanium target at 200 kHz and different duty cycles: (a) voltage and (b) current.
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Figure 2.9 (a) Energy distribution of impinging Ar\(^+\) ions incident on the growing coatings during sputtering Ti target with DC or pulsed DC of different frequencies and (b) flux of the Ar\(^+\) ions in three energy ranges as well as the sum at different p-DC frequencies (substrate grounded).

In particular, the impinging ions in the intermediate and high energy bands became more and more dominant with increasing p-DC frequency, delivering much higher energy for impingement to the growing coatings. To confirm this point, the product of the time-averaged ion count in each energy bin and the energy scale under the IED curves in Figure 2.7a and Figure 2.9a was integrated over the measured energy range and the results are shown as energy flux in Figure 2.10.

Figure 2.10 Energy flux delivered to the growing interface by impinging Ar\(^+\) ions: (a) during sputtering C with 1.25A current and (b) during sputtering Ti with 2.5A current DC or p-DC at different frequencies. The hatched part of the columns is the missed flux due to cutoff of the high energy ions beyond the limit of the energy spectrometer.

It is clear that the energy flux of impinging Ar\(^+\) ions under high frequencies p-DC sputtering was two orders of magnitude larger than that delivered at DC sputtering. Due to different electrical characteristics conductivity and sputtering behavior of different target materials, in particular, p-DC sputtering graphite target delivers even higher energy flux of impinging ions than sputtering titanium target (e.g. \(1.26 \times 10^{15}\) versus \(2.69 \times 10^{14}\) eVs\(^{-1}\)cm\(^{-2}\) at 350 kHz), although the nominal sputtering current was half of the latter case.
(1.25 A versus 2.5 A). However, the energy flux dropped significantly at low p-DC frequencies, for instance at 100 kHz or lower. The key parameters of concurrent ion impingement are the flux of the impinging ions and energy delivered. The enhanced total ion flux measured in Figure 2.7c and Figure 2.9b can be ascribed to the higher average plasma density under p-DC sputtering. In view of this, p-DC discharge is able to transform more electrical energy into the average plasma density and electron temperature than compared to the DC discharge, even if the average power delivered to both the discharges is the same. In other words, p-DC discharge more efficiently transfers plasma energy to the growing thin coating. The Ar$^+$ ion energy distribution spectra clearly demonstrated that the ion counts in the high energy bins were lower than those in the low energy bins. However, due to the wide energy spread, the total flux of the high energy ions delivered in the period B increases with increasing pulse frequency and it becomes comparable to the flux of those low energy ions delivered during the period A and C at high pulse frequencies (see Figure 2.7c and Figure 2.9b).

In the pulsing regime of the asymmetric bipolar pulsed DC power supplies, the duration of the pulse transition period B is a system constant of approximately 200 ns independent of the pulse frequency and duty cycle. As pulse frequency increases, the proportion of the transition period B in a pulse cycle increased and the overshoot voltage increases. Therefore, its contribution to the delivery of impinging Ar$^+$ ions of high energy must increase as well. Furthermore, cathode current waveforms reveal that the discharge electron current during the cathode overshoot period B noticeably increases with pulse frequency\textsuperscript{7}, besides the reversal of the flow direction. The lack of bulk electrons during this period causes the plasma sheath adjacent to the grounded substrate/orifice to expand more with increasing pulse frequency. As a result, the volume of ion sheath in the front of the orifice is getting larger with pulse frequency and consequently the number of ions attracted onto the growing coating or into the energy spectrometer during the pulse transition period B increases as shown in Figure 2.7c and Figure 2.9b. These effects result in a much higher total energy flux to the substrate.

In comparison with the high flux of impinging Ar$^+$ ions, the flux of ions of sputtered material was rather low even under p-DC sputtering.\textsuperscript{7} The energy distribution of Ti$^+$ ion was very similar to the IED curves of Ar$^+$ ions presented in but the counts were nearly two orders of magnitude lower in all the energy bins. Similarly, the counts of C$^+$ ions were three orders of magnitude lower than that of the Ar$^+$ ions for all the p-DC frequencies.

