

MASARYKOVA UNIVERZITA

PŘÍRODOVĚDECKÁ FAKULTA

ÚSTAV FYZIKY A TECHNOLOGIÍ PLAZMATU

Diplomová práce

BRNO 2024

MICHAL FLEISCHER

Variace dielektrických bariérových výbojů běžně používaných pro průmyslové aplikace

Diplomová práce

Michal Fleischer

Vedoucí práce: Mgr. Jakub Kellar, Ph.D. Brno 2024

Bibliografický záznam

Autor:	Bc. Michal Fleicher Přírodovědecká fakulta, Masarykova univerzita Ústav fyziky a technologií plazmatu
Název práce:	Variace dielektrických bariérových výbojů běžně používaných pro průmyslové aplikace
Studijní program:	Fyzika
Studijní obor:	Fyzika plazmatu a nanotechnologií
Vedoucí práce:	Mgr. Jakub Kelar, Ph.D.
Akademický rok:	2021/2024
Počet stran:	xi + 72
Klíčová slova:	Dielektrický bariérový výboj; DCSBD; HDCSBD; Optická emisní spektroskopie; osciloskopická měření; kontaktní úhel; adheze; polymery; nízkoteplotní plazma; X-ray photoelektronová spektroskopie; spektroskopie atomických sil; UV- digitální tisk; povrchová úprava

Bibliographic Entry

Author:	Bc. Michal Fleicher Faculty of Science, Masaryk University Department of Plasma Physics and Technology
Title of Thesis:	Dielectric barrier discharges variations commonly used for industrial applications
Degree Programme:	Physics
Field of Study:	Plasma physics and nanotechnology
Supervisor:	Mgr. Jakub Kelar, Ph.D.
Academic Year:	2021/2024
Number of Pages:	xi + 72
Keywords:	Dielectric barrier discharge; DCSBD; HDCSBD; Optical emission spectroscopy; Oscilloscopic measurements; Contact angle; Adhesion; Polymers; Low-temperature plasma; X-ray photoelectron spectroscopy; Atomic force spectroscopy; UV digital printing; Surface treatment

Abstrakt

Tato práce se zabývá studiem dielektrických bariérových výbojů (DBD, z angl. dielectric barrier discharge) při atmosférickém tlaku, s hlavním zaměřením na Difúzní Koplanární Povrchový Bariérový Výboj (DCSBD, z angl. Diffuse coplanar surface barrier discharge) vyvinutý prof. M. Černákem a jeho týmem. DCSBD získalo pozornost pro svou účinnost při úpravě povrchu obrovské škály materiálů jako třeba polymerů, textilií nebo biomateriálů, příkladem mohou být semena plodin. Součástí téhle práce je zkoumání DBD, zejména konfigurace nesoucí technický název Half-DCSBD jako kompaktní jednotka s upravenou speciální konfigurací DCSBD. Rozšiřování využití plazmové úpravy pro modifikaci povrchů vede ke snaze aplikovat tuhle metodu i v jiných průmyslových odvětvích jako je UV-digitální tisk. Práce se zabývá řešením výzvy jako je adheze podkladů typických pro tento průmysl. Bodem zájmu byly elektrické vlastnosti HDCSBD ale také vibrační a rotační teplota plazmatu produkované konfigurací HDCSBD a porovnání s průmyslově využívaným DCSBD. V práci byla pozorována efektivita napájení pro jednotlivé výboje. Plazmové zdroje byly dále zkoumané za pomoci optické emisní spektroskopie k posouzení vibračních a rotačních teplot a ověření vhodnosti HDCSBD pro využití v oblasti povrchové úpravy. Dále se práce také zabývá aplikací plazmových zdrojů pro modifikaci polykarbonátu a polyethylenu s hliníkovým podkladem určených pro UV-digitální tisk. Pro optimalizování aplikace byly využité různé analytické metody k vyhodnocování smáčenlivosti, změn povrchové energie, měření adhezivních vlastností ale také pozorování chemických a morfologických změn, které vznikly plazmovou úpravou. Výsledky přispívají k porozumění konfigurace HDCSBD a její aplikaci v průmyslu UV-digitálního tisku.

Abstract

This thesis addresses the study of dielectric barrier discharges (DBD) at atmospheric pressure, with a focus on the Diffuse Coplanar Surface Barrier Discharge (DCSBD) developed by Prof. M. Černák and his team. DCSBD has gained attention for its effectiveness in surface modification of a wide range of materials such as polymers, textiles, or biological elements, for example crop seeds. Part of this work involves investigating DBD, particularly the configuration currently known as Half-DCSBD, as a compact unit with a modified special configuration of DCSBD. The expanding use of plasma treatment for surface modification leads to efforts to apply this method in other industrial sectors such as UV digital printing. The thesis addresses challenges such as adhesion of substrates typical for this industry. The focus was on the electrical properties of HDCSBD as well as observing vibrational and rotational temperatures of molecules in the plasma produced by HDCSBD configuration and comparison with industrially used DCSBD. The efficiency of power supply was calculated for each of observed discharges. Plasma sources were examined using optical emission spectroscopy to assess vibrational and rotational temperatures and verify the suitability of HDCSBD for surface treatment applications. Furthermore, the thesis also deals with the application of plasma sources for the modification of polycarbonate and polyethylene with an aluminum substrate intended for UV digital printing. Various analytical methods were used to optimize the application, including evaluating wettability, changes in surface energy, measuring adhesive properties, as well as observing chemical and morphological changes resulting from plasma treatment. The results contribute to understanding the HDCSBD configuration and its usability in the UV digital printing industry.

ZADÁNÍ
DIPLOMOVÉ PRÁCE

Akademický rok: 2023/2024

Ústav:	Ústav fyziky a technologií plazmatu
Student:	Bc. Michal Fleischer
Program:	Fyzika
Specializace:	Fyzika plazmatu a nanotechnologií

Ředitel *ústavu* PŘF MU Vám ve smyslu Studijního a zkušebního řádu MU určuje diplomovou práci s názvem:

Název práce:	Dielectric barrier discharges variations commonly used for industrial applications
Název práce anglicky:	Dielectric barrier discharges variations commonly used for industrial applications
Jazyk závěrečné práce:	angličtina

Oficiální zadání:

Dielectric barrier discharges are widely used in industry. This fact alone is making any serious study of their properties highly interesting one. During this two year work students will compare several dielectric barrier discharges found in laboratories of the Department of physical electronics with high industrial application potential on grounds of their thermal properties, optical emission properties, electrical properties etc.

Vedoucí práce:	Mgr. Jakub Kelar, Ph.D.
Konzultant:	RNDr. Zlata Kelar Tučková, PhD.
Datum zadání práce:	9. 12. 2021
V Brně dne:	1. 5. 2024

Zadání bylo schváleno prostřednictvím IS MU.

Bc. Michal Fleischer, 7. 1. 2022

Mgr. Jakub Kelar, Ph.D., 12. 1. 2022

Mgr. Dušan Hemzal, Ph.D., 25. 1. 2022

Poděkování

Na tomto místě bych chtěl v první řadě poděkovat mému vedoucímu, Mgr. Jakubovi Kellarovi Ph.D., který i přes problémy do mě vložil svou důvěru a pomohl mi celou cestou při psaní této práce. Zároveň bych chtěl poděkovat RNDr. Zlatě Kellar Tučkové, Ph.D., která mi byla až do předání oporou a podporovala mě v průběhu celého magisterského studia. Jejich nekonečná trpělivost s mou osobou mi umožnila psaní této práce a vytvoření její finální podoby, která stojí před Vámi. Spravovat své studium a zároveň zvládat každodenní nástrahy pracovního a osobního života není nikdy snadné, proto bych na tomto místě chtěl poděkovat nejen opět mému vedoucímu doktorovi Kellarovi a doktorce Kellar Tučkové, ale i mé rodině, přítelkyni, dlouholetým přátelům a kolegům, kteří při mně stáli v každé chvíli a pomohli mi dojít až do tohoto bodu.

Prohlášení

Prohlašuji, že jsem svoji diplomovou práci vypracoval(-a) samostatně pod vedením vedoucího práce s využitím informačních zdrojů, které jsou v práci citovány.

