STUDIES ON DIAMOND-LIKE CARBON AND NOVEL DIAMOND-LIKE CARBON POLYMER HYBRID COATINGS DEPOSITED WITH FILTERED PULSED ARC DISCHARGE METHOD

Esa Alakoski

ORTON Orthopaedic Hospital
ORTON Research Institute
The Invalid Foundation
Department of Medicine, University of Helsinki
and
Helsinki University Central Hospital, Helsinki, Finland

ACADEMIC DISSERTATION

To be presented, with the permission of the Medical Faculty of the University of Helsinki, for
public criticism in the auditorium of the Invalid Foundation,
Tenholantie 10 on November 4th, 2006 at 12 noon.

HELSINKI 2006

Supervised by:

Professor emeritus Asko Anttila, PhD, Physics
University of Helsinki
ORTON Research Institute

Veli-Matti Tiainen, PhD, Physics
ORTON Research Institute

Reviewed by:

Professor Juha-Pekka Hirvonen, PhD, Physics
Institute for Energy (IE)
Joint Research Centre (EU)
Petten (Netherlands)

Professor Nureddin Ashammakhi, MD, PhD
Institute of Biomaterials
Tampere University of Technology

Discussed with:

Professor emeritus Folke Stenman, Dr. Tech.
Molecular Physics
Department of Physical Sciences
University of Helsinki

ISBN 952-9657-33-1 (printed version)
ISBN 952-10-3408-4 (PDF version)
ISSN 1455-1330
Yliopistopaino
Helsinki 2006
http://ethesis.helsinki.fi/

Cover photo: A carbon-polymer arc discharge.
Plasma is bright and dense as it flies through the
ring-shaped anode. The sample can be seen on the left.

E. Alakoski: **Studies on diamond-like carbon and novel diamond-like carbon polymer hybrid coatings deposited with filtered pulsed arc discharge method**, University of Helsinki, 2006, 45 p.+appendices, ISSN 1455-1330, ISBN 952-9657-33-1 (printed version), ISBN 952-10-3408-4 (PDF version)

Classification (INSPEC): A8100
Keywords (INSPEC): diamond-like carbon, tetrahedral amorphous carbon, filtered pulsed arc discharge (FPAD) method, adhesion, quality, plasma energy, novel coatings, novel materials, hydrophobic phenomena, contact angle, sliding angle

ABSTRACT

The main obstacle for the application of high quality diamond-like carbon (DLC) coatings has been the lack of adhesion to the substrate as the coating thickness is increased. The aim of this study was to improve the filtered pulsed arc discharge (FPAD) method. With this method it is possible to achieve high DLC coating thicknesses necessary for practical applications.

The energy of the carbon ions was measured with an optoelectronic time-of-flight method. An *in situ* cathode polishing system used for stabilizing the process yield and the carbon ion energies is presented. Simultaneously the quality of the coatings can be controlled. To optimise the quality of the deposition process a simple, fast and inexpensive method using silicon wafers as test substrates was developed. This method was used for evaluating the suitability of a simplified arc-discharge set-up for the deposition of the adhesion layer of DLC coatings. A whole new group of materials discovered by our research group, the diamond-like carbon polymer hybrid (DLC-p-h) coatings, is also presented. The parent polymers used in these novel coatings were polydimethylsiloxane (PDMS) and polytetrafluoroethylene (PTFE).

The energy of the plasma ions was found to increase when the anode-cathode distance and the arc voltage were increased. A constant deposition rate for continuous coating runs was obtained with an *in situ* cathode polishing system. The novel DLC-p-h coatings were found to be water and oil repellent and harder than any polymers. The lowest sliding angle ever measured from a solid surface, 0.15 ± 0.03°, was measured on a DLC-PDMS-h coating.

In the FPAD system carbon ions can be accelerated to high energies (≈ 1 keV) necessary for the optimal adhesion (the substrate is broken in the adhesion and quality test) of ultra thick (up to 200 µm) DLC coatings by increasing the anode-cathode distance and using

high voltages (up to 4 kV). An excellent adhesion can also be obtained with the simplified arc-discharge device. To maintain high process yield (5μm/h over a surface area of 150 cm^2) and to stabilize the carbon ion energies and the high quality (sp^3 fraction up to 85%) of the resulting coating, an *in situ* cathode polishing system must be used. DLC-PDMS-h coating is the superior candidate coating material for anti-soiling applications where also hardness is required.

CONTENTS

LIST OF PUBLICATIONS

This thesis is based on the following six scientific papers that are referred to using Roman numerals (I-VI):

I. Adhesion and quality test for tetrahedral amorphous carbon coating process, E. Alakoski, M. Kiuru, V-M. Tiainen, A. Anttila, Diamond and Related Materials, 12, 2003, 2115-2118.

II. Preparation of diamond-like carbon polymer hybrid films with filtered pulsed arc discharge method, A. Anttila, V-M. Tiainen, M. Kiuru, E. Alakoski, K. Arstila, Surface Engineering, 19, 2003, 425-428.

III. Low sliding angles in hydrophobic and oleophobic coatings prepared with plasma discharge method, M. Kiuru and E. Alakoski, Materials Letters, 58, 2004, 2213-2216.

IV. Energy dependence of the carbon plasma beam on the arc voltage and anode-cathode distance in the pulsed arc discharge method, E. Alakoski, V-M. Tiainen, Diamond and Related Materials, 14, 2005, 1451-1454.

V. A simplified arc-discharge set-up for high adhesion of DLC coatings, E. Alakoski, M. Kiuru, V-M. Tiainen, Diamond and Related Materials, 15, 2006, 34-37.

VI. Effect of continuous *in situ* cathode polishing on plasma yield and energy in filtered pulsed arc discharge system, E. Alakoski, V-M. Tiainen, M. Kiuru, Diamond and Related Materials, 15, 2006, 1677-1681.

All the above-mentioned papers are a result of group work. In a small research group the contribution of and the amount of work demanded from an individual is naturally significant. Also, strictly defining the contribution of an individual is usually not practical everybody has to participate in all the aspects of the research. However, this is an asset rather than a limitation.
The author's main contribution for the papers of this thesis has been participating in the development, the maintenance and the operation of the deposition system as well as the

measurement data analysis and publication (Papers I-VI). The author planned and conducted a significant amount of the surface topography measurements needed in the development of the quality and adhesion analysis method presented in Paper I. The author conducted the coating resistivity measurements and the hardness measurements for Paper II, and together with doctor Kiuru the contact and sliding angle measurements and surface topography measurements for Paper III. The author developed the video microscope image analysis method used for contact and sliding angle measurements in Papers II and III. In Paper IV the author conducted the literature searches and participated in the development and construction of the measurement system and in the carbon plasma energy determinations. The author of this thesis played a crucial role in the birth process of Paper V as it was his background research that brought the work of the Russian Irkutsk group to the knowledge of the rest of the research group. The author also planned and conducted the TRIM simulations and surface topography measurements for Paper V. In Paper VI the author conducted the literature searches and was responsible for the sample preparation and the operation of the deposition system. The plasma energy and process yield determinations for Paper VI were conducted by the author together with doctors Tiainen and Kiuru. The author of this thesis was an active participant in the writing process of all the articles and is the corresponding author and as such responsible for writing the main part of the texts of Paper I and Papers IV-VI. The author has also been responsible for the maintenance and organizing of the laboratory.

The papers are published in internationally refereed scientific journals. The arithmetic mean of the impact factors of the journals in the present work is over 100% higher than the median of all papers in the field of materials science[1] (according to ISI Web of Knowledge). Four of the six papers are published in the most prestigious journal in the field of diamond-like coatings, Diamond and Related Materials.

The Diamond group of ORTON Research Institute is a part of the Medical, Dental and Veterinary Biomaterial Research Group (BRG). The BRG is one of the National Groups of Excellence appointed by the Academy of Finland at the beginning of 1999. Experimental work for these papers was done at facilities of the University of Helsinki and at Anders Langenskiöld laboratory in ORTON Research Institute.

Papers I-III were also used in the thesis of M. Kiuru.

---

[1] ISI Web of Knowledge^{SM}, Journal Citation Reports$^{®}$, 2005 edition.

1 INTRODUCTION

Diamond is a material of extremes. It is the hardest material known to man, it has a very high thermal conductivity, a high electrical resistivity and it is transparent almost in the whole spectral region. It also has a low coefficient of friction against most other materials. Adding to these extreme properties the facts that it is chemically inert and biocompatible, it is evident that diamond is the superior candidate material for solving numerous materials-related problems in engineering and technology.

The exceptional properties of diamond arise from the strong covalent bonds between the neighbouring carbon atoms. In diamond, four identical molecular bonding orbitals are formed as one *s* orbital and three *p* orbitals are hybridised. These so called sp^3-hybridised orbitals arrange tetrahedrally with bonding angles of 109°. In natural diamond the carbon atoms form a densely packed cubic lattice. Our coatings however are amorphous and present no long-range order. The “diamond-likeness” of such coatings depends on the amount of sp^3 diamond bonds in the structure and “high quality” is widely used as a synonym for high sp^3 fraction. In a pure carbon coating the rest of the bonds are normally sp^2-hybridised graphite bonds.

The nomenclature of amorphous carbon coatings with properties similar to natural diamond is the subject of some debate. The terms more widely in use are diamond-like carbon (DLC) and tetrahedral amorphous carbon (ta-C). DLC is a general term used for coatings with any fraction of diamond bonds and ta-C is a more specific term for hydrogen free coatings with higher sp^3 fraction (>70 %) [1,2]. Although criticised for being illogical, the descriptive term amorphous diamond (AD) is sometimes also used. It seems much more informative to people not so involved in the DLC community. The term DLC polymer hybrid (DLC-p-h) was selected for the new type of materials developed in our laboratory, because they contain a significant amount of diamond bonds. For consistency and simplicity, the term DLC is used throughout this thesis.

The method used for deposition of DLC coatings in the current study is the filtered pulsed arc discharge (FPAD) method. The FPAD deposition system is essentially a pulsed plasma generator. Gilmour and Lockwood published pioneering work on pulsed plasma generators in 1972 [3]. Maslov et. al were the first to use pulsed plasmas in the deposition of DLC [4]. In a pulsed plasma generator the plasma is generated between two electrodes in a vacuum. An igniter system is used to vaporise and ionise part of the cathode material (hence the name cathodic arc). The "ignition plasma" provides a conducting path between cathode and anode and the main discharge is initiated. Any good electrical conductor (in our case graphite) can be used as the cathode. The plasma is ejected in the form of a high velocity and highly directional plume through a ring shaped anode. A solenoid is connected in series with the plasma accelerating stage (cathode-anode pair), a tuning resistor and the main capacitor to control the impedance and to focus and guide the plasma plume. The rate of the vaporisation of the cathode material for each coulomb of charge emitted is approximately 10^{-7} kg/C and the velocity of the plasma is in the order of 10^4 m/s [3]. This means that the pressure in the arc spots is extremely high (e.g. in tantalum 95 times that of atmospheric pressure) [3]. High thermal-elastic stresses, induced by the high temperature gradients existing near the cathode spots also result in particle ejection. In our system the curved solenoid filters out most of these neutral graphite particles that unaffected by the magnetic field move along straight trajectories towards the vacuum chamber walls [3,5].

FPAD has many advantages compared to other methods of preparing DLC coatings. High yield [VI] makes FPAD attractive for industrial purposes. The process takes place essentially at room temperature, which makes it suitable for a much wider variety of substrate materials than e.g. CVD. The FPAD grown films also have very low impurity concentrations and contain practically no hydrogen [6,7]. The pulsed operation makes FPAD very reliable because the thermal control of the deposition system is easier to arrange. Coating runs of several days and the preparation of coatings of several hundreds of micrometers in thickness are possible [8,VI]. Despite the magnetic filtering some of the neutral graphite microparticles reach the growing coating, due to multiple scattering [9]. From the point of view of tribological applications this is not only a downside, as in atmospheric conditions graphite particles can act as a solid lubricant, and thus further reduce the friction and wear of the contacting surfaces.

The Diamond Group led by Professor Asko Anttila has intensively studied DLC coatings since the mid 1980's [10-18]. Some representative experimental properties on the coatings together with the analysis method used can be found in Table 1. The group's main focus over the last ten years has been industrial and medical applications of tribological coatings, especially DLC coated artificial hip implants [11,13]. Tests conducted in bovine serum with an accredited hip simulator showed that diamond coating reduces the wear of the hip implant by a factor of 10^6 compared to common commercially available hip implants [12]. In accelerated chemical corrosion tests DLC coating also reduced the corrosion of a common CoCrMo alloy by a factor of 10^5 [14]. The suitability of tantalum for a buffer layer against corrosion in DLC coated artificial hip joints was tested with commercial CoCrMo acetabular cups. A 4-6 μm layer of tantalum on a CoCrMo cup reduces the corrosion of the cup by a factor of 10^6 [15,16].