Besides the enhancement of the flux and energy distribution of impinging ions, another significant feature of p-DC magnetron sputtering is the expansion of the plasma.\textsuperscript{7} At higher pulse frequency, the plasma covers the entire substrate and also fills in the whole chamber. It is this expanded plasma that keeps the growing coating under intensive
and in particular continuous impingement when passing from one target to another in a closed-field configuration of multi-targets sputtering system. At 350 kHz, the enhanced flux and impinging energy of argon ions to the growing coatings and the grounded walls bring about increased generation of secondary electrons. These electrons are accelerated back to the plasma and gain kinetic energy through the plasma sheath which enables them to excite or ionize atoms and molecules of working gas. As a result of this processes, glow discharge was observed not only between the target and substrate but also in the whole chamber.\(^7\)

Thus, \(\text{Ar}^+\) ion energy flux delivered to the substrate strongly depends on the shape and magnitude of the cathode voltage overshoot (pulse transition period \(B\)) and also on the material of which the target is made. A difference between magnitudes of ionization potential, sputtering yield and secondary electron emission coefficient of carbon and titanium can affect plasma parameters, cathode voltage and current waveforms. These parameters are then crucial in determining the plasma intensity and ion energy flux onto the growing coating.

2.3 Characterization techniques:

2.3.1 Grazing incidence X ray diffraction:

The principle of this technique is based on the detection of a diffracted beam when the Bragg diffraction condition \(2d_{hkl} \sin \theta = n\lambda\) is fulfilled, where \(d\) is the space between the planes, \(\theta\) is the diffraction angle, \(n\) is the order of the diffraction peak and \(\lambda\) is the wavelength of the x-rays.

![Figure 2.11 Geometries for a) bulk analysis and b) thin coating analysis showing differences in the beam path lengths.](image)

It is sometimes very difficult to analyze thin coatings due to their small diffracting volumes, which result in low diffracted intensities compared to the substrate and background. This combination of low diffracted signal and high background make it very difficult to identify the phases present. Accordingly, special techniques must be used
when analyzing thin coatings. The most common technique for analyzing thin coatings as thin as 100 Å is to use a grazing incidence angle arrangement combined with a parallel beam geometry. By increasing the path length of the incident X-ray beam through the film, the intensity from the film can be increased so that conventional phase identification analysis can be run. Figure 2.11 compares the grazing incidence angle geometry used for thin coating with the more common, \( \theta/2\theta \) geometry used for bulk analysis. In the conventional \( \theta/2\theta \) geometry, a parafocusing arrangement is used where the X-ray source and the detector slit are at the focal points of the incident and diffracted beams, respectively. For the thin coating arrangement, on the other hand, the incident and diffracted beams are made nearly parallel by means of a narrow slit on the incident beam and a long soller slit on the detector side. In addition, the stationary incident beam makes a very small angle with the sample surface (typically 1° to 3°), which increases the path length of the X-ray beam through the coating. This helps to increase the diffracted intensity, while the same time, reduces the diffracted intensity from the substrate. Overall, there is a dramatic increase in the film signal to the background ratio. Since the path length increases when the grazing incidence angle is used, the diffracting volume increases proportionally. This is the reason for the increased signal strength. During the collection of the diffraction spectrum, only the detector rotates through the angular range, thus keeping the incident angle, the beam path length, and the irradiated area constant. The long soller slit on the receiving side allows only those beams that are nearly parallel to arrive at the detector. This has an added advantage of reducing the sensitivity to sample displacement from the rotation axis.

\[ \text{Figure 2.12 Grazing incidence XRD spectra of about 1µm thick TiC/a-C:H nanocomposite coating deposited on Si with a TiCr interlayer inbetween.} \]

A single circle diffractometer (Bruker D8 ADVANCE) was used with an grazing angle of 1.5°, with a CuK\( \alpha \) radiation (\( \lambda=1.540 \) Å) generator operated at 40kV and 40mA. Figure 2.12 is a typical grazing incidence XRD spectra of TiC/a-C:H nanocomposite coating, where the nanometer range size of the diffracting TiC crystals causes broadening of the peaks. The average size (d) of the nanocrystallites can be estimated from the full
width at half maximum (FWHM) of the peaks and its diffraction angle by using Scherrer equation:

\[ d = 0.9 \frac{\lambda}{\cos \theta \cdot \text{FWHM}_{\text{peak}}} \]  \hspace{1cm} (2.4)

where the FWHM should be introduced in radians to maintain the unit of \( \lambda \) for \( d \).

2.3.2 AFM

Figure 2.13 Picture of AFM (Veeco NanoScope IIIa and Dimension 3100 AFM).