Brno 6. května 2024

.....
Michal Fleischer

Contents

Introduction	1
Kapitola 1. Theoretical Part	3
1.1 Plasma	3
1.1.1 Plasma Criteria	5
1.2 Applications of Plasma	6
1.3 Dielectric Barrier Discharge	7
Kapitola 2. Experimental Setup and diagnostic methods	12
2.1 Equipment description	12
2.2 Measurement of electrical properties	13
2.3 Optical Emission Spectroscopy	14
2.3.1 Vibrational Temperature	16
2.3.2 Rotational Temperature	16
2.4 Analytical setups for plasma treatment evaluation	17
2.4.1 Surface Free Energy and Contact Angle	17
2.4.2 Measurements of Adhesion	20
2.4.3 Cross-cut Test	22
2.4.4 Chemical Characterization	23
2.5 Morphological Characterisation	24
2.5.1 Atomic Force Microscopy	25
2.5.2 Scanning Electron Microscopy	27
Kapitola 3. Results of experiments and discussion	30
3.1 Power efficiency	31
3.1.1 DCSBD	31
3.1.2 HDCSBD	35
3.2 Optical emission spectroscopy of plasma sources	39
3.3 Wettability and Adhesion of Treated substrates	42
3.4 XPS measurements of treated polymers	51
3.5 Morphological observations of treated polymer substrates	54
3.6 Cross-Cut test - Ink Adhesion	56
Conclusion	60

Bibliography	63
Publication activity	68

Introduction

This thesis addresses dielectric barrier discharges (DBD) operating at atmospheric pressure. Department of Plasma Physics and Technology at Masaryk University in Brno has a long history of researching these discharges. A common plasma source for LTP treatment called Diffuse Coplanar Surface Barrier Discharge (DCSBD) was developed by prof. RNDr. M. Černák, CSc. and his team at Comenius University in Bratislava. This dielectric barrier discharge became a main focus for great amount of scientific publications especially for surface treatment of different materials. [1, 2, 3]. Low-temperature plasma (LTP) treatment is commonly used for surface modification, as it improves surface free energy, adhesive properties of the material, or overall wettability of the sample. One of the main advantages of DCSBD is its large treatment area in comparison with commonly used LTPs such as industrial corona or plasma jet, the overall homogeneity of created plasma and no limitation for sample dimensions which cannot be said for industrially used volume barrier discharges.

The DCSBD is widely used for surface modification. It shows favorable results in plasma treatment of biological samples such as seeds of different crops which was a point of discussion in my bachelor's thesis [4]. The discharge has shown improvement of surface properties for textile, fibers, wood and glass or different groups of polymers [5, 6].

As the research of DBD progresses, the usage of LTPs is starting to spread into different industry sectors. One of recent applications is large-format UV-digital printing [7, 8]. One of the main challenges of this printing method is a selection of correct substrate materials with desired properties. Commonly used polymers tend to have a smooth surface with a low surface energy which often causes insufficient adhesion of inks used for UV-digital printing. The adhesion also varies on the color used for the printing or the pattern of the printed image. Adhesive properties or abrasion resistance then affects the final product's usage.

One of the DCSBD most limiting components is the cooling system. The simplest configuration for cooling system of DCSBD is an oil pump with implemented cooling mechanism (such as fan, cold flowing water, etc.). The oil is used as a dielectric that is in direct contact with electrodes. The oil needs to be constantly cooled down to prevent overheating of the plasma source.

In this thesis, we focus on special configuration of DCSBD with a technical name Half-DCSBD (HDCSBD). This setup utilizes simpler cooling system which is further discussed in the sections of this work. Another distinction lies in the position of electrodes which are built into ceramic, and not being covered by special oil. There are numerous studies of DCSBD. One such publication is thesis of Mgr. J. Kelar, Ph.D. [9], which is an extensive study of DCSBD parameters. Due to its high coverage of DCSBD electrical properties

of plasma unit as well as thermal properties of the particles inside of plasma for various generators and frequencies of transformers, we conducted just selective measurements for DCSBD.

The HDCSBD electrical properties and thermal properties of molecules underwent analysis and were compared to the properties of DCSBD. We conducted measurement to access the efficiency of a high voltage source used to supply power for HDCSBD as well as for voltage source of DCSBD used in industry. HDCSBD properties were measured for different input powers as well as different temperatures of plasma. As a method to obtain information about generator efficiency, we used classical method for calculating power in plasma from definition of electrical power as the product of voltage and current integrated over a given period of observed signals measured by oscilloscope. For final calculation, a program was written in Python3 to locate maximums and minimums of measured signals, correctly set measured period and calculate power in plasma using the mentioned definition.

An optical emission spectroscopy was conducted on the HDCSBD as well as on DCSBD powered by generator and transformer with maximum input power and frequency commonly used in industrial applications. This measurement accesses rotational temperatures of OH^- molecules and vibrational temperatures from vibrational lines of molecules of nitrogen. To calculate these temperatures, we used software made by doc. Mgr. Zdeněk Navrátil, Ph.D., Spektrum Analyzer 1.7 [10]. These properties of HDCSBD were compared with industrially used DCSBD to emphasise the similarity of these sources.

Final goal of this thesis was using HDCSBD and DCSBD to successfully and effectively plasma modify surface of polycarbonate (PC) and polyethylene-aluminium (Pe-Al) substrate, called Dibond, used for UV-digital printing. To achieve the best results, number of different analysis and experimental tests were done on these samples. We have identified process variables such as treatment time or treatment distance for optimal LTP treatment and used them in tests. Samples underwent the wettability and surface free energy measurements to observe changes in dependence on used plasma source and process variables. As of the adhesion properties of the substrates, we have conducted peel-force measurements and standard crosscut test used in printing industry after printing the various patterns with different colors. The morphological changes and chemical composition of activated samples after the LTP treatment were studied using x-ray photoelectron spectroscopy, atomic force microscopy, scanning electron microscopy and confocal microscopy. Part of the results collected during work on this thesis was used to write scientific publication and published in impacted journal [11].

Chapter 1

Theoretical Part

1.1 Plasma

The word plasma has a lot of meanings. In physics, it describes one of the four fundamental states of matter. Matter in this state contains high amount of charged particles (electrons and ions) that interacts with neutral atoms and molecules. Charged particles bounded in such a state interact with each other through the Coulomb forces and keep the collective behavior. Although it sounds like the presence of excited particles primary sets plasma apart from other states of matter, to actually call something plasma, it needs to meet certain criteria which are briefly discussed in this section using information from well respected sources [12, 13, 14]

Fundamental states of matter are divided in to 4 known states (5 if we consider the Bose-Einstein condensate [15]) that is solid, liquid, gas and mentioned plasma. To describe the main differences between these states, we should talk about the strength of the bonds between the particles for each matter. From observation of our daily lives, we know, what gas is. Gasses have a low density, able to easily expand and have fast reactions to changes of temperature and pressure. This is due to the atoms and particles inside the matter are not particularly attracted to each other. For liquids, the shape is more defined. The particles are more attracted to each other, giving it a more uniform shape depending on the container they are in. If something is solid, it is commonly hard to deform and keeps shape unless enough force is used to change it. This is because the the particles and atoms of the matter are bonded with a strong forces.

To transform one state of matter to another, we need to either make the bonds stronger or weaker. To determine state of the matter, we can look at the kinetic energy of the particles. With the increase of kinetic energy we observe decrease of bonding energy. To increase kinetic energy, we can raise the temperature of the matter. If we increase the temperature of, for example, water to the known 100°C, it starts to evaporate, changing to the water vapor, the gaseous state of water. The energy or heat needed for phase transition is called latent heat.

Plasma is created by phase transition from gas. Gas has already almost no attractive forces between molecules and particles. If we add energy to the gas, for example, with heating the gas or creating a local electric field, we can observe more than the increase of the kinetic energy. As the energy rises, so the Independence of the particles inside of the molecules

or atoms, leading to the ionization interactions. This results into creation of ionized gas, plasma. Common occurrence of plasma in nature is thermal plasma, for example Sun, where the temperatures are high enough to create thermal ionization interactions.

If plasma is just a gas with ionized particles, what makes it different from the point of how the particles are bonded and interact with each other? One of the important properties of plasma is the collective behaviour of charged particles. The collective behaviour exists because of long-distance Coulomb forces through which the particles interact. This also means, that while the plasma is neutral in macroscopic scope, moving particles create small electromagnetic fields which affect the dynamics of the plasma. These fields tend to exclude each other on a large scale, leading to the macroscopic neutrality.

Laboratory plasma is commonly created by inducing the ionization processes [16]. The knowledge of these processes is important, as the properties of plasma are determined by the dominant ones. This way, we can create a wide range of ionized gases that are different in their temperature, ionization level, the density of the particles or even the stability. As an example, there will be briefly discussed method mostly used for analysis (Laser Induced Plasma) and a method used in industry (Plasma Discharges).

One of the common methods to create artificial plasma is called laser induced plasma (LIP), where we achieve this state of matter by high energy laser pulses. These pulses are focused on a single point of the matter leading to the vaporization, atomizing and finally ionization, thus creating plasma [17]. The matter breakdown to create laser induced plasma is a threshold phenomena, depending on the properties of the laser as well as on properties of the material. Breakdown process by longer pulses is more dominated by thermal processes while shorter pulses lead to dominant electrostatic processes. The common usage of laser induced plasma is spectroscopy, where plasma created this way is analysed by spectrometer [18, 19]. This method called laser-induced breakdown spectroscopy (LIBS) is used for better understanding of chemical properties for certain materials [20].