The FPAD method is a complicated process and depends on numerous different parameters. In Figure 1 the deposition equipment and vacuum systems used in the preparation of the novel DLC polymer hybrid coatings are presented.

Paper I of this thesis presents a new, simple and inexpensive method to evaluate the coating process as a whole. The single most important parameter of the process is the adhesion of the coating to the substrate. If adhesion fails, everything fails. An essential factor in the preparation of adhesive DLC coatings is good control of plasma energy. Paper IV presents a method for controlling the carbon plasma energies. By increasing the anode-cathode distance and using high deposition voltages the plasma acceleration can be increased. The plasma energies were measured with the time-of-flight method. Another method for measuring plasma energies is the Doppler-shift method presented in our earlier paper [17].

A push towards the preparation Paper V of this thesis was given by the work published by an Irkutsk-based Russian research group. They use a somewhat similar set-up as ours for producing highly ionised ions with extremely high ion energies [19-22]. The main differences in their set-up compared with our one are the lack of the filtering solenoid and small geometry

Table 1. Some experimental properties of FPAD grown DLC coatings [6,7]

Property	Analysis method	
sp^3 fraction at optimum deposition energy	ESCA	85 %
Density	DSA	3.3 g/cm^3
Hardness	Nanoindenter	80 GPa
Overall purity	Nuclear methods	> 99 at.-%
Hydrogen content	ERDA	< 0.1 at.-%

(e.g. diameter of their cathode is only 1 mm). In Paper V, we showed that by removing the solenoid from our system high carbon ion energies, sufficient ion mixing in the interface and consequently high adhesion of DLC coatings can be achieved by using a very simple high-energy unit. This high energy unit can be used for the preparation of the adhesion layer whereas the actual high quality coating is deposited with a separate unit. The removal of the filtering solenoid naturally increases the number of the graphite particles in the adhesion layer. However, this does not have an adverse effect on the adhesion of the DLC coating as the carbon ion dose needed for the deposition of the adhesion layer is very low and thus the amount of particles reaching the adhesion layer is also very low.

Paper VI gives experimental information on the control of another important factor for the deposition of thick, high quality DLC coatings, namely sufficient plasma yield. By using continuous *in situ* cathode polishing, stable process yield can be maintained for weeks, practically until the cathode material has been fully utilised. The polishing also stabilizes the carbon ion energy and thus the quality of the resulting coating. Without cathode polishing the plasma yield drops in a very short time and the carbon ion energy increases. This means inferior coating quality and deposition times at least five times longer than with cathode

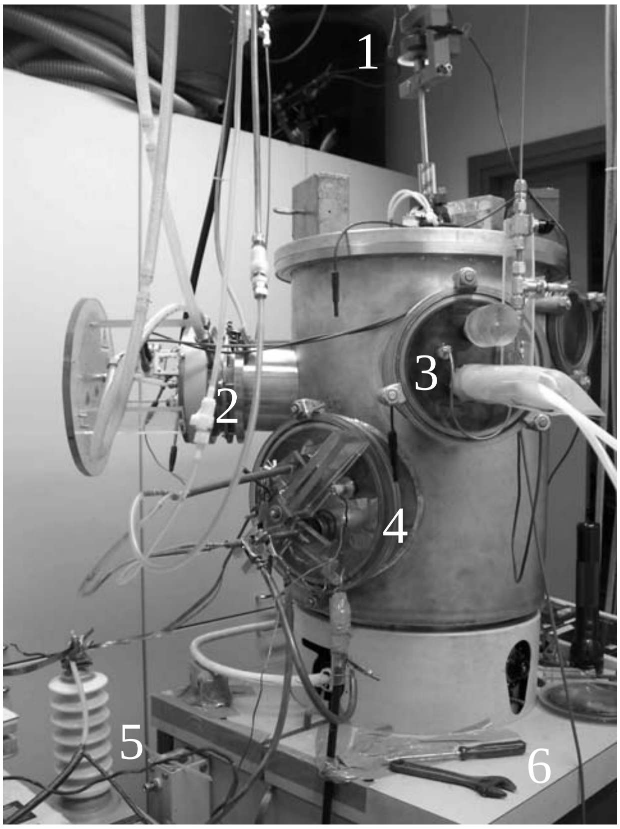


Fig. 1. A photograph of the FPAD deposition equipment and vacuum system.

1. *Sample holder and manipulator*

2. *Ar sputter cleaning apparatus* (see Fig. 3)

3. *Magnetron sputtering apparatus,* used for the deposition of metallic coatings and intermediate layers.

4. *Modified FPAD unit,* used for the deposition of the novel DLC polymer hybrid films (see also Fig. 7).

5. *The main capacitors*

6. *The frame* (inside; fore vacuum and oil diffusion pumps).

polishing. For example in our current set-up the deposition time of 50 µm thick coating would increase from 10 to 50 hours. However, this effect can be used when high ion energies are needed.

As a result of a failed FPAD experiment a coating with interesting properties was formed. It could not be marked with any pens and neither commercial stickers nor tapes could be attached to it. This led to modification of the FPAD system and to discovery of a whole new group of coating materials, the DLC polymer hybrids (DLC-p-h). The DLC-p-h coatings and the coating process are currently being patented [18]. For the time being the polymers used in the hybrid coatings are the most common commercial non-stick materials, polydimethylsiloxane (PDMS) and polytetrafluoroethylene (PTFE). Paper II presents the preparation method of these novel coatings, their chemical compositions and their physical properties. Paper III focuses on the exceptional non-stick properties of the DLC-p-h coatings. An extremely low sliding angle of 0.15 ± 0.03° was measured on the DLC-PDMS-h surface with a 20 µl distilled water droplet. This is currently the lowest sliding angle ever measured for a solid surface.

2 REVIEW OF THE LITERATURE

The FPAD method used for deposition of DLC coatings in the present work is unique in the world. The equipment used in the deposition of DLC was designed and built at our laboratory. No other method that can produce DLC coatings up to 200 µm in thickness was found in the literature. Most analysis methods used in the present work were also developed by our research group. Thus, relevant information relating to our work is very scarce in the literature.

2.1.1 DLC deposition methods

To harness the superiority of diamond to surfaces, a wide range of methods of preparing DLC coatings have been developed during the years. These methods can roughly be divided into two categories, chemical vapour deposition methods (CVD) and physical vapour deposition (PVD) methods. Chemical methods use some hydrocarbon gas (such as methane) as a precursor and the resulting coatings are usually polycrystalline. For these reasons CVD coating are full of grain boundaries and contain significant amounts of hydrogen. The processing temperature is also in most cases quite high (>600 °C), which severely limits the choice of substrate materials. The most commonly used PVD methods are sputtering [23,24], pulsed laser deposition (PLD)

[25,26], mass selected on beam (MSIB) [1,27], and cathodic arc [2,3,28,29, I-VI]. Sputtering is a very common method of depositing thin films in the industry. Its main disadvantage in depositing DLC coatings is a low ratio of energetic ions to neutral species, and thus is does not produce the hardest films [30]. PLD is a method in which carbon plasma is created using high power (I>10 W/cm^2) pulsed ND:YAG and Excimer lasers. The problems of PLD are the presence of contaminating graphite particles in the plasma stream and insufficient adhesion of thick coatings [25,26]. MSIB is an excellent method for preparing high quality DLC coatings [27]. However, high cost, the size of the equipment and low process yield make MSIB suitable for laboratory purposes only. The coatings for this work were deposited using a variant of the cathodic arc method developed at our laboratory, the FPAD method [28,29].

2.1.2 Energies of the carbon ions in vacuum arcs

According to the literature, carbon ion energies in vacuum arcs are usually measured using either an ion source [31] or plasma-source set-up [32,33]. In the ion source set-up [31] an ion extraction voltage grid is used for the extraction of a carbon ion beam from a carbon plasma source, whereas in the plasma source set-up [33] no ion extraction voltage grid is used. The ion source set-up [31] uses a time-of-flight method with a Faraday cup detector. A modulation is introduced into the arc current and the energy of the carbon ions can be measured from the delay between the arc current modulation and the ion current modulation using an oscilloscope. If a special deflection gate is used information on the ion charge-state can be obtained [31].

In the plasma source set-up [33] a Faraday-cup cannot be used as the transverse magnetic field used in it for suppressing secondary electrons would affect plasma flow. Instead of a Faraday cup a negatively biased collector electrode (Langmuir probe) is used. With the plasma source set-up no charge-state information is obtained. This is not a drawback in conventional carbon vacuum arcs, as usually only singly charged ions are present in the plasma (see also 2.1.3) [34-38]. In some energy measurements of cathode materials of low atomic mass, such as carbon, the ion extraction system may have been the cause for systematic errors [33]. To avoid such problems the use of an ion source set-up is recommended for cathode materials of low atomic mass only when charge-state resolution is necessary [32].

The energies of the carbon ions in conventional vacuum arc systems (arc currents, 100-600 A) in the absence of external magnetic field are about 20 eV and seem to be independent of the arc current [32,39]. Higher currents simply mean that more plasma forming cathode spots are created. The character of the spots does not change. However, much higher carbon ion energies are observed in vacuum sparks [17-22,32,IV,V], in the transition region between vacuum arcs and sparks [38] and by using high currents and strong external magnetic fields [40].

2.1.3 Charge state fractions of the carbon ions in vacuum arcs

According to several measurements only singly charged ions are present in arc discharge carbon plasmas [34-38]. However, the production of higher charge states for carbon has also been reported in the literature. The ionisation state is mainly determined by the power input per plasma particle [32]. The increase in the power density leads to an increase in the electron temperature of the plasma. The higher charge states are enhanced, as the electrons are the main contributors of the ionisation process [41].

Bugaev *et al.* [41] studied the generation of multiply charged ions in vacuum arc discharges. According to them higher charge-states can be obtained by using high magnetic fields. Using a magnetic field of “several tenths of Tesla” near the cathode region they observed distributions of 29%, 58%, 13% for C^+, C^{2+} and C^{3+} respectively. The second method of increasing the average charge is by superimposing high current bursts (1 kA, 4 μs) into the arc. Also the magnetic field of the arc current provides an increase in the average charge of the plasma ions, but this increase is only considerable in arc currents higher than 1 kA [41].

Usually, higher charge states are also present at the beginning of each arc [42,43]. This is the so-called spark phase of the arc. In fact, Anders *et al.* [32] called our short plasma pulses as carbon vacuum sparks. The spark phase is characterised by arc like current levels (100-600 A), but the anode-cathode voltage is significantly higher (>>20 V) than in the actual arc phase [38]. Because the ionisation state is mainly determined by the power input per plasma particle, the higher charge states in the high current and high voltage spark phase are evident, as also the number of plasma particles is smaller at the beginning of each arc [32]. The duration of the spark phase depends on the discharge circuit and electrode geometry [44] but usually the charge-state distributions reach their semi-steady-state distribution when the pulse duration is longer than 100 μs [45]. According to Anders *et al.* [38] e.g. in a 3 μs carbon plasma arc the charge states determined were 91.4 % and 8.4 % for C^+ and C^{2+} and in a 150 μs arc only the C^+ state was present. For comparison, in our high energy plasma unit the pulse duration is about

15 μs and the peak current can be as high as 13 kA with an anode-cathode voltage of 6 kV [17,I].

2.1.4 Stress in DLC

The main reason for the adhesion problems of DLC coatings has been the formation of high internal compressive stresses during the growth process. The internal stresses in high-quality DLC coatings can be in the order of 10 GPa [46,47]. These stresses are thought to be necessary to stabilise the sp^3 phase of the coating during the deposition in the so-called subplantation process [30]. Ferrari *et al.* [48] expressed doubts on the necessity of stress in the stabilisation of the sp^3 phase but even they admitted that to “easily reach the highest quality DLC coatings stress may be necessary”. The data of McKenzie *et al.* [49] and Fallon *et al.* [46] indicate a clear dependence of stress on sp^3 fraction.

Several methods to relieve the internal stress of DLC coatings have been studied. Such methods include annealing [50], incorporating metal, silicon or boron in the coating during deposition [51-53], using substrate biasing [54,55] and ion irradiation [56]. These methods seem to be effective in reducing at least some of the stress [57]. However, the properties of DLC coatings (hardness, wear resistance, electrical resistivity) that are considered to be useful in many applications may change [58]. Friedmann *et al.* [50] reported complete stress relief by using post deposition thermal annealing (2 min. in 600°C). The thickness of the stress free film on silicon was 1.2 μm. By using several steps of deposition and annealing they reported that they had grown DLC films up to 10 μm in thickness, without losing the near diamond-like hardness of the films. The method seems to be effective but cumbersome. Annealing can also induce graphite rich layers in the coatings [59]. Such layers cannot be detected using normal surface analysis methods e.g. electron energy loss spectroscopy (EELS) or electron spectroscopy for chemical analysis (ESCA) and can only be revealed by methods, which possess sufficient depth resolution like cross sectional transmission electron microscopy (TEM) [59].