In this work, the surface morphology of the nanocomposite coatings, and the surface roughness evolution of the coatings with sliding distance were investigated by a Digital Instrument NanoScope IIIa and Dimension 3100 atomic force microscope (Figure 2.13) with a Si tip of nominal 10 nm radius in tapping mode. The atomic force microscope (AFM) was invented by Binning et al. in 1986. The AFM measures the forces acting between a fine tip and a sample. The tip is attached to the free end of a cantilever and is brought very close to a surface. Attractive or repulsive forces resulting from interactions between the tip and the surface will cause a positive or negative bending of the cantilever. The bending is detected by means of a laser beam, which is reflected from the back side of the cantilever. Figure 2.14a shows the basic concept of AFM. The AFM is mainly based on probe, which represents a micromachined cantilever with a sharp tip at one end, which is brought into interaction with the sample surface. Each probe has different specifications and shape. V-shaped cantilevers are the most popular (but also there are rectangular), providing low mechanical resistance to vertical deflection, and high resistance to lateral torsion. Cantilevers typically range from 100 to 200 µm in length, 10 to 40 µm in width, and 0.3 to 2µm in thickness.
Integrated cantilevers are usually made from silicon (Si) or silicon nitride (Si₃N₄). They are characterized by their force constant and resonant frequency. An optical detection system and electronics for the management of scanning procedures and data acquisition are necessary. To detect the displacement of the cantilever, a laser is reflected off the back of the cantilever and collected in a photodiode. The diode is divided into four parts, as seen in Figure 2.14b. When the laser is displaced vertically along the positions top (B-A) and bottom (D-C), there exists a bending due to topography, while if this movement is horizontal left (B-D) and right (A-C), it produces a torsion due to “friction” (lateral force). The differential signal between the top two elements and the two bottom elements provides a measure of the vertical deflection of the cantilever. Similarly, the differential signal between the sum of the two left elements and the sum of the two right elements provides a measure of the torsion in the cantilever.

The AFM can be used in different modes of operations. In the so-called contact-AFM mode, the tip makes soft “physical contact” with the surface of the sample. The deflection of the cantilever $\Delta x$ is proportional to the force acting on the tip, via Hook’s law, $F=-k \times \Delta x$, where $k$ is the spring constant of the cantilever. In contact-mode, the tip either scans at a constant small height above the surface or under the conditions of a constant force. In the constant height mode, the height of the tip is fixed, whereas in the constant-force mode the deflection of the cantilever is fixed and the motion of the scanner in $z$-direction is recorded. By using contact-mode AFM, even “atomic resolution” images are obtained. For contact mode AFM imaging, it is necessary to have a cantilever which is soft enough to be deflected by very small forces and has a high enough resonant frequency to not be susceptible to vibrational instabilities. Silicon Nitride tips are used for
contact mode. In these tips, there are 4 cantilever with different geometries attached to each substrate, resulting in 4 different spring constants. To avoid problems caused by capillary forces which are generated by a liquid contamination layer usually present on surfaces in air, the sample can be studied while immersed in a liquid. This procedure is especially beneficial for biological samples.

In non-Contact Mode, the probe operates in the attractive force region and the tip-sample interaction is minimized. The use of non-contact mode allowed scanning without influencing the shape of the sample by the tip-sample forces. In most cases, the cantilever of choice for this mode is the one having high spring constant of 20-100 N/m so that it does not stick to the sample surface at small amplitudes. The tips mainly used for this mode are silicon probes.

Another mode of operation is Tapping mode (intermittent contact mode). The force measured by AFM can be classified into long-range forces and short range forces. The first class dominates when we scan at large distances from the surface and they can be Van der Waals force, capillary forces (due to the water layer often present in an ambient environment). When the scanning is in contact with the surface the short range forces are very important, in particular the quantum mechanical forces (Pauli Exclusion Principle forces). In tapping mode-AFM the cantilever is oscillating close to its resonance frequency. An electronic feedback loop ensures that the oscillation amplitude remains constant, such that a constant tip-sample interaction is maintained during scanning. Forces that act between the sample and the tip will not only cause a change in the oscillation amplitude, but also change in the resonant frequency and phase of the cantilever. The amplitude is used for the feedback and the vertical adjustments of the piezoscanner are recorded as a height image. Simultaneously, the phase changes are presented in the phase image. The advantages of the tapping mode are the elimination of a large part of permanent shearing forces and the causing of less damage to the sample surface, even with stiffer probes. Different components of the sample which exhibit difference adhesive and mechanical properties will show a phase contrast and therefore even allow a compositional analysis. Silicon probes are used primarily for Tapping Mode applications.

In summary, in these modes we can work in different environments: air, liquid and vacuum. In contact mode the tip touches the sample surface, which leads to a high force and allows manipulation of the sample. The disadvantage is that the AFM tip may be contaminated by the sample. The opposite happens in the noncontact mode, where the tip stays at a distance above the sample. In tapping mode the tip touches the surface periodically therefore manipulation of the sample, as well as contamination of the tip is possible.
2.3.3 Tribological testing:

Friction is the dissipation of energy between sliding bodies. The coefficient of friction is calculated from the ratio of frictional force to applied normal force. There are many designs of friction measuring setups: these can be classified in terms of range of load, range of speed, atmosphere in which they function, reciprocating vs. continuous motion, rotating vs. linear motion, spherical or cylindrical or flat shapes of sliding members, etc. Many setup configurations are available for purchase but all are variants of the basic motion-producing and force-measuring components.