In plasma discharges, we create ionization processes by accelerating charged particles. Acceleration is due to the high local electric field leading to increase of particles speed. Higher velocity leads to higher kinetic energies, which increases a change of ionizing collisions. This type of plasma is called non-thermal plasma. Since lighter particles react more significant to the changes of electric field, electrons gain more kinetic energy than heavy ions. This creates electrons with high temperature, or rather said, thermodynamic temperature while ions and neutral particles keep their low temperature.

As we add energy to the plasma, we can achieve large temperatures. Commonly, we divide plasma into the low temperature and high temperature plasma. The high-temperature plasma is considered when the temperature is higher than 10^6 K [21]. Temperature in this case refers to kinetic energy of each particle in plasma. This plasma is often found in space around the stars or in thermonuclear reactors such as COMPASS in Prague with Tokamak setting [22], to create a plasma or thermonuclear fusion. Lower temperatures are typically created artificially in laboratories or industries that use plasma, for example, on surface treatment. Furthermore, if the plasma is in thermodynamic equilibrium, we talk about thermal plasma. Non-thermal plasma is then without thermodynamic equilibrium. There are many interactions in plasma. We can observe collisions of charged particles together, or a charged particle with neutral. While charged particles are interacting through Coulomb forces and magnetic field induced by moving, neutral particles interact through

induced polarization. Depending on the ratio of these interactions, we call plasma either strongly ionized or weakly ionized plasma. Weakly ionized plasma has most of the interactions based on collisions of charged particles with neutrals. As the amount and importance of collisions within charged particles rises, so does the ionization of the plasma. If all interactions within plasma are based on collisions of only charged particles, it becomes a fully ionized plasma.

1.1.1 Plasma Criteria

As it was already mentioned, plasma is not just a simple ionized gas. There are few criteria that the matter has to fulfill, to call it plasma. One of these criteria is the length of the plasma. To understand this criterion, we must introduce the Debye length:

$$\lambda_D = \left(\frac{\epsilon_0 k / q_e^2}{n_e / T_e + \sum_j z_j^2 n_j / T_j} \right)^{1/2} \approx \left(\frac{\epsilon_0 k T}{n_e e^2} \right)^{1/2} \quad (1.1)$$

where ϵ_0 is vacuum permittivity, k is the Boltzmann constant, q_e is an electron charge, n_e is electron concentration, T_e is the temperature of the electrons and z_j is proton number of the atom. We can simplify this equation with assumption, that in low temperature plasma, the ion contribution is insignificant in comparison of electrons. On the right side, e is elementary charge. We can interpret Debye length as a maximum distance, where charged particles interacts with other charged particles. It shields charged particles from interacting with others that are beyond the Debye length. This is a result of collective behaviour. The criteria of matter to be called plasma is therefore, that the length of the plasma L , has to be many times larger than that of Debye length:

$$L \gg \lambda_D \quad (1.2)$$

For typical plasma discharge, the Debye length is approx. 10^{-4} m. The Debye length can be extended to meters if we consider plasma created by stars in space. To create plasma we need a certain amount of charged particles. The specific amount, after which the matter can be called plasma, is tightly bonded with the Debye length. If we imagine a sphere with the radius of Debye length, we can express this criterion as:

$$n_e \lambda_D^3 \gg 1, \quad (1.3)$$

where n_e is concentration of electrons. This equation means, that the number of electrons inside imaginary Debye sphere must be much higher, than 1.

We already mentioned the concept of macroscopic neutrality. If there are no external forces affecting the charged particles inside the plasma and plasma is in equilibrium state, then for small fragment of plasma volume, with the right density of charged particles becomes neutral. The particles inside plasma tend to create microscopic electromagnetic fields of positive and negative. These charges are equal; therefore they cancel each other, creating no surface charge or electric field. To express mathematically, the criterion means, that the concentration of positively charged particles equals to concentration of negatively charged particles:

$$n_e = \sum n_i, \quad (1.4)$$

where n_i is concentration of ions. This criterion is also called a quasineutrality. Plasma with a significant excess of charge is called non-neutral plasma and electric fields play a dominant role in the behaviour of the matter [23, 24].

Macroscopic neutrality can be affected by external forces. If plasma is taken out of equilibrium state, it responds with the collective move of charged particles to return in such a state. These oscillation create a so called plasma frequency. The term plasma frequency is an important timescale and can be calculated for various charged particles. However, the frequencies often become too high, preventing the relatively heavy ions from reacting. As electron oscillations tend to be far more important for plasma properties, plasma frequency is often referred to plasma electron frequency [12]:

$$\omega_{pe} = \left(\frac{n_e e^2}{m_e \epsilon_0} \right)^{\frac{1}{2}}, \quad (1.5)$$

where m_e is mass of the electron.

1.2 Applications of Plasma

The early plasma research dates back to 1857 where W. Siemens [25] used atmospheric discharge to generate ozone or in 1879 by Sir William Crookes where he calls the same medium by name "radiant matter" [26]. Since then, plasma was systematically studied all over the world, bringing new understanding of physics and new technologies with it. From explaining the collective behaviour of electron gasses inside the solids to thermonuclear fusion and plasma propulsion engines for spacecrafts. The rapid increase of plasma studies lead to creation of industrial plasma, which is often divided into the high pressure (atmospheric) plasma or low pressure plasma.

Low pressure plasma is often used for deposition, creation of thin layers of various materials for their properties like conductivity or hardness. A commonly used method for such a deposition is magnetron sputtering, which uses specifically formed magnetic field to transfer particles of requested material to the surface of the substrate, creating a thin layer [27]. Another method is plasma-enhanced chemical vapor deposition or PECVD which uses different precursors in gas state to deposit thin layers of material [28].

Atmospheric plasma found its use in surface modifications. The main pros of this approach are the cost of the operation for such a device as well as compatibility. The most common method to create atmospheric plasma in industries is in the form of barrier discharges which will be explained later in section 1.3. Low temperature plasma (LTP) treatment is a common application for activation, cleaning and improving adhesion properties of the surfaces. It use can be also found in creation of ozone [29]. Activation of surface found its way in to the different parts of industries such as biomedical applications for sterilization [30] or textile treatment to improve dye absorption [31]. The popularity of LTP treatment reach to even more common industries such as printing and coating [11].

As plasma is more and more researched, we are able to use it in different ways. In modern industry, plasma is often used to cut different conductive materials [32]. Semiconductor

industry utilizes plasma in more ways, such as cleaning medium, modifications before deposition processes and etching. As a charged medium, plasma is also finding its way to the scanning electron microscopy where plasma in different gasses is used to replace Gallium focused ion beams to prevent a Ga implantation and make the method less invasive [33].

1.3 Dielectric Barrier Discharge

Atmospheric barrier discharges found numerous applications in industry. Setup of these discharges will be discussed in this section is dielectric barrier discharge (DBD). Their construction is different in using the dielectric layer built in the interelectrode layer to bring different properties of plasma [34]. DBDs were first utilized to create ozone by W. Siemens and later on became a standard use for surface modification of different materials to improve the wettability, adhesive properties or composite a very thin layers [35, 2].

As it was said, DBD consist of dielectric layer covering at least one electrode. This configuration prevents from creation of arcs and spark between the electrodes as it limits the amount of electrons transferring between the electrodes. Another advantage of the dielectric layer is that the coverage of the electrode increases the lifespan of the discharge since its preventing corrosion of the electrodes. In modern industry commonly used dielectric is ceramic but different materials can be used such as glass or polymers due to the high dielectric strength to withstand even higher voltages and different thermal, mechanical and chemical properties. The choice of dielectric is important as it significantly affects the properties of created plasma. As the charge collects on the surface of dielectric, we use alternating current (AC) to reverse the electric field at regular intervals, causes charges to oscillate back and forth leading to the more uniform coverage of the surface. The frequency of AC can range from radio frequencies up to microwave frequencies (kHz to GHz). This wide range also brings different properties of created plasma. Different setups also include different distance between the electrodes. Some configuration leave small gaps between the electrodes in distance of millimeters while others uses distance measured in centimeters. Input voltage depends on the gas that the plasma is getting ignited. For ambient air, the typical input voltage is in the range of tens of kV while in rare gasses the plasma can be ignited even under 1 kV. Wide range of parameters to construct DBD leads to different configurations. Most common configurations are volume discharges (VD), coplanar discharges (CD) and surface discharges (SD).