As no-one has presented an easy method for preparing stress-free high quality DLC coatings, our focus has been on improving the adhesion [I,IV,V] rather than on stress relief. In some applications, such as the micro-electromechanical devices (MEMS) stress-free films are required [55,57,60]. However, in many industrial and medical applications, e.g. the artificial hip joints the main problem is not the stress. If sufficient adhesion of thick high quality DLC coatings can be achieved, coatings with high internal stresses can be utilised [11-14].

2.1.5 Non-stick properties of surfaces

A whole new group of materials, the DLC-polymer-hybrids, is presented in this thesis [II,III]. These coatings combine the excellent mechanical properties of diamond with the non-stick properties of polymers. The property usually referred to when describing the non-stick properties of materials is the contact angle of a distilled water droplet [61,II,III]. A surface is defined to be hydrophobic, if the contact angle of water on it is higher than 90°. If the contact angle is below 90° it is called hydrophilic [62]. Low surface energy materials show high contact angles and high surface energy materials show low contact angles. The contact angle can be measured from a static droplet (static contact angle) or e.g. from a droplet sliding down an inclined plane (dynamic contact angle) [63,64,II,III]. The dynamic contact angle can be measured either from the advancing (leading) end or from the receding (tail) end of the droplet. The difference between receding contact angle and advancing angle is the so-called contact angle hysteresis [65-69,II,III]. The contact angle hysteresis is used to measure how well a droplet moves on a tilted surface [65,70]. However, the sliding behaviour can be measured directly by measuring the critical tilt angle at which the droplet starts to slide down an inclined plane called the sliding angle of the droplet [II,III]. It is important to notice that high contact angles do not always mean low sliding angles [71, II, III]. This means that the term hydrophobicity should not be used as a synonym for the “true repellency” of water. To evaluate a surface that “truly repels” liquids one has to study the behaviour of droplets on near horizontal tilt angles [71,II,III].

2.1.6 Ultrahydrophobic surfaces

The maximum contact angle attainable on a flat surface only by lowering the surface energy is 120° [72]. However, one can fabricate so-called ultrahydrophobic (sometimes also called super-hydrophobic) films with contact angles higher than 150° by combining appropriate surface roughness with surfaces having low surface energy [73-79]. Because of the limited contact area between the solid and water, chemical reactions are thought to be limited on such surfaces [73,74]. Unfortunately higher roughness also commonly means poorer mechanical properties [73]. This fact severely limits the practical use of ultrahydrophobic films. Sliding angles of surfaces are rarely mentioned in the literature [77-80]. Before our work the lowest sliding angle has been reported by Miwa *et al.* [80]. They measured a sliding angle of ~ 1° from an ultrahydrophobic surface prepared from an AlOOH-ethanol mixture coated with a thin layer of fluoroalkysilane. The surface of their film consisted of assemblies of needle-like structures. In a needle-like structure the contact area between the droplet and the surface is very small and the droplet slides on an air cushion [80]. The problems of such surfaces in addition to poor mechanical properties are ageing and decay under demanding conditions [65,73].

2.1.7 Modification of the hydrophobicity of DLC films

DLC films themselves are only mildly hydrophobic [81]. However, they can be made more hydrophobic, e.g. by incorporating fluorine [82-84]. These fluorinated DLC films are prepared from hydrocarbon-fluorocarbon gas mixtures. Their hydrophobic properties can reach the performance of PTFE and they show relatively high hardness and wear resistance (~5 GPa) [85-87]. Their stability under thermal stress can, however, be questionable [88]. The hydrophobicity of DLC films can also be modified by incorporating metals in them (Ni, Fe, Al) [89] or by surface treatments with different gas plasmas (Ar, O_2, CF_4, H_2) [90]. No studies on the sliding behaviour of droplets on modified DLC surfaces were found in the literature.

3 CURRENT STUDY

3.1 AIMS

The aims of the current study have been:

1. Improving the FPAD coating process for the deposition of DLC coatings for medical and industrial applications

2. Developing the DLC-polymer-hybrid coating process

This work is basic research and it has not always been to predict the direction of the research beforehand. Chance sometimes plays an important role. The discovery of the DLC-p-h coating is a good example of this.

3.2 MATERIALS AND METHODS

3.2.1 Preparation and deposition of the samples

The sample substrates are first polished using commercial polishing apparatus (Fig. 2). The sample polishing is started using SiC grinding papers. The final polishing is done with polycrystalline diamond suspensions and polishing cloths. The RMS roughness of the polished samples is in the range of a few tens of nanometers and the finished surface is mirror fine. The roughness of the samples is of secondary importance; the essential thing in polishing is avoiding sharp edges and ridges in the finish. Sharp edges can act as stress raisers and may result in the delamination of the DLC coating.

Cleanliness of the samples is naturally also important when depositing thin films. The samples are cleaned in an ultrasonic washer first using acetone to remove the remains of the polishing suspension. Acetone is also efficient in removing fat and greases. The pre-vacuum cleaning is finished in an ethanol bath and blowing possible external particles away from the sample

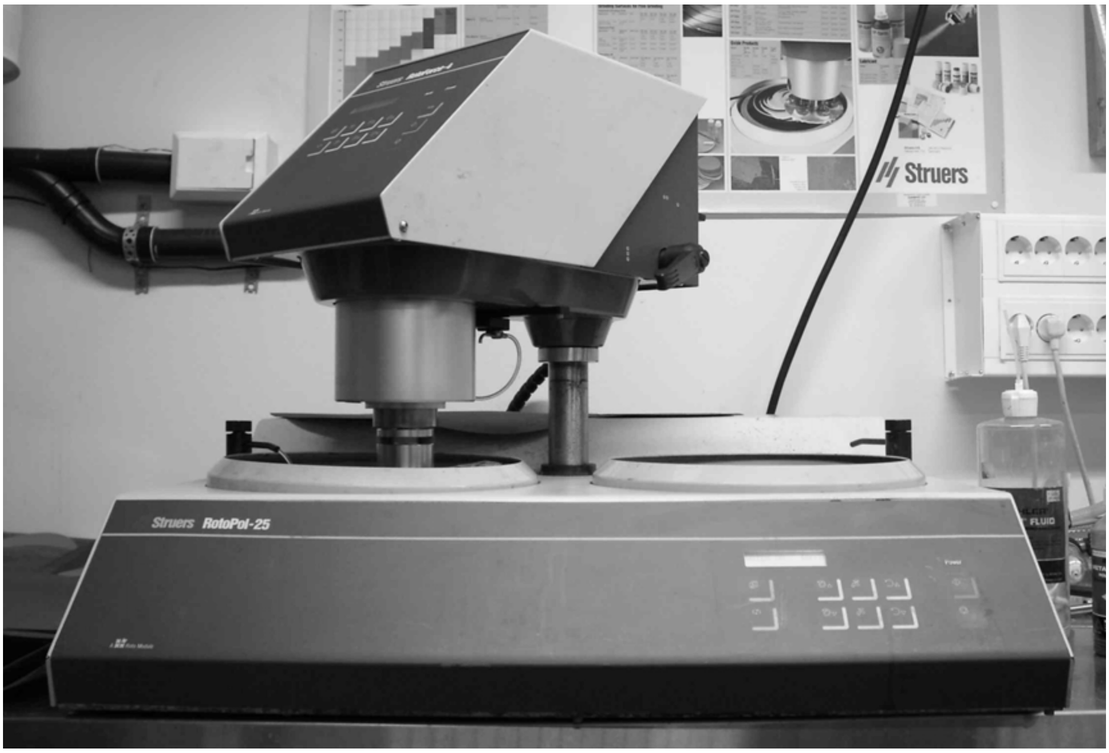


Fig. 2. A photograph of the Struers Rotopol-25 commercial polishing machine.

surface with pressurised nitrogen gas. To remove possible water and other residue contaminants and native oxide layers from the surface, the samples are further cleaned in vacuum by argon sputtering [91]. We use a Russian manufactured sputtering unit (Fig. 3) for this purpose. This technology was originally developed for use as a propulsion system for space probes and it has been modified for sputter cleaning. In several years of use the unit has proven itself robust, effective and nearly maintenance free, needing only vacuuming every once in a while. Morshed *et al.* [92] reported that argon sputter cleaning can also alter the composition of the native oxide layer on the surface of stainless steel AISI316L (an important material for the application of DLC coating on artificial hip joints). It seems that there is an optimal etch time to maximise adhesion consistent with the removal of chromium and iron oxides from the surface and leaving a residue of nickel oxide. In our experience, all these cleaning stages are important since omitting any one of the cleaning stages may result in the delamination of the coating.

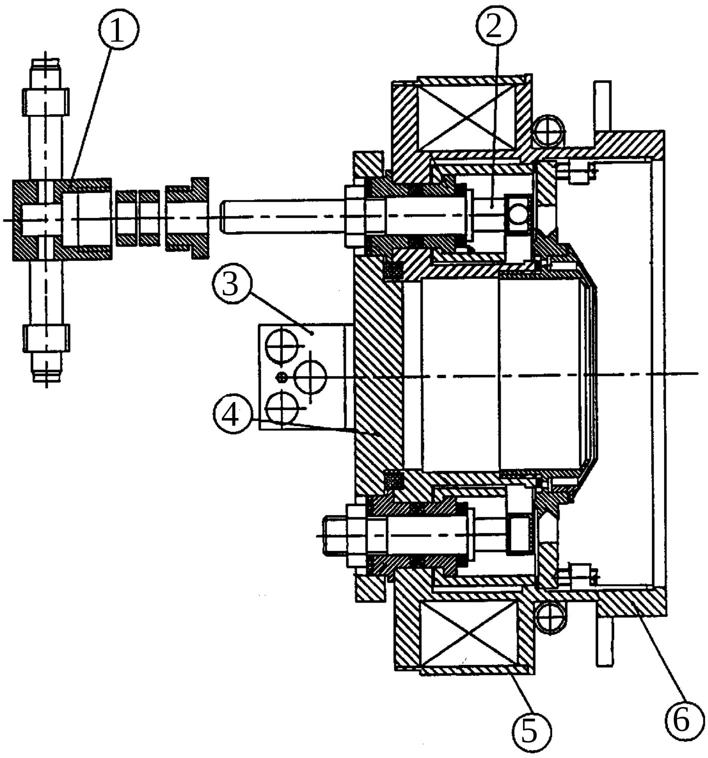


Fig. 3. A Russian manufactured sputtering unit. The technology was originally developed as propulsion system for space probes and has been modified for sputter cleaning. The working gas used in our system is high purity (99.999%) argon. **1**. *Cooling water inlet* **2**. *Anode* **3**. *Electrical connections* **4**. *Gas inlet* **5**. *Magnet* **6**. *Frame (acts as the cathode).*

The actual coating deposition is started using high carbon ion energies to achieve an interfacial mixing in the adhesion layer. Energies used are significantly higher [I,IV,V] than the optimal energy (~100 eV) for the sp^3 bond formation [1,2,93,94]. Some ~200 eV carbon ion energy should be enough for sufficient interfacial mixing, but the higher energies enhance the mixing and thus also the resulting adhesion [I,IV,V]. The mixing layer was deposited using a separate high energy FPAD unit. A second FPAD unit, with optimal carbon ion energies was then used for the deposition of the actual high quality (sp^3 fraction > 80 %) DLC coating [I,VI]. In this unit, an *in situ* cathode polishing system is used. Cathode polishing stabilizes the process yield and the energy of carbon plasma ions [VI].

3.2.2 Carbon ion energy measurements

Good ion energy control is a necessary requirement for the deposition of well-adherent high-quality DLC coatings. Our research group has developed two successful methods for plasma energy determinations; namely the optoelectronic time-of-flight [95,96,IV] method and the Doppler-shift method [17].