![Figure 2.15 Schematic of ball on disk configuration (CSM High temperature tribometer).](image)

A ball-on-disk configuration (Figure 2.15) is used in this study and described here. A flat or a sphere indenter is loaded onto the test samples with a precisely known weight. The pin or ball in mounted on a stiff lever, designed as a frictionless force transducer. As the disc rotates, the resulting frictional forces acting between the pin and the disc are measured by very small deflections of the lever using a LVDT sensor. Wear behavior for both the pin and the samples can be analyzed by measuring the respective volume loss during a specific friction run. This simple method facilitates the determination and study of friction and wear behavior of almost every solid state material combination, with varying time, contact pressure, sliding velocity, temperature, humidity, lubricants, etc.

The coatings were deposited on Si wafer, which were glued on steel disks and Φ6 mm 100Cr6 steel and Si₃N₄ ball counterparts were used to study the tribological performance of the coatings. The tests were performed for 10000 laps at a sliding speed of 10 cm/s, normal load of 5 N, at room temperature (20-23 °C), and constant relative humidity of 50%. The wear track radius in the range of 8-10 mm was used. 3D confocal micrographs of the wear tracks on the coatings were captured to measure the wear volume for calculation of the wear rates of the coatings. In the ball-on-disk configuration an area of the ball is continuously in contact with the coating, whereas the corresponding areas on the coated sample are in contact only once during a lap. The wear rate of the
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coatings is defined as the volume of wear per unit track length, per Newton of normal load and per lap. Although the calculated value of the wear rate according to this definition is exactly the same as calculated from the total sliding distance of the ball (equal to the product of laps and perimeter of the wear track), its physical meaning is different from the commonly used dimension “mm³/Nm” of wear rate. The latter is valid only for the configuration of a coated ball sample sliding against a disk. The wear volume of the steel ball, after the tribotest, was calculated by approximating the worn volume to a spherical cap. Since the height of the cap is much smaller than the ball radius R (3 mm), the wear volume can be approximated to \( \frac{\pi d^4}{64R} \) where \( d \) is the wear scar diameter.

Optical and confocal microscopy was used to characterize the transfer film formed on the steel ball after the tribotest. The thickness of the transfer film was measured on three-dimensional images (512×512 pixels) of the wear scar on the steel ball, captured by confocal microscope after ultrasonically removing the wear debris. The WSxM® 4.0 Develop10.2 free software was used to select the pixels having transfer film on the confocal micrograph. The average and maximum thickness of the transfer film was then calculated by considering the z values all these pixels.

2.3.4 Confocal microscope:

![Confocal microscope diagram](image)

**Figure 2.16 Operating principle of Confocal microscope, where BS is beam splitter, MO is multiple pinhole disc. Only the light reflected from the surface which is in focus is transmitted to the CCD camera. (Nanofocus® µsurf confocal microscope).**

A confocal microscope is typically used to capture topographic height images over micrometer scales. A Nanofocus® confocal microscope was used to capture 3D images.
of wear tracks on the coatings, in order to calculate the wear rate, and also was used to characterize the transfer film formed on the ball counterparts after sliding against the coatings. The schematic of the confocal microscope is shown in Figure 2.16. The whole sensing head of the confocal microscope moves vertically by a stepper motor and/or only the objective moves in the vertical direction (z axis) by means of piezo drive. The unit scans a batch of various height levels of the surface to be measured. As whole areas are usually measured, the sample is not moved laterally during a measurement. The size of the measurement area depends on the applied objective and is listed in Table 2.1.

Table 2.1 Measurement field values, working distance, resolution and other optical parameters for different objectives used for confocal imaging:

<table>
<thead>
<tr>
<th>Objective</th>
<th>20X</th>
<th>50X</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measurement field (µm x µm)</td>
<td>700x660</td>
<td>290x280</td>
</tr>
<tr>
<td>Numerical Aperture</td>
<td>0.46</td>
<td>0.8</td>
</tr>
<tr>
<td>Working distance (mm)</td>
<td>3.1</td>
<td>0.66</td>
</tr>
<tr>
<td>Vertical resolution (nm)</td>
<td>40</td>
<td>15</td>
</tr>
</tbody>
</table>

The surface to be measured is illuminated through the microscope by an external xenon light source. Only those light beams which are focused on the detector (CCD chip) reach it. All unfocused light beams; i.e. all which are not at the same height are displayed by a pinhole. In such a way, a single point can be measured. The pinhole of the measurement head consists of a rotating Nipkow disk with approximately 120000 pinholes, which acts as multiple point sources scanning the surface. Surface areas which are at the same height level are mapped on the CCD chip. These height level records can then be joined to form a 2 or 3 dimensional image.