When it comes to DBD, the ignited plasma can have two main modes, depending on the properties of DBD or surrounding conditions, such as the type of gas, etc. These modes are called diffuse mode and filament mode. Although certain geometric setup leads to creation of diffuse mode, the most common mode is filamentary. In this mode, the plasma is created by tens of thousands of microdischarges (thickness in units of μm) which are so called, filaments [36]. Since the width of the filaments is comparably smaller than the common plasma length using DBD, filaments fill the discharge zone with dependence on input voltage. Filaments contain a significantly more ionizing particles in comparison with surrounding gas. It is important to say, that the gas in these filaments doesn't reach critically high temperatures. This is due to the limited current that can flow through microdischarges as well as a small lifespan of discharge due to the dielectric. This contributes to the usage

of DBDs as a surface modification technology for temperature sensitive materials.

Volume dielectric barrier discharges

One of the most common DBD configuration is the Volume Dielectric Barrier Discharge (VDBD). The configuration is shown in Figure 1.1. It consists of two parallel electrodes where at least one of them is covered by dielectric material. In general, the discharge is created between these electrodes at the interelectrode distance of few mm. Numerous microdischarges cross the gas gap and connect electrodes [37]. The charge in plasma is then collection of so called microdischarges and surface discharge on the dielectric. These microdischarges can increase their width to appear homogeneous. The main advantage of this method is the volume of plasma that can be ignited. Disadvantages leads to inhomogeneous plasma and local excitation of the material and limited thickness of treated material [2].

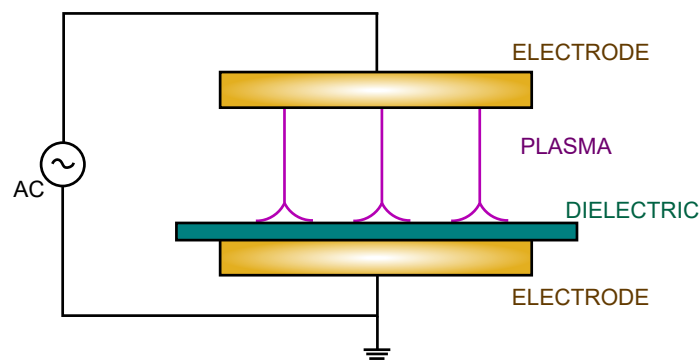


Figure 1.1: Geometric representation of VDBD with an AC power supply.

Surface dielectric barrier discharges

The geometric representation of surface dielectric barrier discharge (SDBD) can be seen in Figure 1.2. The setting consists of one electrode being completely covered by dielectric while the other thinner electrode sits on top of the electrode parallel to the first one. The discharge then develops along the surface of the dielectric which area is proportional to the input voltage and it also consists of microdischarges. The advantage of this setup is its high density of the plasma. This is at the expense of short lifespan for electrodes as plasma is in direct contact with one of the electrodes.

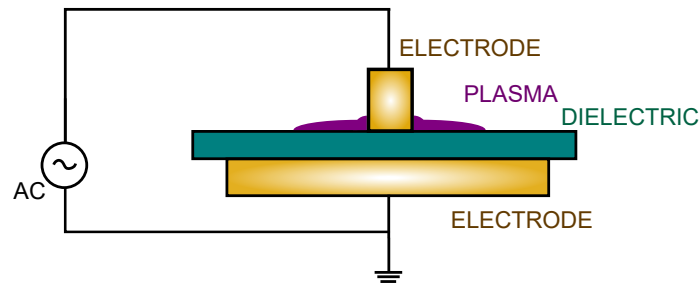


Figure 1.2: Geometric representation of SDBD with an AC power supply.

Coplanar dielectric barrier discharges

Figure 1.3 shows the geometric representation of Coplanar Dielectric Barrier Discharge (CDBD). Due to the advanced modern technology we are able to create electrodes with a very small distance between them (in the units of μm) and coat them with the dielectric layer. As there cannot exist any spark or discharge inside the dielectric layer, the microdischarges occur at the top of the dielectric, creating an imaginary bridge between the electrodes. Advantages of such a configuration lays in complete separation of electrodes from plasma, ensuring high lifespan as well as creation of homogeneous and uniform plasma at its surface with correct setting.

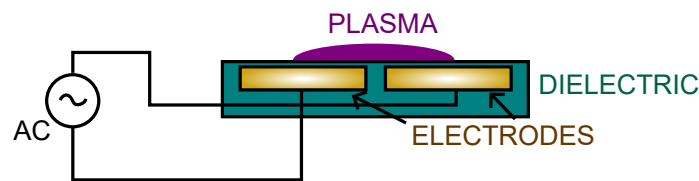


Figure 1.3: Geometric representation of CDBD with an AC power supply.

Diffuse coplanar surface barrier discharge

Diffusive mode occurs most commonly in CDBD. To achieve this mode, there are specific conditions for the length of the gap between electrodes, the frequency of excitation signal, thickness of dielectric barrier or the gas in which the ignition proceeds. The creation of diffusive mode also depends on the pressure in the discharge zone, but as this thesis main focus are atmospheric discharge, this factor is not of significance here. There are dielectric barrier discharges that are able to create this two modes at the same time.

Diffuse coplanar surface barrier discharge (DCSBD) was created by Prof. RNDr. Mirko Černák CSc. and his group at Comenius University in Bratislava with a cooperation of Masaryk University in Brno [38]. The schematic image of DCSBD is shown in Figure 1.4. Widely applied and produced ceramic (Al_2O_3) is used as a dielectric layer at the top of electrodes. These electrodes are then covered in oil of special properties as a secondary dielectric to prevent electrical breakdown between the electrodes. The oil also works as a cooling element. There is a wide range of DCSBD using different interelectrodes distances as well as width of the electrodes, the amount of electrodes, thickness of ceramic or the

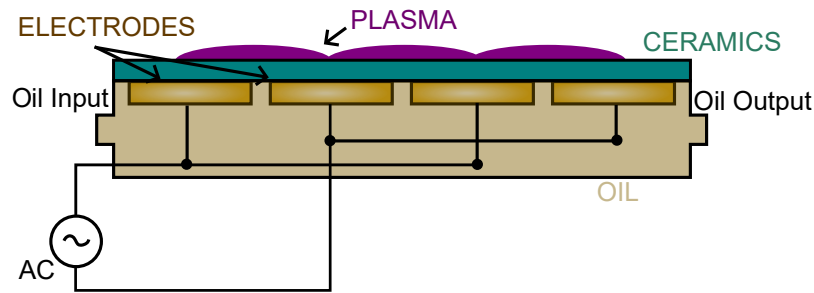


Figure 1.4: The simplified scheme of DCSBD.

shape of electrodes. For the purpose of this thesis, we are gonna only consider setup with electrodes of 1.5 mm width and interelectrode distance of 1 mm. The shape of electrodes looks like two combs opposite to each other in close proximity. The thickness of ceramic is 0.6 mm. The complexity of this configuration is mirrored in so called macroscopic homogeneity of generated plasma. This is due to the filaments created at a surface being close to each other, creating a full coverage of the discharge zone. As it was already mentioned, the filaments in coplanar barrier discharge creates a bridge between electrodes. In case of DCSBD, this bridge is prolonged by diffusive part which location is directly above the electrodes, thus filaments connect the diffusive parts. Figure 1.5 shows the plasma generated by DCSBD with an input power of 400 W by generator with 15 kHz transformer. This property is one of the main reasons why it is commonly used for surface treatment for a wide range of materials [1, 2, 11, 39].

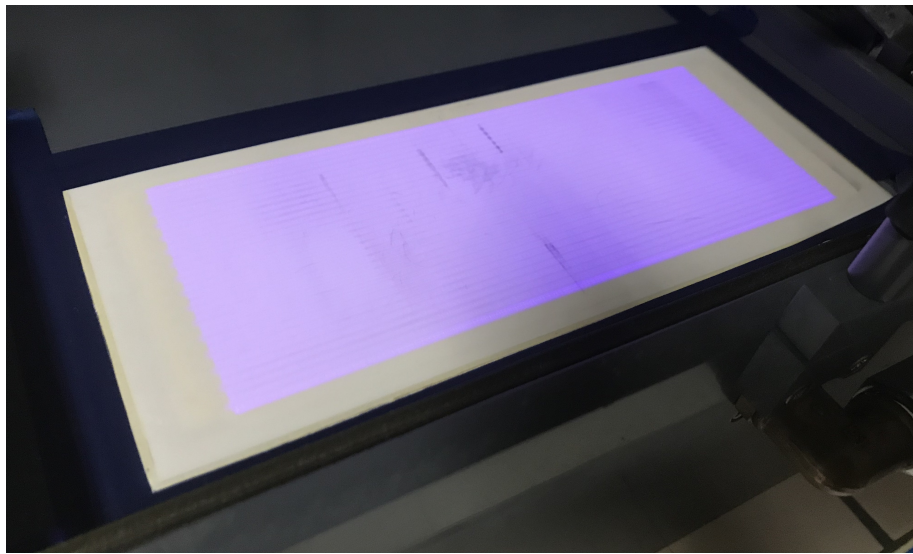


Figure 1.5: The DCSBD ignited by the generator with 15 kHz transformer and input power of 400 W.