Both methods are based on observing the characteristic light emitted by the carbon plasma pulses. In the time-of-flight method [IV] two observation points from the flight path of the plasma pulse are chosen. Light from these observation points is led to photo diodes using collimated optical fibres and converted to electronic signals. The signals are then amplified for an oscilloscope using an external amplifier. The delay between the signals from the two fibres gives the time-of-flight, t of the plasma pulse. As the distance between the observation points, s is known the speed, v and energy, E of the plasma pulse can easily be calculated, using the familiar equations:

$$v = \frac{s}{t} \quad , \; E = \frac{mv^2}{2} \tag{1}$$

In the Doppler-shift method [17] collimated optical fibres are placed at known angles relative to the main axis of plasma flow. As one fibre sees the plasma flying away from it and the other fibre flying towards it, the characteristic light from the ions is correspondingly red shifted for the first and blue shifted for the second. The light from the fibres is led to a crossed dispersion spectrograph and the line spectrum is recorded on a film. The spectrum is photographed using a CCD-videomicroscope and converted to line profiles using image analysis software. The Doppler-shifts and the corresponding plasma ion energies are calculated from the centroids of the peaks in the line profiles. Estimates of the charge state distributions can also be obtained by comparing the intensities of the peaks to their tabulated values.

3.2.3 Stabilizing the process yield and energies of carbon ions

Another important factor for the deposition of thick, high quality DLC coatings for practical applications is sufficient process yield. By using continuous *in situ* cathode polishing [VI], stable process yield can be maintained for weeks, practically until the cathode material has been fully utilised. Cathode polishing also stabilizes the energies of carbon ions for the production of high quality DLC.

The cathode polishing effect is achieved by rotating the cathode against an alumina sheet. The rotation rate of the cathode is rather low, 0.5 rpm, but sufficient for cathode polishing. The low rotation rate reduces the stress on the vacuum feed-troughs thus increasing their life span. Air pressure pushes the cathode towards an alumina sheet that is inclined at an angle of 2-3°. As the rotating cathode pushes against the alumina sheet edge a lathing effect is produced. The sharpness of the alumina sheet edge naturally affects the wear rate of the cathode surface. Excessive cathode wear rates should naturally be avoided.

3.2.4 The simplified high energy device

An Irkutsk based Russian research group uses a somewhat similar arc discharge device to ours for producing highly ionised ions with surprisingly high energies. However, their system has no particle filtering solenoid and its geometry is smaller e.g. the diameter of their cathode is only 1mm. The discovery of the Irkutsk system from the literature led us to test whether we could use our larger system for producing similar results. For this purpose we modified an existing arc-discharge device (cathode diameter: 10 mm) by removing the solenoid. The operation of the system, i.e., its capacity of producing carbon ion energies high enough for the deposition of the adhesion layer of DLC coatings was then tested with the adhesion and quality method of section 3.2.6 (I).

3.2.5 Quality of DLC

The sp^3 fraction measurements for Papers I and II were done using the ESCA method. This method is also known by the name X-ray photoelectron spectroscopy (XPS). In ESCA monochromatic X-rays are used for producing photoelectrons from the sample. The binding energy of the electrons of a given element depends on the chemical surroundings of that element. The chemical composition of the sample can thus be deduced by measuring the energy spectrum of the photoelectrons. As the escape depth of electrons is in the range of a few nanometers careful sample preparation and a good vacuum are essential requirements [97].

For the sp^3 fraction measurements in Paper I Al K_α X-rays were used and the C 1s core level spectra were analysed. The 1s photoelectron spectrum of pure carbon is a single, wide peak and is deconvoluted to its two main contributors at 284.4 eV and 285.2 eV, from sp^2 and sp^3 hybridised carbon atoms, respectively [98,99]. In Fig. 4 the C 1s spectra of natural diamond and pure graphite can be seen and in Fig. 5 the spectrum of a DLC with 77% sp^3 fraction is shown. From these spectra it is easy to see that ESCA provides a straightforward and direct method for evaluating the sp^3 fractions DLC coatings.

The ESCA analysis for Papers I and II was purchased from the Centre for Chemical Analysis at the Helsinki University of Technology. One must point out that due to the high cost of the analysis (several hundred Euros per measurement point) ESCA measurements of our coatings are seldom done and other cheaper and more practical methods are in dire need. In practical coating work the quality analyses of our coatings were done using test coating runs on aluminium foils and evaluating the brightness of the Newtonian rings of the coatings (optical transparency increases as the sp^3 fraction increases, as diamond is optically transparent and graphite is not) [VI]. The method is good, but difficult to quantify. Another excellent method for rough quality approximations is measuring the electrical resistance (resistivity increases as the sp^3 fraction increases, as diamond is an insulator and graphite is a conductor) of deposited coatings. A new method that was developed and is used in our laboratory to test the deposition parameters of our system, is the adhesion and quality test explained in Paper I and in section 3.2.6.

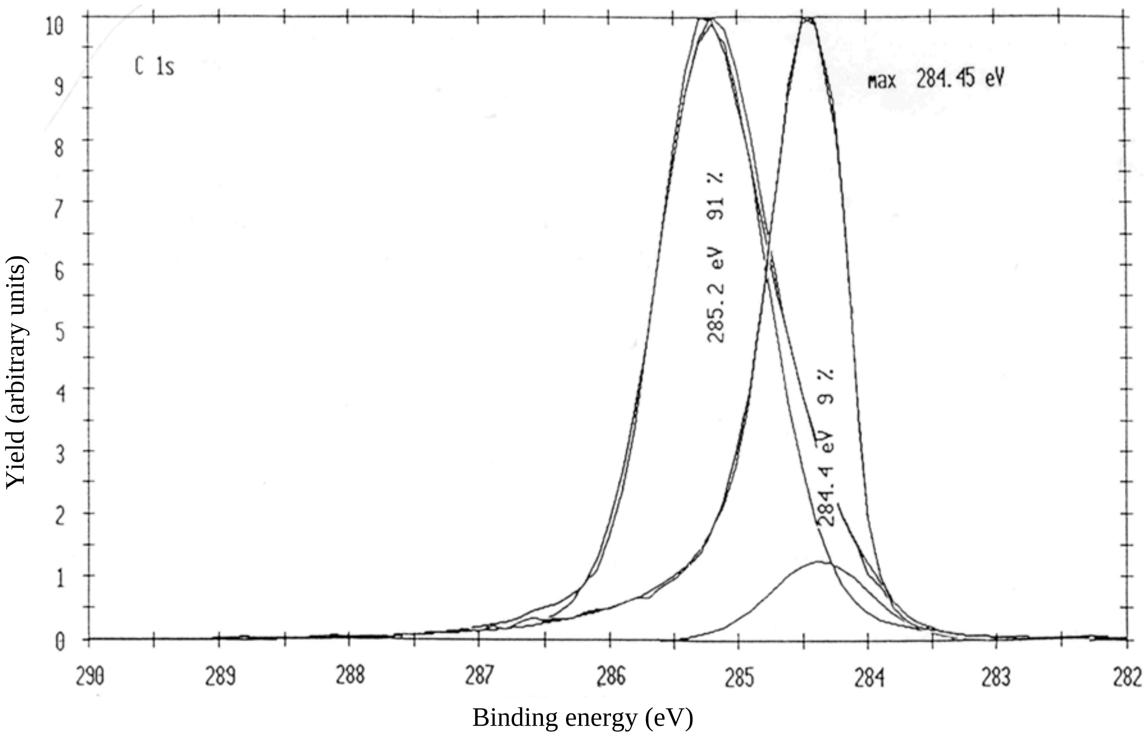


Fig. 4. ESCA spectra of natural diamond and pure graphite. The left peak is from natural diamond and has been deconvoluted into components corresponding to diamond and graphite bonds. Note that because of the graphite rich surface layer the sp^3 fraction is only 91%. The right peak is from pure graphite.

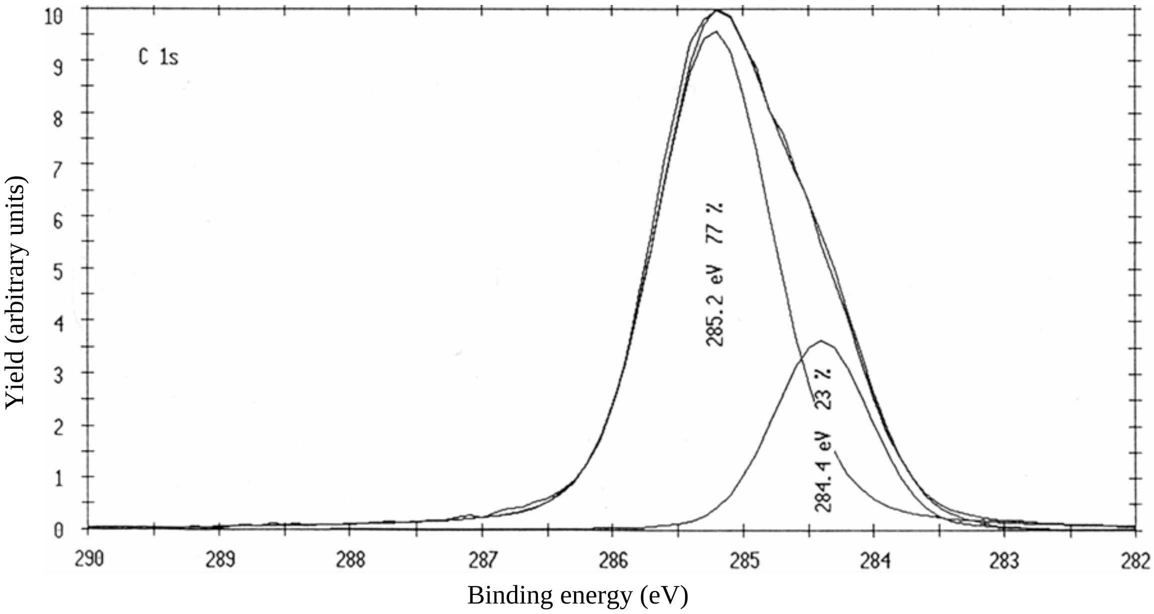


Fig. 5. ESCA spectrum of a DLC coating with an sp^3 fraction of 77%. The peak has been deconvoluted into components corresponding to diamond and graphite bonds.

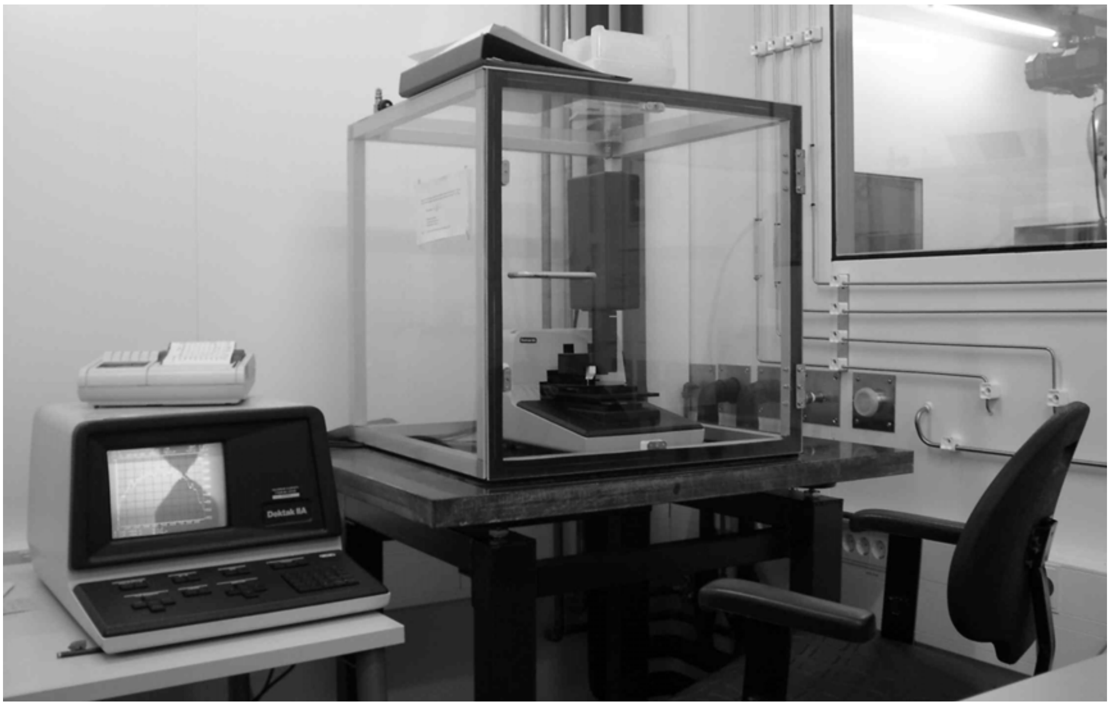


Fig. 6. A photograph of the stylus profiler (Dektak IIa), used for surface topography measurements.

3.2.6 Adhesion and quality of DLC

Methods that are usually used for testing the quality (sp^3 -fraction) of DLC coatings, such as ESCA and EELS are expensive, difficult and slow. In some applications, such as the artificial hip joint the coatings have to be flawless and a fast test is needed to control the deposition parameters. In Paper I, a fast method that takes advantage of the correlation between the quality and internal stress of the coating is presented. The method tests the coating process as a whole.