2.3.5 Raman spectroscopy

The chemical structure of the coatings was studied by Raman spectroscopy. Raman spectroscopy is a standard nondestructive tool for the characterization of crystalline, nanocrystalline, and amorphous carbons. Raman is light scattering by the change in polarisability $\chi$ due to lattice vibration

\[ \chi^{(k)} = \chi_0 + \frac{d\chi}{dq} Q(k,q) \quad (2.5) \]

where $\chi$ is the polarisability at wavevector $k$, and $Q$ is the amplitude of phonon of wavevector $q$. This change in polarisability causes an inelastic scattering of an incident photon $(\omega,k)$ into the scattered photon $(\omega',k')$. $(\omega$ is the phonon frequency). In amorphous materials, Raman spectrum corresponds to vibrational density of states (VDOS) $G(\omega)$ weighted by the appropriate matrix element $G(\omega)$ according to the Shuker-Gammon formula

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The above equation describes quite well the Raman spectra of a-Si and a-Ge, which are sp³ bonded only, by using a broadened version of the crystalline VDOS as $G(\omega)$. The visible Raman spectra of disordered carbons are in marked contrast. The Raman spectra of all disordered carbons are dominated by the relatively sharp G and D features of the sp² sites. This is because the π states are much more polarisable due to much greater cross section than that of σ states. The Raman spectra of DLC mainly show one or two prominent features, the G peak around 1580–1600 cm⁻¹ and the D peak around 1350 cm⁻¹. The Raman spectrum is considered to depend on (1) clustering of the sp² phases, (2) bond disorder, (3) presence of sp² rings or chains, and (4) the sp²/sp³ ratio. These factors act as competing forces on the shape of the Raman spectra, as shown schematically in Figure 2.17.

![Figure 2.17 Schematic diagram of influences on the Raman spectra. A dotted arrow marks the indirect influence of the sp³ content on increasing G position.](image)

The key property of interest in DLC is the sp³ content. Raman spectroscopy is widely used on DLC’s, and for a given restricted range of conditions, it is possible to indirectly derive the sp³ content. The spectra are fitted by a Breit-Wigner-Fano (BWF) line for the G peak and a Lorentzian for the D peak. The BWF line shape is given by:

$$I(\omega) = \frac{n(\omega) + 1}{\omega} C(\omega) G(\omega)$$  \hspace{1cm} (2.6)

where $I(\omega)$ is the peak intensity, $n(\omega)$ is the peak position, $C(\omega)$ is the broadening function, and $G(\omega)$ is the underlying vibrational density of states. The full width at half maximum (FWHM) and $Q$ are assumed as the full width at half maximum (FWHM) and $Q^{-1}$ is the coupling or skewness coefficient.
The Lorentzian line shape is recovered in the limit $Q^{-1} \to 0$. Note that because of skewness, the maximum of BWF occurs at

$$\omega_{\text{max}} = \omega_0 + \frac{\xi}{2Q} \quad (2.8).$$

Ferrari and Robertson\textsuperscript{12} have shown that it is possible to classify the Raman spectra of amorphous carbon with a three stage model, ranging from graphite to ta-C, as shown in Figure 2.18. The DLC based coatings studied in this work fall in stage 2 and hence it is described here. For the other stages, a reference is made to Ref. 12. In stage 2, defects are progressively introduced into the graphite layer, causing its phonon modes to soften, particularly the G peak. The Shuker-Gammon formula applies, and the VDOS is no longer that of graphite. The end of stage 2 corresponds to a completely disordered, almost fully sp\textsuperscript{2}-bonded a-C consisting of distorted sixfold rings or rings of other orders (≈ maximum 20% sp\textsuperscript{3}). The G peak decreases from 1600 to ≈1510 cm\textsuperscript{-1} and $I(D)/I(G) \to 0$. This indicates an introduction of sp\textsuperscript{3} sites into a structure composed only of sixfold rings.\textsuperscript{12}
All measurements were recorded under the same conditions (10 s of integration time and 10 accumulations) using a 100x magnification objective and a 100 µm pinhole. The spectra were analyzed by the fitting procedure described above.

References

1 P.J. Kelly, R.D. Arnell, Vacuum 56 (2000) 159