The common problem with DCSBD is the need of oil for cooling and as a dielectric. The flow of oil is provided by a sophisticated cooling system which significantly rises the price and makes the whole setup less compact. Due to this fact, a DBD with technical name Half-DCSBD (HDCSBD) was created. Figure 1.6 shows the schematic image of the HDSCBD.

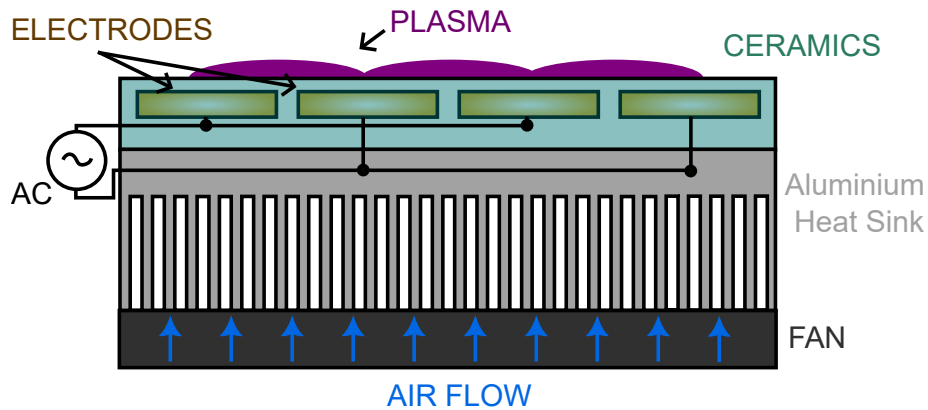


Figure 1.6: The simplified scheme of HDCSBD with the shown air flow.

HDCSBD is more compact solution at the cost of halved discharge zone (indicated by the name, Half-DCSBD). The electrodes are no longer in oil but inside the ceramic. This unique approach is manufactured by KYOCERA Inc. (Kyoto, Japan), designed and protected by Masaryk University. Since the electrodes are no longer inside the cooling oil, the whole cooling system was replaced with an industrial aluminium heat sink and a fan underneath with an adjustable voltage source to control airflow and cool the heat sink. Figure 1.7 shows the top view of HDCSBD while supplied by generator with internal adjustable transformer at approx. 20 kHz and input power of 200 W. Part of this thesis is to measure properties of plasma generated by HDCSBD and compare them with industrially used DCSBD.

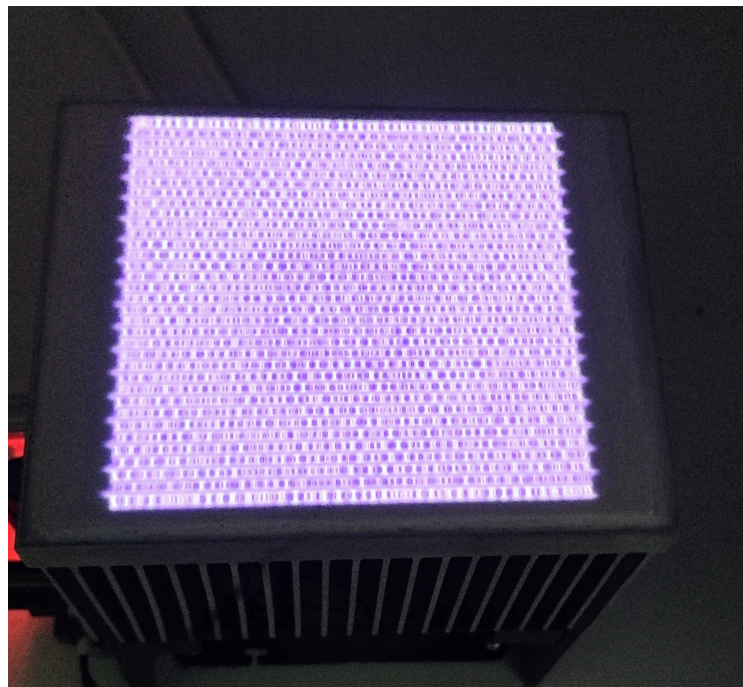


Figure 1.7: HDCSBD ignited by the generator with approx 20 kHz transformer and input power of 200 W.

Chapter 2

Experimental Setup and diagnostic methods

2.1 Equipment description

In this thesis, two distinct plasma sources with different setups were used for the measurements. The first discussed setup involves DCSBD as the plasma source. The discharge is connected to the power generator through 15 kHz transformer and cooling system to cool oil used as a dielectric material inside the unit. The setup can be seen on image 2.1 without the cooling system. All of the measurements conducted in this study were performed in ambient air with an input power of 400 W that was measured with a digital wattmeter OM 402PWR. This arrangement allowed for a thorough investigation of the plasma discharge characteristics and surface treatment of our substrates.

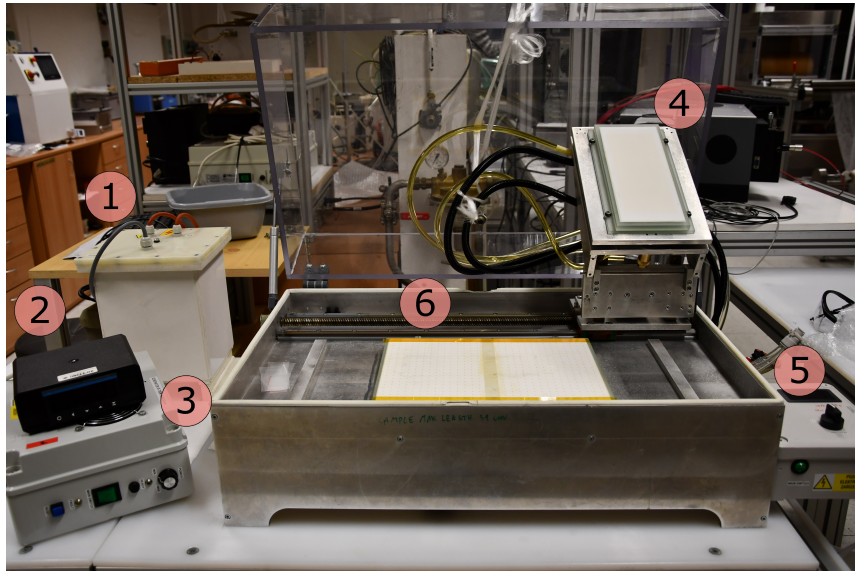


Figure 2.1: Setup for plasma treatment using DCSBD: 1) 15 kHz transformer, 2) wattmeter, 3) power generator, 4) movable cantilever with DCSBD, 5) actuator, 6) chamber with ceramic plate that allows undersuction of sample to prevent attraction of sample to the plasma source.

For the second setup, the HDCSBD is included as a plasma source. HDCSBD is furthermore connected to the generator with input power up to 250 W, utilizing internal transformer operating at approx. 20 kHz. Since HDCSBD does not use oil, the cooling system was replaced with an aluminum heat sink and a cooling fan. It is important to note that during surface treatment, HDCSBD replaced DCSBD in the movable cantilever shown in figure 2.1(5). The transformer and generator were also exchanged. The complete setup is shown in figure 2.2.



Figure 2.2: Setup that was used with HDCSBD as a plasma source: **1)** Power generator with internal transformer, **2)** wattmeter, **3)** 24 V generator connected to fan and thermocouple, **4)** HDCSBD, **4a)** Aluminium heat sink, **4b)** logistics to adjust input voltage for cooling fan.

2.2 Measurement of electrical properties

Generation of plasma discharge leads to the power losses due to various factors, such as thermal or dielectric losses. While measuring the time dependence of current and voltage, we can calculate electrical power in plasma using the equation:

$$P = \frac{1}{T} \int_t^{t+T} I(t) U(t) dt, \quad (2.1)$$

where T is a period of alternative signal, $U(t)$ is progression of voltage and $I(t)$ represents the current progression with a time dependency t . During the measurements of current and voltage, it is important to have a stable discharge considering the thermal losses that can vary with the plasma temperature [40]. Furthermore, the method is fairly complicated as we need to achieve integration of all filaments in one period. The measurements were made using Pearson M4100 current transformer as an electrical device to measure the alternating

current. The coil works on a maximum working current of 500 A with a conversion factor of 1V:1A. To measure progression of voltage we used two high-voltage probes Tektronix P6015A. These probes have maximum working voltage of 50 kV and dividing ratio of 1000:1. For monitoring of the signal we used oscilloscope Teledyne Lecroy, WaveRunner 6100A with a bandwidth of 1 GHz and a sampling frequency of 10 GSa/s. This high-speed capability allows for the observation of microdischarges within a single discharge period. For measurement of input power into the high voltage generator, wattmeter OM 402PWR was used. It is noteworthy that the setup was used for both plasma sources discussed in this thesis. To calculate power, a simple software was written in Python 3.9, which finds points for zero voltage, then saves maximums and minimums to set period and integrates the product of calculated voltage and current. The typical graph for the time dependence of voltage and current can be seen in figure 2.3.