Earlier, we noticed that the internal stress of the coating can break and peel off the surface of a silicon wafer if the adhesion and the quality of the coating are sufficient [100]. By using identical silicon wafers as test substrates this observation can be used to evaluate the quality of the coatings by a simple visual inspection. If the adhesion is not sufficient the coating delaminates without breaking the silicon substrate. With good adhesion the coating peels off by breaking the silicon surface. The quality of the coating can be determined from the thickness of the thinnest possible coating peeling off with the substrate. Lower peeling thickness means that the internal stress and quality of the coating (sp^3 fraction) is higher. Higher peeling thickness means that the internal stress and consequently the quality of the coating is lower. The peeling effect is usually measured using a profiler (Fig. 6). Quality calibration can be made using other methods. In our case the quality calibration was made with the ESCA method purchased from the Centre for Chemical Analysis at the Helsinki University of Technology. According to the calibration made for the measurements in Paper I the peeling thickness is a very sensitive analysis method. The thinnest coating layer that broke the silicon surface was 0.5 μm and the thickest was 1.5 μm and the sp^3 fractions of the coatings were 85% and 80%, respectively. The most time consuming part of this test is the vacuum pumping. The time required for the test is approximately 1 hour. The material cost of the method is the cost of the silicon wafer. In addition, once the calibration has been made the repeatability of the test is excellent as the coating is amorphous and homogenous and the substrate silicon wafers are identical. The test is simple, sensitive, fast, inexpensive and reliable.

3.2.7 Deposition of DLC-polymer hybrid films

The development of the DLC-p-h coatings is an example of the role of chance in science. In a failed DLC experiment, PDMS (polydimetylsiloxane) that was used as an electrical insulator was accidentally vaporised amidst the carbon plasma and a film of interesting properties was formed. The film could not be marked by any marker pens and neither stickers nor tapes could

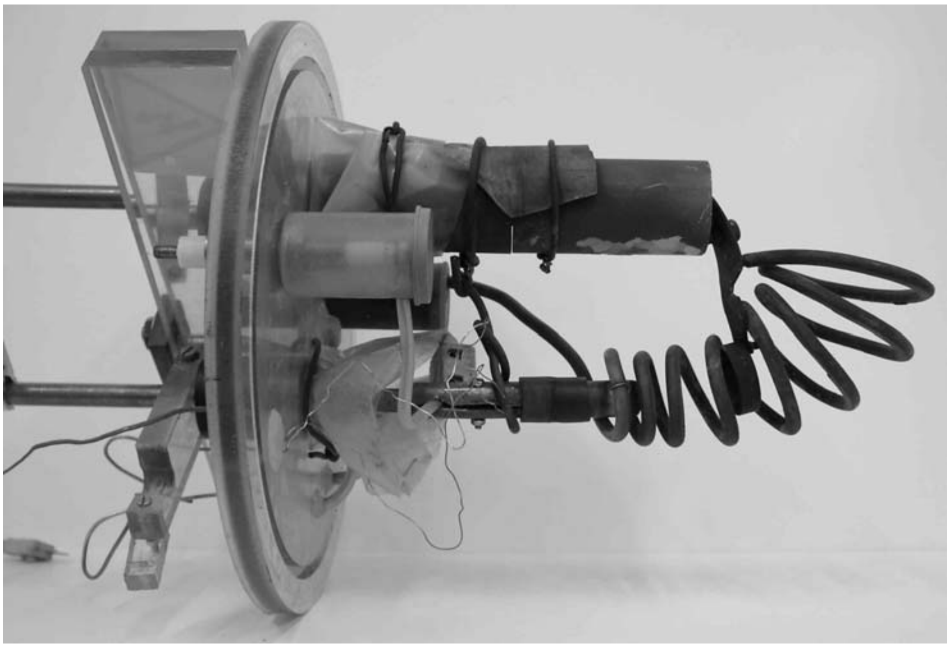
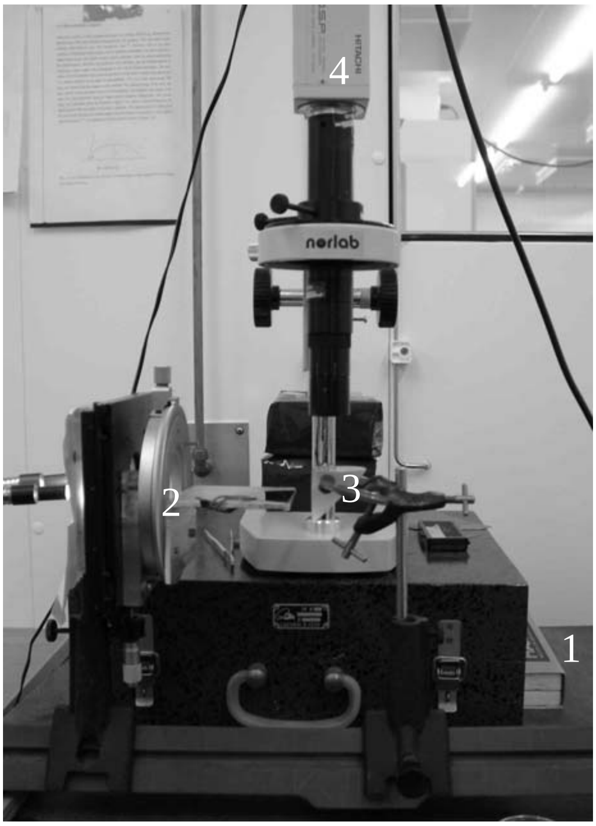


Fig. 7. A photograph of the modified FPAD unit used to deposit DLC - polymer -hybrid coatings

Fig. 8. A photograph of the contact angle and sliding angle measurement apparatus. The apparatus is constructed on (**1**) s*tone table* and consists of a (**2**) *tiltable sample table*, (**3**) *prism* and (**4**) *CCD-videomicroscope.* Analysis of the photographed droplets is performed using suitable image analysis software.



be attached to it [II]. This led us to modify the FPAD system to produce similar coatings in a controlled manner. The modified FPAD unit can be seen in Fig. 7. The DLC-p-h coatings combine the exceptional mechanical properties of the DLC coatings and the non-wetting properties of the “parent” polymer. By controlling the amount of the polymer component vaporised and sputtered by the carbon plasma (in effect controlling the pulse frequency of the system) coatings with a wide range of mechanical and wetting properties can be deposited. The method and the novel coatings are currently in the patenting process [18,II,III].

3.2.8 Contact and sliding angle measurements

The apparatus that we have used to measure the contact and sliding angles of our DLC-p-h coatings for Papers II and III is built on a stone table and consists of a tiltable sample table, a prism and a CCD-videomicroscope (Fig. 8). Analysis was performed using suitable image analysis software. For samples with the lowest sliding angles another apparatus with a higher precision for the tilt angle was constructed [III]. A larger plane (20x60 cm) with an axle in one end was used to maximise the measurement accuracy. Before the measurement the plane was carefully set to be horizontal (in both x and y directions) using a spirit level. The sliding angle was determined from the height of the free end of the tilted plane.

3.3 RESULTS AND DISCUSSION

3.3.1 The motivation for thick DLC coatings

DLC coating is a ceramic material. The stress-strain behaviour of ceramic materials is usually measured using a transverse bending test (ASTM C1161). A rod of length L is supported from its opposite ends and an increasing bending force F is applied to the middle of the rod (see Fig. 9). Using the test for a specimen of a rectangular cross section, the load at fracture F_f can be calculated from the equation

$$F_f = \frac{2bd^2\sigma_{bd}}{3L} \tag{2}$$

where σ_{bd} is the stress at fracture, sometimes called bend strength (an important mechanical parameter for brittle ceramics), b is the width and d the thickness of the rod [101]. The coating-substrate system differs of course from a simple rod. The coating and the substrate have different elastic properties. This may have an effect on the strength of the coating-substrate system. However, the rod example can be used as the first approximation to illustrate the effect of thickness on the strength of DLC coatings. The physical meaning of Equation (2) is that the

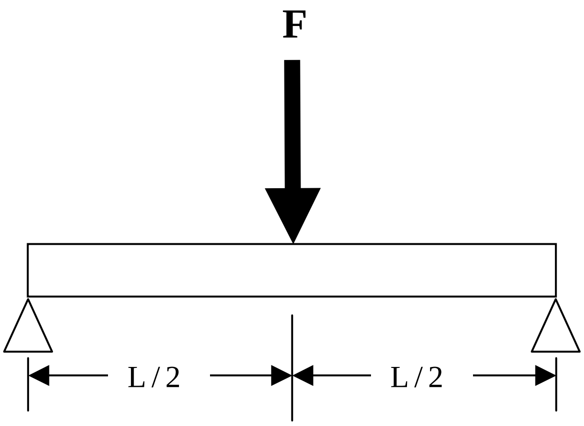


Fig. 9. A three point loading scheme for measuring the stress-strain behavior and bend strength of brittle ceramics.

force needed to “break” the coating is proportional to the square of the coating thickness. If the coating thickness is increased from 1 μm to 10 μm, the breaking force increases to 100-fold, and the force needed to break the coating of 100 microns in thickness is 10000-fold. This explains why thin DLC coatings fail and thick coatings “pass” in hip joint simulator tests. If the adhesion is sufficient, thick coatings are able to withstand several orders of magnitude greater forces. From the viewpoint of load-bearing applications the importance of thick well-adhesive coatings is thus evident.

Although there are some reports on the deposition of reasonably thick (1-25 μm) DLC coatings [50,54,102-104], our group is, according to our knowledge, presently the only research group in the world that can routinely deposit coatings of several tens of micrometers in a coating run of practical duration (at our current set-up our maximum deposition rate is approximately 6 μm/hour on an area of 10 cm^2). The thickest coatings we have so far deposited are 200 μm and we have not reached the upper limit in thickness yet [14]. However, depositing coatings of hundreds of microns requires several days, which is rather cumbersome, as the system requires constant monitoring to avoid changes in the deposition parameters. Anyhow, our routine thickness of tens of microns is more than enough for practical tribological applications of DLC coatings, such as, artificial hip and knee implants.

3.3.2 Vacuum

A common layman’s question when hearing for the first time about diamond coatings is: “Isn’t it expensive?” The answer is, no more expensive than the equipment used for the deposition of the coatings (excluding the cost of human labour). The most expensive parts of the deposition system are the vacuum chamber and the pumping systems. A better vacuum usually means less residual gas impurities in the coatings and also better adhesion of the coatings. However, the downside is that a better vacuum also means higher material, equipment and maintenance costs. Moreover, vacuum pumping is time consuming. The evident conclusion is that finding the optimal operating conditions is essential for a cost-effective industrial scale DLC deposition system.

The deposition of DLC coatings with the FPAD method takes place at room temperature in a vacuum of approximately 10^{-4} Pa. Although this pressure is nine orders of magnitude lower than atmospheric pressure, there are still 10^{10} residual gas molecules in each cubic centimetre.

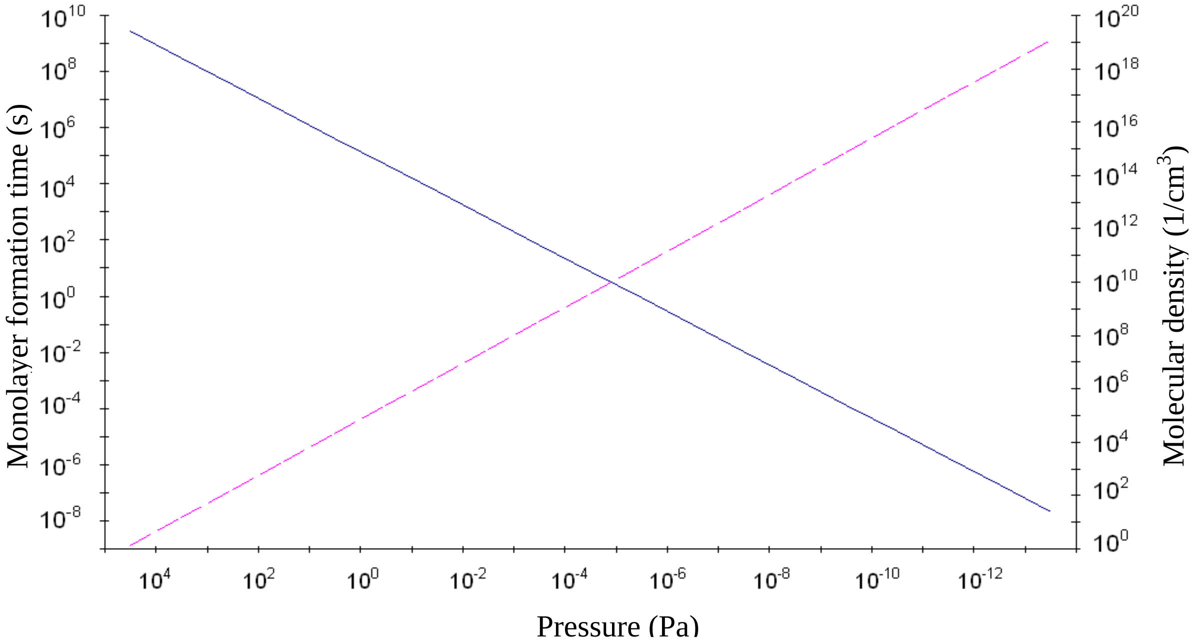


Fig. 10. A graph showing the molecular density (solid line) and the monolayer formation time (dotted line) as a function of the pressure. Molecular density is shown for nitrogen at 20 °C and monolayer formation time for hydrogen at 20 °C.

Considering the impingement of residual gases on surfaces in a vacuum the meaning of these large numbers becomes understandable. The characteristic contamination time τ_C for complete monolayer coverage of a surface containing 10^{15} atoms/cm^2 can be calculated from the equation (derived from the kinetic theory of gases):

$$\tau_C = 2.14 \cdot 10^{-10} \frac{(MT)^{\frac{1}{2}}}{P} \sec \qquad (3)$$

where M is molecular weight, T is the absolute temperature and P is the pressure which is given in Pa [105]. Assuming that all impinging atoms stick, at atmospheric pressure and ambient temperature a surface is covered by a monolayer of hydrogen in $1.3\cdot10^{-9}$ sec and at our deposition pressure of 10^{-4} Pa the contamination time is still 1.3 seconds. A summary of the way pressure affects gas density, and monolayer formation times can be found in Fig. 10.

The fact that the surface of the substrate is covered by a monolayer of residual gas almost instantly in our deposition pressures has to be remembered when depositing coatings. The actual coating deposition must be started immediately after the sputter cleaning of the substrate surface. In our system the energetic nature of our plasma ions [17,I,IV,V] helps to keep the surfaces clean, as the carbon ions are able to sputter away the residual gases stuck to the growing surfaces. This is evidenced by the low impurity concentrations (< 1 at.-%) of our coatings measured with nuclear methods [7].

3.3.3 The substrate

Earlier, our group has shown that to achieve well-adherent, thick, high-quality DLC coatings, it is essential to use suitably soft (<3 GPa, Vickers) substrate materials [8]. On harder substrates the maximum thickness of an adhesive DLC layer is in the order of a few hundred nanometers, due to high internal compressive stresses of the coatings. For example, the maximum thickness of high-quality (sp^3 fraction 85%) DLC deposited on commercial silicon wafers with our deposition set-up is 500 nm. However, this fact can be used to test the deposition process as explained in section 3.2.6.

Another necessary prerequisite for the substrate is that it must be a carbide former. A typical well behaving substrate material is the low carbon stainless steel AISI316L (in which the carbide former is chromium). On the other hand, direct deposition of DLC on copper fails, although it is a soft material, because it does not form carbides.

Thick coatings can also be deposited on harder substrates, but then a proper intermediate coating material such as tantalum [15,16] must be used. In soft materials such as plastics substrate surface deformation and sample heating by the high deposition rate may cause problems [8].

3.3.4 Energies and charge state fractions of the carbon ions in FPAD

Our energy and charge state results [17] differed drastically from those earlier measured from arc discharge plasmas [34]. Strong populations of doubly (23%) and triply (73%) ionised carbon were observed [17]. The relative intensities of the spectral lines for the 4+ charge state were very low in our measurement range and were not detected. However, based on ionisation energy considerations (E_{i3+} = 47.9 eV vs. E_{i4+} = 64.5 eV [106]) and the normally continuous shape of experimental charge-state distributions the existence of the 4+ state is likely. The energies of the carbon ions were found to depend on the charge-state and were 32, 110, and 250 eV for 1+, 2+ and 3+ states, respectively [17].

The huge difference in the current (200 A vs. 7.5-10 kA) is the main explanation for the higher charge states, but also the high magnetic field (0.8 T for a 20 loop straight solenoid with 10 kA current) and short pulse duration have their enhancing effect on the plasma electron temperature and ionisation [41,43].

The energy of the plasma ions was found to depend on the anode-cathode distance [IV]. Increasing the anode-cathode distance increases the energy of the carbon ions. Also the discharge voltage has a strong effect on the energy of the plasma ions, provided that the geometry is appropriate. When the distance between the cathode and anode was 4.6 cm, increasing the discharge voltage from 3000 V to 4000 V increased the energy of the plasma ions from 100 eV to 720 eV [IV]. These energies are sufficient for the production of the adhesion layer of DLC coatings.

The measurements in Paper V indicate that the carbon ion energies achieved with the simplified system may be still significantly higher, up to 4 keV [19,V]. The method of the Irkutsk group is based on the idea that the high current rise rate of a vacuum spark produces highly unbalanced plasma with enhanced ion acceleration [21]. In our system the current rise rate without the filtering solenoid is clearly higher [V]. However, according to the adhesion and quality test (I, section 3.2.6) adhesion with the simplified system is excellent but not perfect. Many craters were produced on the silicon wafer, but the whole surface was not broken as it is in the case of optimal adhesion [V]. The possible explanation for better adhesion in the filtered case is better plasma confinement and higher plasma density, which reduces interference due to interactions with residual gases. It can also be argued that the energy dispersion of the carbon plasma beam is higher when the filtering solenoid is not used [V].

In the actual DLC deposition unit a continuous cathode polishing system is used. The polishing stabilizes the carbon ion energies and thus also the quality of the resulting coating. Without cathode polishing the process yield drops in a very short time and the carbon ion energy increases. This would mean deposition times at least five times longer than with cathode polishing. For example in our current set-up the deposition time of 50 μm thick coating would increase from 10 to 50 hours. Without cathode polishing, plasma ion energy increases and the quality of the DLC coating changes.

Table 2. Properties of non-stick polymers PDMS and PTFE [101,107]

Property	PDMS	PTFE
Density (g/cm^3)	1.1-1.6	2.17
Elongation at break (%)	100-800	200-400
Resistivity (Ωm) at 20 °C	10^{13}	10^{17}
Temperature range of use (°C)	-115 to 315	-240 to 205
Chemical resistance	Good, resistant against weak acids	Excellent, resistant against strong acids

3.3.5 Properties of the “parent” polymers PDMS and PTFE

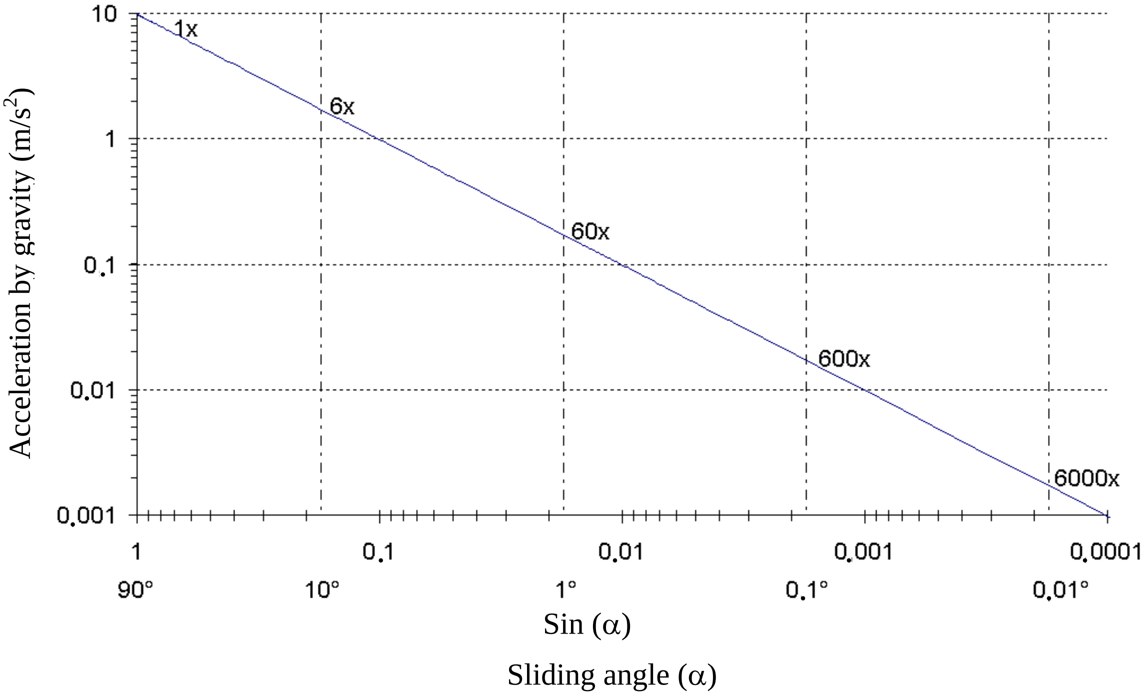
The polymers used in novel DLC-p-h coatings were polydimethylsiloxane (PDMS) and polytetrafluoroethylene (PTFE). PDMS is a representative of a family of polymers called polysiloxanes, more widely known by their trade name silicones. PDMS is an excellent electrical insulator and a common non-stick material. Its limitations are poor mechanical properties and limited chemical resistance. Another common non-stick polymer, PTFE (trade name teflon®) was also selected for the polymer component of our hybrid coatings. Its advantage compared to PDMS is its high chemical resistance. The representative properties of the used parent polymers PDMS and PTFE can be seen in Table 2.

3.3.6 Properties of the DLC-polymer hybrid films

DLC-p-h coatings with a wide range of physical properties can be prepared with the FPAD method. The Vickers hardness values of the DLC-PDMS-h coatings varied from 1 GPa to 70 GPa according to deposition speed [II]. The sp^3 fraction of 70% measured with ESCA corresponds well with the high hardness [II]. Higher deposition speed means a higher amount of the polymer component and better hydrophobicity and lower hardness. It should also be noted that the coatings are not isotropic as the DLC-polymer cathode heats up during the deposition process and the evaporation and sputtering of the polymer is enhanced towards the end of the deposition.

Both types of hybrid films showed high contact angles for water but DLC-PDMS-h coatings showed as a rule much lower sliding angles than DLC-PTFE-h. For the aforementioned reason, Papers II and III focused more on the DLC-PDMS-h coating. However, because of the higher chemical resistance of PTFE, DLC-PTFE-h coating might be more suitable for some applications, e.g. molds in the chemical industry.

Measuring very low sliding angles is not a simple task as the accelerating force is very low at low planar tilt angles. This is illustrated in Figure 11, where the accelerating force by gravity is plotted as a function of the sliding angle. With a tilt angle of 1° the accelerating force has decreased by a factor of 60 and with the tilt angle of 0.01° by a factor of 6000 from the angle of 90°. An extremely low sliding angle 0.15 ± 0.03° was measured on the surface of DLC-PDMS-h coating with a 20 µl distilled water droplet. This is currently the lowest sliding angle measured on a solid surface [III].



Sliding angle (α)

Fig. 11. A log-log plot of the acceleration by gravity of a droplet as a function of the sliding angle. The numbers in the plot give the comparison factor with the accelerating force at angle of 90°.

4 CONCLUSIONS AND FUTURE PROSPECTS

Thick high quality DLC coatings can be prepared with the FPAD method. The deposition of thick coatings has been made possible with the proper selection of the substrate material and/or with the use of intermediate layers such as tantalum. The tantalum acts both as an adhesion-improving layer and as a buffer layer against corrosion. Another essential requirement for achieving good adhesion of DLC coatings, is starting the deposition with high plasma ion energies to ensure sufficient interfacial mixing [I,IV,V]. With a properly constructed high-energy plasma unit, high carbon ion energies and good interfacial mixing can be achieved. Thick, well-adherent coatings are required for industrial and medical applications, such as artificial hip joints. With a proper substrate, suitable intermediate layer, interfacial mixing [I,IV,V] and thick well-adherent coatings all the technical problems related to DLC coated artificial hip joints can be solved as shown in our simulator experiments [12-15].

DLC coated artificial hip joints were first studied during the boom of diamond coating research in the late 80’s and early 90’s. These experiments failed systematically due to adhesion problems and insufficient coating thicknesses [108]. This led to deep suspicions of DLC coatings in the hip joint industry. These prejudices die hard and are currently one of the main obstacles to the commercialisation of DLC coated hip joints.

One important aspect of depositing DLC coatings for medical and industrial applications is maintaining sufficient process yield, so that deposition times remain reasonable. In the FPAD system sufficient process yield is maintained by using an *in situ* cathode polishing system [VI]. Unstable operation of the system may also have an adverse effect on the properties and adhesion of the DLC coatings. Cathode polishing stabilizes the carbon ion energies and thus also the quality of the resulting coating. Without cathode polishing the energy of plasma ions increases, resulting in quality changes in the growing coating and the process yield decreases, resulting in deposition times at least five times longer.