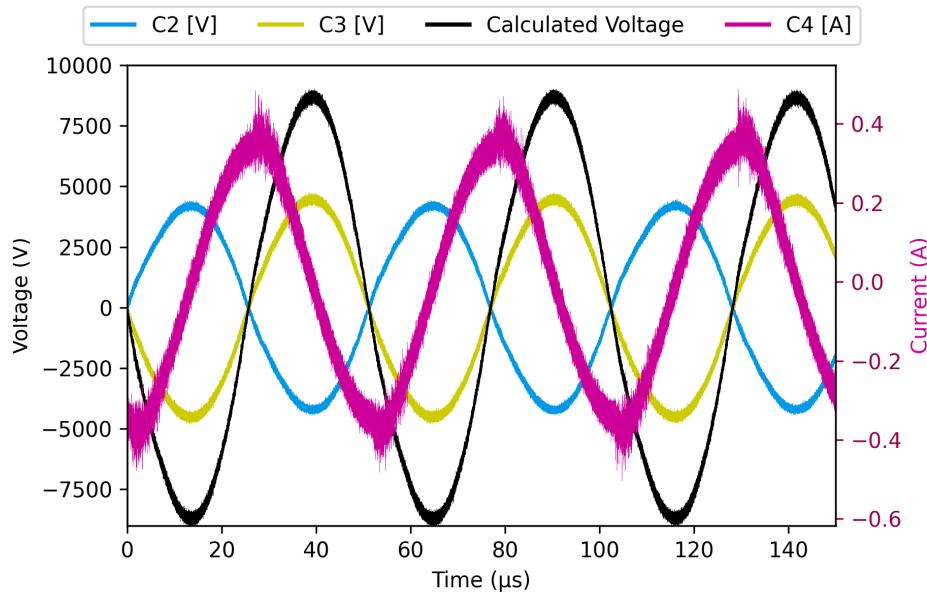


Figure 2.3: Typical waveforms of voltage and current in HDCSBD with a power input of 150 W using a transformer with frequency of approx. 20 kHz.

Where C2 and C3 are measured voltages by two high-voltage probes. Calculated voltage is difference between C3 and C2 and C4 is measured time dependency of current measured by current transformer.

2.3 Optical Emission Spectroscopy

Optical emission spectroscopy (OES) is widely used for plasma diagnostics. Most common parameters that can be observed by OES in plasma are vibrational, rotational and excitation temperature. Although different approaches can be used, for example Langmuir probe, OES is non-invasive and simpler to execute [41]. This section was processed using information from [42].

OES is the analysis of the light emitted by a medium, in our case plasma. Electrons colliding with gas molecules leads to the excitation. Molecules in excited states tend

to relax, lowering their potential energy to the lowest unoccupied electronic state. This happens by spontaneous emission. The radiation emitted by this process is then observed as the light emitted by a medium. In general physics, electromagnetic radiation shows a broad spectrum of wavelengths, ranging from ultraviolet (UV) to infrared regions (IR).

Device used to measure the OES is called a spectrometer. There are more ways to collect the light emitted by the plasma. The emitted light or radiation can be collected directly onto the input slit in a spectrometer or by optical fiber. The radiation can also be transferred directly to the monochromator using a pair of optical lenses. Dispersed light is then directed to the detector which can for example be a photomultiplier. Using input slits helps us to increase or decrease the emitted light collection. While working with plasma, to maintain efficient detection, rapid analysis is important. Way to maintain good resolution over a wider range is with a usage of spectrometer implemented with fast turning or spinning grating.

A common detectors used in spectrometers are Charge Coupled Device (CCD) or Intensified Charged Coupled Device (ICCD) cameras. CCD is a semiconductor chip that collects light and creates electrical charge proportional to the intensity of the emitted light. This electric charge is then shifted around the CCD device to the charge amplifier and changed to the voltage. The sensitivity of CCP allows for collection of radiation of small intensity. For even smaller intensities there is a need of better amplifier. ICCD consist of CCD connected to image intensifier, consisting of photocathode, micro-channel plate and phosphor screen [43]. It's simple device consist of photons generating photoelectrons accelerated to the micro-channel plate that works as an amplifier. Amplified electrons then reach phosphor screen leading to creation of photons transfered to CCD by optical fibers. ICCD was not used in this thesis. Figure 2.4 shows typical arrangement for components of spectrometers.

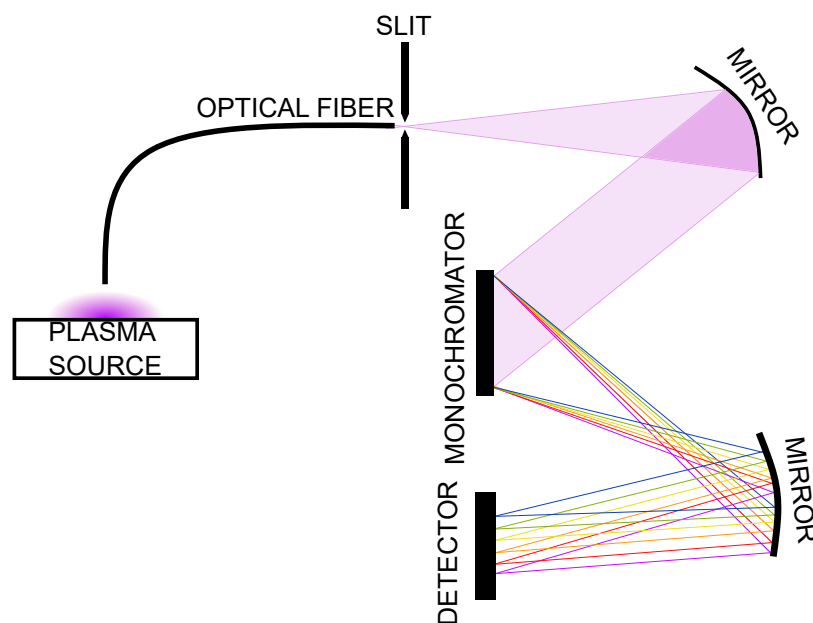


Figure 2.4: Schematic arrangement of common spectrometer with movable diffraction grating as a monochromator and CCD detector.

2.3.1 Vibrational Temperature

The following subsections are under presumption of local thermodynamic equilibrium. All the measurements mention in these subsections were done by software made by doc. Mgr. Zdeněk Navrátil, Ph.D., Spektrum Analyzer 1.7 [10]. Let's imagine a diatomic molecule as an anharmonic oscillator. Anharmonic oscillator is a system where if disrupted from balance, the restoring force is not proportional to the displacement [44]. To measure intensity of a vibrational lines, we need to consider every vibrational motion. We can follow equation:

$$I = C \cdot \frac{q_{v'v''}}{\lambda^4} e^{-\frac{E_v}{kT_v}} \quad (2.2)$$

Where C is constant, v' and v'' are vibrational quantum numbers of upper and lower state, λ is wavelength of emitted light, k is Boltzmann constant and E_v is energy of vibrational movement of diatomic molecule around equilibrium position. The Franck-Condon faktor $q_{v'v''}$ equals the square of overlap integral and represents the relative strength of line. By taking the logarithm of this equation, we obtain pyrometric line that helps us determine temperature based on the intensity of the lines:

$$\ln \frac{I_{v'v''} \lambda^4}{q_{v'v''}} = -\frac{1}{kT_v} E_v + C \quad (2.3)$$

$$\tan \alpha = -\frac{1}{kT_v} \quad (2.4)$$

From slope we can calculate vibrational temperature T_v .

2.3.2 Rotational Temperature

We follow the example set in section about vibrational temperature. Rotational movement of the diatomic molecule can be compared to a solid rotor that is rotating perpendicular to the bond axis between the nuclei of the two atoms [44]. Intensity of a rotational line can be written as:

$$I = C \cdot \frac{S_{J'J''}}{\lambda^4} e^{-\frac{E_J}{kT_r}}, \quad (2.5)$$

where $S_{J'J''}$ is stands for Hönl–London factor, T_r is rotational temperature, J', J'' are rotational quantum numbers of upper and lower state, and E_J is energy of the rotational movement done by the diatomic molecule. We can achieve pyrometric line the same way by taking the logarithm of intensity equation:

$$\ln \frac{I_{J'J''} \lambda^4}{S_{J'J''}} = -\frac{1}{kT_r} E_J + C, \quad (2.6)$$

$$\tan \alpha = -\frac{1}{kT_r}, \quad (2.7)$$

where we again calculate rotational temperature from slope of the equation.