Interfacial mixing in the adhesion layer of FPAD deposited DLC coatings can be improved by increasing the energy of the carbon plasma ions. We have shown that carbon plasma can be accelerated to sufficient energies by increasing the anode-cathode distance and by using sufficiently high arc voltages [IV]. With a simplified arc discharge device even higher carbon ion energies are possible [V]. In fact, the energies achieved with our system were so high [IV,V] that this method for plasma acceleration should be investigated for use in fusion experiments. Currently fusion experiments are conducted with huge and mega-expensive TOKAMAK reactors. By colliding pulsed plasma beams together it might be possible to achieve fusion with a smaller, simpler and immensely cheaper system. Although this idea might sound far-fetched the gains of succeeding in such experiments are so high that they warrant a try.

The main problems of present artificial hip and knee implants are usually related to wear and corrosion in the human body environment. Mechanical stress and wear debris can lead to aseptic loosening or mechanical failure of the implant. Also the corrosion products of most present implant materials may have adverse health effects. High quality DLC is the superior coating material for preventing wear and corrosion related problems of human implants. The corrosion of DLC is minimal and its wear is near the detection limit. Even if the DLC coating delaminates, the DLC particles will probably have negligible negative health effects, as they are pure carbon and thus naturally biocompatible. Of course the coatings have to be thick enough to withstand the high stresses present in a human knee or hip joint. The FPAD method has shown itself to be reliable method for producing such thick high quality DLC coatings. In fact it is currently the only reported method in the world that can achieve this.

With a slight modification of the FPAD deposition system a whole new group of materials, the DLC-polymer-hybrids, can be deposited [II]. Currently we have experimented with the most common so-called non-stick materials, PDMS and PTFE as the polymer component, but other polymers can also be used. The hybrid coatings are harder than any polymers and have retained the excellent hydro- and oleophobic properties of the polymers [II,III]. The DLC-PDMS-h coating has superior non-stick properties and has already found its first application in the protection of moulds used in the preparation of PDMS electrospray chips used in electrospray ionisation mass spectrometry [109]. The use of DLC-PDMS-h to increase the lifetime of plastic moulds is a promising industrial application of the coating. The biocompatibility and the possible biomechanical applications of the novel DLC-p-h coatings will be studied in the near future. The anti-soiling properties of DLC-p-h coatings make them very promising for applications that require hemocompatibility such as artificial heart valves.

NOMENCLATURE

AD	Amorphous diamond, a popular term for a material that has amorphous structure and possesses properties similar to natural diamond.
AISI316L	Low carbon acid resistant stainless steel alloy, contains iron,18% chromium, 10% nickel and 3% molybdenium.
Amorphous	Without any long range order.
Cathode polishing	A method of stabilising the process yield, energy of the carbon plasma and quality of the resulting coating by continuously abrading the cathode against an alumina sheet during the deposition.
CCD	Charge-coupled device, a semiconductor device used as an optical sensor in digital cameras. Stores charge and transfers it sequentially to an amplifier and detector.
CVD	Chemical vapour deposition, general name for methods in which the film deposition occurs via chemical processes through the gas phase.
DLC	Diamond-like carbon, a general term for material with sp^3 diamond bonds.
DLC-p-h	Diamond-like carbon polymer hybrid, a new group of materials developed by the ORTON Diamond Group that has diamond-like and polymer-like properties.
DLC-PDMS-h	Diamond-like carbon polydimethylsiloxane hybrid, a novel coating with polydimethylsiloxane and carbon with diamond bonds.
DLC-PTFE-h	Diamond-like carbon polytetrafluoroethylene hybrid, a novel coating with polytetrafluoroethylene and carbon with diamond bonds.
DSA	Doppler shift attenuation. An ion beam method for obtaining the density of DLC coatings and requiring a very high level of technical expertise.
EELS	Electron Energy Loss Specroscopy. A materials analysis technique based on the energy loss of electrons as they travel through a sample.
ERDA	Elastic recoil detection analysis. An ion beam method for evaluating the elemental compositions of materials.
ESCA	Electron spectroscopy for chemical analysis. A materials analysis technique where photoelectrons are induced from the sample using X-rays. The binding energy of the electrons of a given element depends on the chemical surroundings of that element. By measuring the energies of the photoelectrons the chemical bonds in the sample can be identified. Also known as XPS (X-ray photoelectron spectroscopy).

FPAD method	Filter pulsed arc discharge method, a coating method developed by the ORTON Diamond Group.
Hydrophobicity	The ability of a surface to repel water.
Langmuir probe	A small electrode placed in contact with plasma for measuring its properties. The potential of the electrode is varied while the resulting collection currents are measured.
Nanoindenter	A high technology method of measuring mechanical properties of materials in nanometer scale. Elastic modulus and deformation behaviour are determined from an analysis of the force vs. displacement response measured during indentation of the material.
Nuclear methods	Group of materials analysis methods that are based on nuclear reactions induced in the sample by e.g. proton beam.
MEMS	Micro-electromechanical systems, miniature sensors, motors, transmissions etc.
MSIB	Mass separated ion beam. A laboratory method of producing thin films e.g very high quality DLC films.
Oleophobicity	The ability of surface to repel oils.
PDMS	Polydimethysiloxane, chemical formula $[(CH_3)_2\text{-Si-O}]_{n,}$ hydrophobic, elastic polymer, the most commonly used polysiloxane. Polysiloxanes are better known by their tradename silicones.
PLD	Pulsed laser deposition. A method of depositing DLC films, that utilizes lasers.
Plasma	The most common state of known matter in the universe. Partially ionised gas composed of ions, electrons and neutral species. Electrically neutral, when averaged over all the particles it contains.
PTFE	Polytetrafluoroethylene, the most commonly used hydrophobic fluorocarbon polymer. It is also known by its trade name teflon$^{©}$, chemical formula $[CF_2]_n$.
PVD	Physical vapour deposition, general name for methods in which the film deposition occurs via physical processes through the gas phase. Common PVD methods are e.g. evaporation, sputtering and ion beam deposition.
Sliding angle	Critical angle at which a droplet starts to slide on an inclined plane.
Superhydrophobic	see. Ultrahydrophobic

ta-C	Tetrahedral amorphous carbon, a scientific term for a carbon material that has amorphous structure and contains significant amount of sp^3 diamond bonds (> 80%) and no hydrogen.
TEM	Transmission electron microscopy. An electron microscopy technique based on electrons travelling through a very thin sample.
TOF	Time-of flight, an energy measurement method based on a measurement of a time-of-flight of an object in a known distance.
Tribology	Science of the phenomena in surfaces sliding against each other. Science of friction, wear and lubrication.
TRIM	The transport of ions in matter. A downloadable software for simulating the transport of ions matter. http://www.srim.org/
Ultrahydrophobic	A surface that combines a hydrophobic material with high surface roughness and shows very high contact angles is said to be ultrahydropobic surface. The theorectial maximum for contact angle of a hydrophobic material is approximately 120°.
XPS	X-ray photoelectron spectroscopy. Also known as ESCA.

ACKNOWLEDGEMENTS

Sincere thanks to my supervisor, Professor emeritus Asko Anttila, the founder and prime motor of our research group. Without his ideas and support this work would not have been possible. My second supervisor the current head of the Diamond Group, PhD Veli-Matti Tiainen is thanked for his expertise, enthusiasm, and guidance. Thanks are also due to Professor Reijo Lappalainen from the University of Kuopio. To former and current members of our research group, including Mirjami, Panu, Jouko, Harri, Antti, Petteri, and Timo thanks for creating informal and fun working atmosphere with lots of laughs.

Professor Juhani Keinonen is thanked for letting me conduct research in the Department of Physics in the beginning of this work. The current head of the Accelerator Laboratory, Professor Jyrki Räisänen, gave me all the support in his powers, of which I am accordingly grateful. Both gentlemen are thanked for having made it possible for our group to move on and continue our research also after the National Centre of Excellence status of the Academy of Finland 2000-2005 ceased. The personnel of the Accelerator Laboratory are thanked for their hard work and help at the Kumpula end during our move to ORTON. The help of Raimo Ingren with technical matters of our research group during our years at Siltavuorenpenger and at Kumpula is greatly appreciated. Engineer Seppo Kousa is thanked for his ingenious help in solving some electronic problems in the experiments for this work.

Professors Juha-Pekka Hirvonen and Nureddin Ashammakhi are thanked for their hard work in reviewing this thesis.

The leaders of the BRG Centre for Excellence, Professor Yrjö T. Konttinen and the late Professor Seppo Santavirta, are thanked for their unwavering support of our group in its difficulties. Professor Konttinen has found from his already extremely busy schedule numerous working hours to tend to the matters of our research group. Personally I am extremely grateful for his work in finding the funding for the completion of this work.

The Surgeon-in-Chief of ORTON Invalid Foundation professor Seppo Seitsalo and the Research Director of ORTON Research Institute Docent Dietrich Schlenzka are thanked for providing our group excellent new facilities at ORTON in which to conduct our research. The completion of this work would have been very difficult without these new facilities. The

personnel of ORTON Invalid Foundation and Orton Research Institute, especially P.T., PhD Jyrki Kettunen, are thanked for helping in the restart of our laboratory and in the daily chores.

Warmest thanks and my love to family and friends. You are all in my heart. Your support and understanding have been invaluable. I am extremely lucky of having such warm relationships with my parents, Raija and Asko. They have always been there for me and believed in me, of which I am deeply grateful. And thank you, Pipa, for coming into my life. Your love and warmth have made the last year and a half happy for me and eased the stress of the last months. Matti is thanked for providing me a place to stay when in need and for being such a great friend and my cousin Timo for being like a brother to me.

The financial support of the National PhD Graduate School in Biomaterials and Tissue Engineering, Academy of Finland, Tekes, the Magnus Ehrnrooth Foundation and the Sigrid Juselius Foundation is gratefully acknowledged.

Helsinki, September 2006
Esa Alakoski

REFERENCES

[1] Y. Lifshitz, Diamond Relat. Mater. **8**, 1659 (1999).

[2] D.R. McKenzie, Rep. Prog. Phys. **59**, 1611 (1996).

[3] A. S. Gilmour Jr. and D. L. Lockwood, Proceedings of the IEEE **60,** 977 (1972).

[4] A.I. Maslov, G.K. Dimitriev, Yu.D. Chistyakov, Pribory y Tekhnika Eksperimenta **3**, 2524 (1985).

[5] A. Anders, G.Y. Yushkov, IEEE Trans. Plasma Sci. **30**, 108 (2002).

[6] J.-P. Hirvonen, J. Koskinen, R. Lappalainen, A. Anttila, Materials Science Forum **52-53**, 197 (1989).

[7] J.-P. Hirvonen, J. Koskinen, P. Torri, R. Lappalainen, A. Anttila, Nucl. Instrum. Methods B **53**, 118 (1996).

[8] A. Anttila, R. Lappalainen, V-M. Tiainen, M. Hakovirta, Adv. Mater. **9**, 1161 (1997).

[9] M. Hakovirta, J. Salo, A. Anttila, R. Lappalainen, Diamond Relat. Mater. **4**, 1335 (1995).

[10] A. Anttila: in 'Structure-Property Relationships in Surface-Modified Ceramics, NATO ASI Series', ed. C. J. McHargue *et al.*, Kluwer, The Netherlands, 455 (1989).

[11] V-M. Tiainen, Vacuum **67**, 599 (2001).

[12] R. Lappalainen, M. Selenius, A. Anttila, Y. T. Konttinen, S. Santavirta, J. Biomed. Mater. Res. Part B: Appl. Biomater. **66**B, 410 (2003).

[13] V-M. Tiainen, Diamond Relat. Mater. **10**, 153 (2001).

[14] A. Anttila, R. Lappalainen, H. Heinonen, S. Santavirta, Y. T. Konttinen, New Diam. Front. C. Tech. **9**, 283 (1999).

[15] M. Kiuru, E. Alakoski, V-M. Tiainen, R. Lappalainen, A. Anttila, J. Biomed. Mater. Res. Part B: Appl. Biomater. **66**B, 425 (2003).

[16] E. Alakoski, M. Kiuru, A. Soininen, V-M. Tiainen, A. Anttila, R. Lappalainen, *Tantaalin käyttö suojaavana välikerroksena PVD-timanttipinnoitteiden alla*, FI-patent application 12.3.2002, application number 20020463.

[17] V-M. Tiainen, E. Alakoski, M. Kiuru, A. Soininen, A. Anttila, Eur. Phys. J., Appl. Phys. **22**, ,111 (2003).

[18] E. Alakoski, M. Kiuru, A. Soininen, V-M. Tiainen, A. Anttila, R. Lappalainen, *Timanttisidoksiset hiili-polymeerimateriaalit*, FI-patent application 12.3.2002, application number 20020462.

[19] N. V. Astrakhantsev, V. I. Krasov, V. L. Paperny, J. Phys. D **28**, 2514 (1995).

[20] S. P. Gorbunov, V. I. Krasov, V. L. Paperny, J. Phys. D **30**, 1922 (1997).

[21] M. F. Artamonov, V. I. Krasov, V. L. Paperny, Journal of Experimental and Theoretical physics **93**, 1216 (2001) 6.

[22] M. F. Artamonov, V. I. Krasov, V. L. Paperny, J. Phys. D**34,** 3364 (1997).

[23] J. Schwan, S. Ulrich, H. Roth, H. Eherhardt, S.R.P. Silva, J. Robertson, R. Samlenski, J. Appl. Phys **79**, 1416 (1996).

[24] J.J. Cuomo, J.P. Doyle, J. Bruley, J.C. Liu, Appl. Phys. Lett. **58**, 466 (1991).

[25] A.A.Voevodin, M.S. Donley, J.S. Zabinski, Surf. Coat. Technol. **42-49**, 92 (1997).

[26] Y.Y.Tsui, D.G.Redman, Surf. Coat. Technol. **96-101**, 126 (2000).

[27] M. Hakovirta, J. Salo, R. Lappalainen, A. Anttila, , Phys. Lett. A **205**, 287 (1995).

[28] A. Anttila, J.-P. Hirvonen, J. Koskinen, US Patent 5078848 (1992).

[29] A.Anttila and J. Koskinen, FIN Patent 89725 (1993).

[30] J. Robertson, Mat. Sci. Eng. R. **37**, 129 (2002).

[31] A. Anders, G.Y. Yushkov, J. Appl. Phys. **88**, 5618 (2000).

[32] A. Anders, G.Y. Yushkov, J. Appl. Phys. **96**, 970 (2004).

[33] A. Anders, G.Y. Yushkov, J. Appl. Phys. **91**, 4824 (2002).

[34] W.D. Davis, H.C. Miller, J. Appl. Phys. **40**, 2212 (1969).

[35] I.G. Brown, G. Feinberg, J.E. Galvin, Appl. Phys. **63**, 4889 (1988).

[36] I.G. Brown, X. Godechot, IEEE Trans. Plasma Sci. **19**, 713 (1991).

[37] I.G. Brown, Rev. Sci. Instrum. **65**, 3061 (1994).

[38] A. Anders, IEEE Trans. Plasma Sci. **29**, 393 (2001).

[39] J. Kutzner, H.C. Miller, J. Phys. D **25**, 686 (1992).

[40] E. M. Oks, A. Anders, I.G. Brown, M.R. Dickinson, R.A. MacGill, IEEE Trans. Plasma Sci. **24**, 1174 (1996).

[41] A. S. Bugaev, V.I. Gushenets, G.Y. Yushkov, E.M. Oks, A. Anders, I. Brown, A. Gershkovich, P. Spadke, Russian Physics Journal, **44**, 912 (2001).

[42] J.E. Galvin, I.G. Brown, R.A. MacGill, Rev. Sci. Instrum. **61**, 583 (1990).

[43] A. Anders, I.G. Brown, R.A. MacGill, M. Dickinson, Rev. Sci. Instrum. **67**, 1203 (1996).

[44] G.A. Mesyats, Cathode phenomena in a vacuum discharge, The Breakdown, The Spark, and The Arc, Moscow, Russia:Nauka, (2000).

[45] A. Anders, S. Anders, B. Juttner, I.G. Brown, IEEE Trans. Plasma Sci. **21**, 305 (1993).

[46] A. Anttila, J. Salo, R. Lappalainen, Mater. Lett **24**, 153 (1995).

[47] P.J. Fallon, V.S. Veerasamy, C.A. Davis, J. Robertson, G.A.J. Amaratunga, W.I. Milne, J. Koskinen, Phys Rev. B **48**, 4877 (1993).

[48] A.C. Ferrari, S.E. Rodil, J. Robertson, W.I. Milne, Diamond Relat. Mater. **11**, 994 (2002).

[49] D.R. McKenzie, D. Muller, B.A. Pailthorpe, Phys. Rev. Lett. **67**, 773 (1991).

[50] T.A. Friedmann, J..P. Sullivan, J.A. Knapp, D.R. Tallant, D.M. Follstaedt, D.L. Medlin, P.B. Mirkamiri, Appl. Phys. Lett. **71**, 3820 (1997).

[51] J.C. Damasceno, S.S. Camargo Jr., F.L. Freire Jr., R. Carius, Surf. Coat. Technol. **133-134**, 247 (2000).

[52] B.K. Tay, Y.H. Cheng, X.Z. Ding, Diam. Relat. Mater **10**, 1082 (2001).

[53] M. Chhowalla, Y. Yin, G.A. Amaratunga, D.R. MacKenzie, Th. Frauenheimer, Appl. Phys. Let. **69**, 2344 (1996).

[54] M. Chhowalla, G.A. Amaratunga, J. Mater. Res. **16**, 5 (2001).

[55] D. Sheeja, B. K. Tay, L. J. Yu, S. P. Lau, Surf. Coat. Technol. **154**, 289 (2001).

[56] D.H. Lee, S. Fayeulle, K. C. Walter, M. Nastasi, Nucl. Instrum. Methods Phys. Res. B **148**, 216 (1999).

[57] B.K. Tay, D. Sheeja, L.J. Wu, Diamond Relat. Mater. **12**, 185 (2003).

[58] D. Sheeja, B. K. Tay, J. Y. Sze, L. J. Yu, S. P. Lau, Diamond Relat. Mater. **12**, 2032 (2003).

[59] Y. Lifshitz, Diamond Relat. Mater. **12**, 130 (2003).

[60] J. Robertson, Diamond Relat. Mater. **12**, 79 (2003).

[61] P.C. Hiementz (ed.) Principles of Colloid and Surface Chemistry, Dekker, New York, Basel, 307 (1986).

[62] H.T. Davis, Advances in Engineering Series, Chapter 7, VCH Publishers Inc. (1996).

[63] D.Y. Kwok, A.W. Neumann, Adv. Colloid Interface Sci. **81**, 167 (1999).

[64] L. Makkonen, Langmuir **16**, 7669 (2000).

[65] L.W Schwartz, S. Garoff, Langmuir **1**, 219 (1985).

[66] J.H.Wang, P.M.Claesson, J.L.Parker, H.Yasuda, Langmuir **10**,3887 (1994).

[67] R.E.Johnson, R.H.Dettre, J.Colloid. Interface Sci **62**, 205 (1977).

[68] J.Drelich, Polish J. Chem. **71**, 525 (1997).

[69] R. Blossey, Nature Mater. **2**, 301 (2003).

[70] W. Chen, A.Y. Fadeev, M.C. Hsih, D. Öner, J. Youngblood, T.J. McCarthy, Langmuir **15**, 3395 (1999).

[71] H. Murase, T. Fujibayashi, Prog. Org. Coat. **31**, 97 (1997).

[72] T. Nishino, M. Meguro, K. Nakamae, M. Matsushita, Y. Ueda, Langmuir **15**, 4321 (1999).

[73] A. Nakajima, K. Hashimoto, T. Watanabe, Monatsh. Chem. **132**, 31 (2001).

[74] A. Nakajima, A. Fujishima, Adv. Mater. **11**, 1365 (1999).

[75] T. Onda, S. Shibuichi, N. Satoh, T. Tsujii, Langmuir **12**, 2125 (1996).

[76] S. Ren, S. Yang, Y. Zhao, T. Yu, X. Xiao, Surf. Sci. **546**, 64, (2003).

[77] J.Fresnais, L Benyahia, J.P. Chapel, Poncin-Epaillard F., Eur. Phys. J., Appl. Phys. **26**, 209 (2004).

[78] S.A. Kulinich, M. Farzaneh, Appl. Surf. Sci. **230**, 232, (2004).

[79] S. Li, H. Li, X. Wang, Y. Song, Y. Liu, L. Yiang, D. Zhu, J. Phys. Chem. B **106**, 9274 (2002).

[80] M. Miwa, A. Nakajima, A. Fujishima, K. Hashimoto, T. Watanabe, Langmuir **16**, 5754 (2000).

[81] R.S. Butter, A.H. Lettington, P. Vincenzi (Ed.), New Diamond and Diamond-like Films, Advances in Sci. Technol. **6**, 353 (1994).

[82] D. Flösch, G. Clarotti, K.E. Geckeler, F. Schue, W. Göpel, J. Membr. Sci.**73**, 163 (1992).

[83] J. Seth, S.V. Babu, Thin Solid Films **230**, 90 (1993).

[84] I. Scmidt, F. Hentschel, C. Benndorf, Diamond Relat. Mater. **5**, 1318 (1996).

[85] M. Grischke, A. Hieke, F. Morgenweck, H. Dimingen, Diam. Relat. Mater. **5**, 454 (1998).

[86] M. Hakovirta, R. Verda, X.M. He, M. Nastasi, Diamond Relat. Mater. **10**, 1486 (2001).

[87] L.G. Jacobshon, M.E.H. Maia da Costa, V. J. Trava-Airoldi, F.L. Freire Jr, Diamond Relat. Mater. **12**, 2037 (2003).

[88] H. Yokomichi, T. Hayashi, A. Masuda, Appl. Phys. Lett. **72**, 2704 (1998).

[89] J.S. Chen, S.P. Lau, Z. Sun, G.Y. Chen, Y.J. Li, B.K. Tay, J.W. Chai, Thin Solid Films **398-399**, 110 (2001).

[90] B.K. Tay, D. Sheeja, S.P. Lau, J.X. Guo, Diamond Relat. Mater. **12**, 2072 (2003).

[91] A. –S. Loir, F. Garrelie, C. Donnet, M. Belin, B. Forest, F. Rogemond, P. Laporte, Thin Solid Films **453**, 531 (2004).

[92] M. M. Morshed, B. P. McNamara, D. C. Cameron, M. S. J. Hashmi, Surf. Coat. Technol. **163**, 541 (2003).

[93] S. Xu, D. Flynn, B.K. Tay, S. Prawer, K.W. Nugent, S.R.P. Silva, Y. Lifshitz, W.I. Milne, Phil. Mag. B **76**, 351 (1997).

[94] M. Chhowalla, J. Robertson, C.W. Chen, S.R.P. Silva, C.A. Davis, G.A.J. Amaratunga, W.I. Milne, J. Appl. Phys. **81**, 139 (1997).

[95] J. Salo, Nucl. Instr and Meth. B **95**, 119 (1995).

[96] J. Salo, R. Lappalainen, A. Anttila, Appl. Phys. A **61**, 353 (1995).

[97] L.C. Feldman, J.W. Mayer, Fundamentals of Surface and Thin Film Analysis, 1st edition, Elsevier Science Publishing Co. Inc., 1986.

[98] J. Diaz, G. Paolizelli, S. Ferrer, F. Comin, Phys. Rev. B **54**, 8064 (1996).

[99] P. Merel, M. Tabbal, M. Chaker , S. Moisa, J. Margot, Appl. Surf. Sci. **136**, 105 (1998).

[100] A. Anttila, J. Salo, R. Lappalainen, Mater. Lett. **24**, 153 (1995).

[101] W.D. Callister Jr., Materials Science and Engineering – An Introduction, 5th edition, John Wiley & Sons Inc., (2000).

[102] V.N. Inkin, G.G. Kiprilenko, A.J. Kolpakov, Diamond Relat. Mater. **10**, 1103 (2001).

[103] Q. Wei, J. Sankar, J. Narayan, Surf. Coat. Technol. **146-147**, 250 (2001).

[104] Y. Oka, Y. Nishimura, M. Yatsuzuka, Vacuum **73**, 541 (2004).

[105] M. Ohring, The Materials Science of Thin Films, 1st edition, Academic Press Inc., (1992).

[106] CRC Handbook of Chemistry and Physics, 82nd edition, CRC Press, New York (2001).

[107] http://www.dupont.com/teflon/films/H-55008-2.html

[108] M.J. Allen, J.E.F Houlton, P.J. Millet, B. J. Myer, N. Rushton, Combined Orthopaedic Research Meeting, Sept. 28-30, Hamatsu, Japan, 189 (1998).

[109] K. Huikko, P. Östman, K. Grigoras, S. Tuomikoski, V-M. Tiainen, A. Soininen, K. Puolanne, A. Manz, S. Franssila, R. Kostiainen, T. Kotiaho, Lab Chip **3**, 67 (2003).