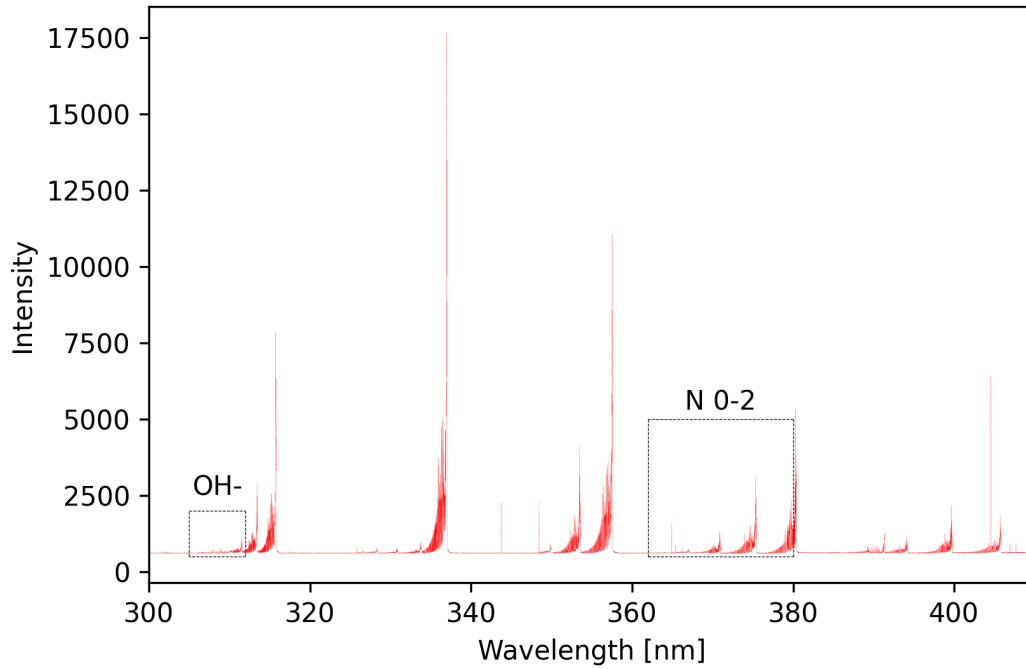


Figure 2.5: Overview image of spectrum during calibration for HDCSBD with input power of 150 W at rising temperature. Images shows regions of interests for OH⁻ and N vibrational bands 0-2.

Experimental setup

For the measurement of OES we used the spectrometer FHR 1000 (Horiba Jobin Yvon, France) with the construction shown in figure 2.4. The spectrometer used dual grating 80 mm × 110 mm and movable diffraction grating. To detect light, optical fiber was set up on holder above the used plasma source approx 7 cm. Detector used for data collection was CCD camera Synapse Plus (Horiba Jobin Yvon, France). Figure 2.5 shows measurement of HDCSBD during preheating powered by 150 W and 20 kHz transformer. During the experiment, we measured the spectrum of OH⁻ in the range of 306-312 nm and the spectrum of nitrogen molecules in vibrational bands 0-2 in the range of 366-382 nm. Software SpectrumAnalyzer 1.7 was used to calculate vibrational temperature for HDCSBD with different power input and temperature of the ceramic.

2.4 Analytical setups for plasma treatment evaluation

2.4.1 Surface Free Energy and Contact Angle

Measurement of SFE (Surface Free Energy) is commonly used in industry and academia to assess the wettability of a material. We can define SFE as a work, denoted by W , required to create a surface area, ΔS . This concept can be mathematically shown in the equation as

follows

$$W = \gamma \Delta S, \quad (2.8)$$

where γ represents the surface tension [$\text{N} \cdot \text{m}^{-1}$]. There are various ways in which to measure SFE, for example, using a special test ink. The method that provides a more precise measurement, assessing not only the total SFE but its individual components, is called the contact angle measurement. The analytical method involves a test liquid of known volume and known properties. The measured contact angle is an angle between the material, the observed test liquid deposited on the surface of the material, and the gas in which the measurement was taken. Further explanation will consist of the notation used in figure 2.6.

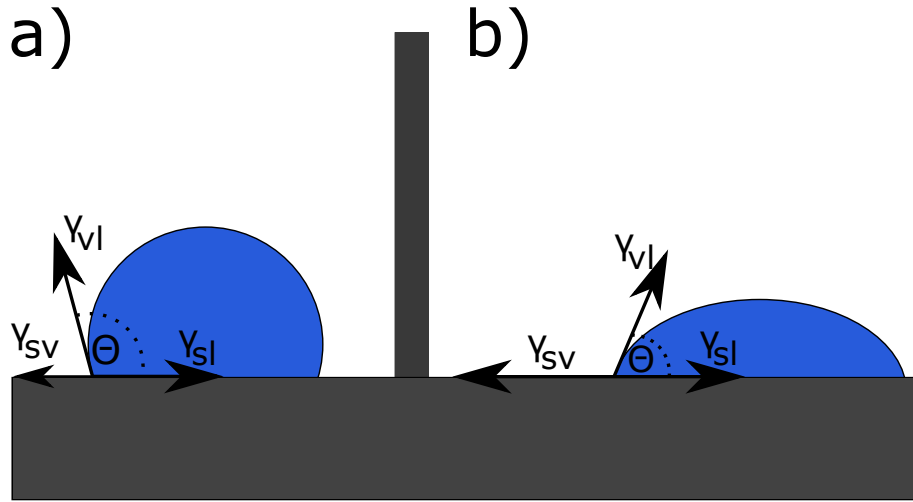


Figure 2.6: The figure shows components of surface tension for different interfaces between matters: water contact angle typical for **a)** hydrophobic and **b)** hydrophilic surfaces.

The notation shown in figure stands for:

γ_{sl} - Surface tension at the interface of solid and liquid

γ_{sv} - Surface tension at the interface of solid and vapor

γ_{vl} - Surface tension at the interface of vapor and liquid

Θ - Contact Angle

To successfully calculate the surface free energy, correct model has to be used. Various models take into account different amount of individual components for SFE and require varying amount of liquids needed to calculate SFE. The simplest and most basic model, from which others were created is the Young-Dupré equation. The model is utilizing Young equation made by Thomas Young (1805):

$$\gamma_{sv} = \gamma_{sl} + \gamma_{vl} \cos \Theta. \quad (2.9)$$

Anthanase Dupré and Paul Dupré modified defined work of adhesion for a solid-liquid system:

$$W_A = \gamma_{vl} + \gamma_{sv} - \gamma_{sl}. \quad (2.10)$$

After substitution back into the Young equation, it leads to:

$$W_A = \gamma_{vl}(1 + \cos \Theta), \quad (2.11)$$

Which represents the equation for solid-liquid adhesion energy in used gas.

Owens-Wendt Model

Made by Owens and Wendt (1969), this model dissects the surface free energy into two components, London dispersion forces, which are weak intermolecular forces as a part of Van der Waals interactions, and polar components formed primarily by the reaction of bonds:

$$\gamma = \gamma^d + \gamma^p, \quad (2.12)$$

where the component with index "d" represents dispersive component and with index "p" is polar component. We can then substitute Young equation:

$$(1 + \cos \Theta)\gamma_l = 2 \left(\sqrt{\gamma_s^d \gamma_l^d} + \sqrt{\gamma_s^p \gamma_l^p} \right). \quad (2.13)$$

At least two liquids with known disperse and polar parts of the surface tension are required to determine the surface free energy of the solid and at least one liquid must have a polar part higher than 0. Furthermore, this equation can be rewritten in a more compact form also known as a Owens, Wendt, Rabel and Kaelble (OWKR) model [45]:

$$\left(\frac{\gamma_l (1 + \cos \Theta)}{2\sqrt{\gamma_l^d}} \right) = \sqrt{\gamma_s^d} + \sqrt{\gamma_s^p} \sqrt{\frac{\gamma_l^p}{\gamma_l^d}}. \quad (2.14)$$

After measuring the contact angle of 2 or more liquids and calculating all variables, this equation can be used to plot as a line and determine the components of surface free energy

Experimental setup

For the analysis of dispersive and polar components within the SFE, we used the OWKR regression model mentioned in this thesis. To achieve the more precise results, we used three liquids with known chemical properties. The used liquids and needed properties are shown in table 2.1.

Liquid	Formula	Temperature	γ_l^d	γ_l^p [mN/m]	γ_l [mN/m]
Water	H ₂ O	20	27.19	45.61	72.8
Diiodomethane	CH ₂ I ₂	20	50.8	0	50.8
Ethylene glycol	C ₂ H ₆ O ₂	20	29.81	18.19	48

Table 2.1: Table of used liquids with needed properties

Setup used for the measurement is shown at the figure 2.7. For estimating the contact angles, an average of 14 droplets of each liquid was deposited on the observed material's surface by a micropipette with a constant volume of 1 μ l. To capture photos to measure the profile of the liquid droplets, a See (Surface energy evaluation) System analyzer (Advex Instruments, s.r.o., Brno, Czech Republic) was used. The standard error of measurement is approx. 1 mJ/m².



Figure 2.7: See System Analyzer used to evaluate contact angles and SFE of used liquids.

2.4.2 Measurements of Adhesion

Even though the water contact angle and SFE provide understanding into surface changes for wettability of the sample, they don't explain changes in adhesive forces. Adhesion can be often described as the tendency of a material or surface to cling to one another. The forces that are responsible for this adhesive behaviour can be categorized as either chemical, dispersive (or adsorptive adhesion, which is a mechanism for intermolecular interactions between molecules of two or more materials) or mechanical. These forces can be observed and further measured.

Experimental Setup

To measure mechanical adhesive forces, the static material testing machine Texture Analyser TA.XT plusC (Stable micro Systems, Surrey, United Kingdom) was used. The testing machine was equipped with a load cell of 50 N range. Experimental setup can be seen on fig. 2.8. Measurements were recorded using Exponent Connect software provided by the machine manufacturer. FINAT method no. 1, the adhesion peel test (specifically, 180° adhesion peel test) was performed on reference and plasma treated samples. For measurement we used a special adhesive tape (TQC Sheen, Rotterdam, Netherlands) calibrated according to the ISO 2409:1999.

To ensure the precise measurement of adhesive forces, all the experiments included calibration for the testing machine. For the calibration of weight, a precisely 1 kg weight was placed on the calibration platform at the top of the loading cell. Afterwards, the software ran the calculations and with the correct weight input from the user nullifies any external forces so the load on the load cell is exactly 1000g. After removing the weight, the load shows 0 N so all outside forces are removed from the measurement. For the second calibration, the calibration of height we cleared the measurement space and set correct

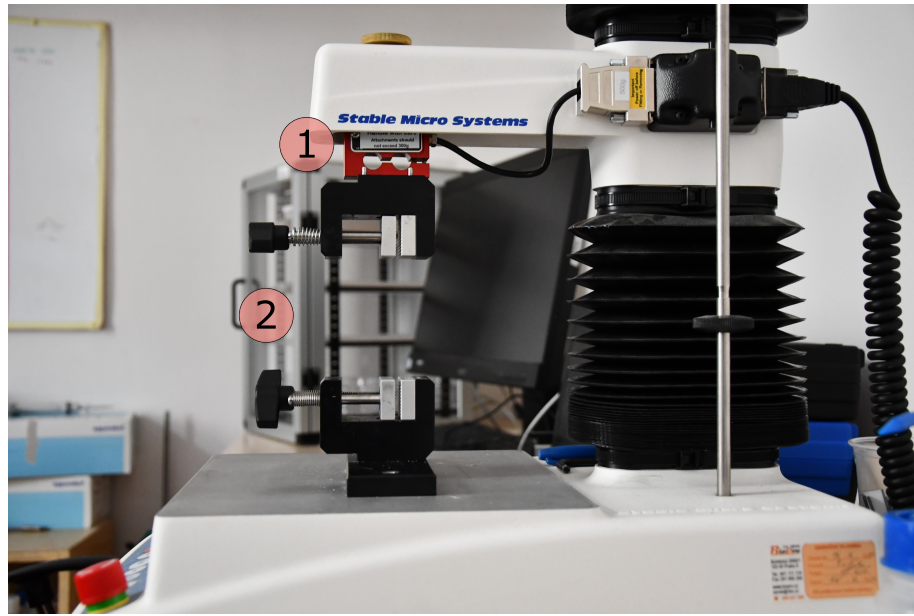


Figure 2.8: Texture analyser Ta.XT plusC used to measure peel force: **1)** load cell and **2)** mechanical chatters.

mechanical chatters (refer to fig. 2.8). The calibration consist of robotic arm slowly lowering the upper chatters down to the bottom of the machine. After the upper chatters reacts to the touch of the lower chatters, it stops and calibrates the position as the lowest point of the measurement environment. After calibrating and setting up the testing method, we prepared the sample for measurement. The preparation of the samples involved applying adhesive tape to the surface of the material. To ensure the repeatability of the process and maintain a consistent force for interlocking the materials, we used a pre-calibrated rolling pin (2 kg) and made 12 passes over the taped area. It was also ensured that the width of the sample is same for all the measurements.

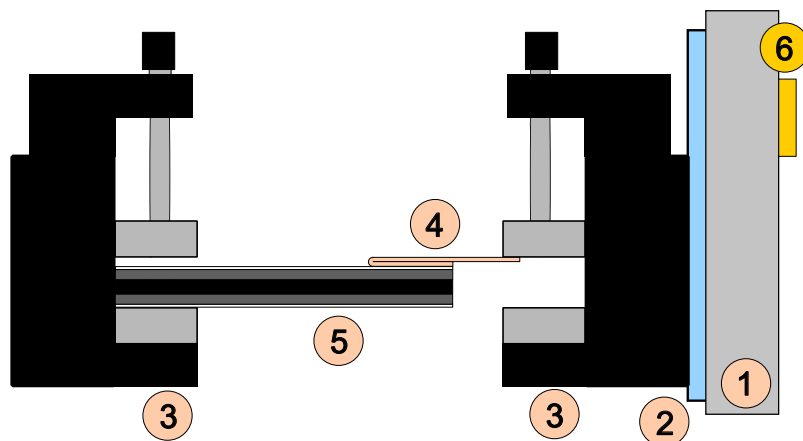


Figure 2.9: Schematic of the experiment: **1)** cantilever, **2)** load cell, **3)** mechanical chatters, **4)** adhesive tape, **5)** sample and **6)** platform with screw conected to loadcell for weight calibration. The schematic is rotated by 90°.

Sample with the tape was placed in to the mechanical chatters of measuring device. Place itself was placed into the robotic arm which after starting the measurement started to move away from sample. Set speed of robotic arm was approx. 10 mm/min on the surface with length of 100 mm, leading to the 10 minutes of time needed for measurement. The measurement was repeated at least on 5 samples. Software measured 500 points per second. The measured data were further processed by excluding clear sings of errors such as unavoidable air bubbles or the beginning of the process, where the strain gauge was just stretching the adhesive tape. The remaining values were averaged. Schematic for the measurement can be seen on fig. 2.9.

2.4.3 Cross-cut Test

Polymers are used worldwide as a foundation for an ink during printing, they are produced by numerous suppliers with a different production processes that can affect the ink adhesion. For that reason, end-users require certain standards for the material, especially for the adhesion of ink on the substrate and printed layer quality. [46]. To test these properties, test method called "Cross-cut" is widely implemented. This method is supposed to evaluate the adhesion of paints and coatings by separating them from the substrate. It's a quick test that uses a cutter to create evenly spaced lattice pattern on the top of the substrate. After the lattice is done, a special adhesion tape is used to cover the sample and removed by quick pull. Lattice is then examined visually to determine the result. Scoring according to the ISO 2409:2013 is shown in figure 2.10. The cross-cut test was used for all the measured samples.

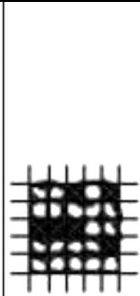
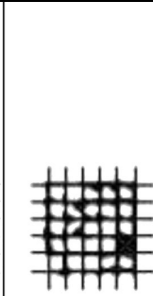
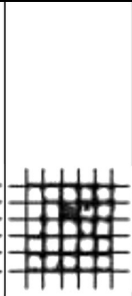
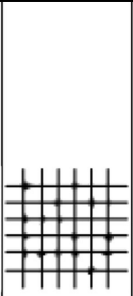
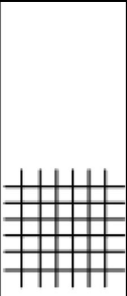
5	4	3	2	1	0	Score
						

Figure 2.10: Scoring of cross-cut test results according to the ISO 2409:2103 with 0 being the best result [47].

Experimental Setup

For the cross-cut test, it was first needed to create a pattern which is gonna be tasted on treated surface. The custom UV LED head (395 nm, 14 W/cm) was used to cure and harden the acrylate-based ink (EFFE811, Effetec s.r.o.) and pattern with 360×1200 DPI resolution. For this test, the samples were in the form of blocks with dimensions of $15 \times$

10 cm². To perform cross-cut we used testing set CC3000 (TQC-Sheen, Rotterdam, The Netherlands) together with tape according to ISO 2409:2007. Cross-cut was performed on patterns printed by a prototype of a UV-digital printing machine (Effetec s.r.o) with the use of HDCSBD technology discussed in this thesis. Patterns and their use will be shown and discussed in Section 3.6. The prototype can be seen in Figure 2.11.

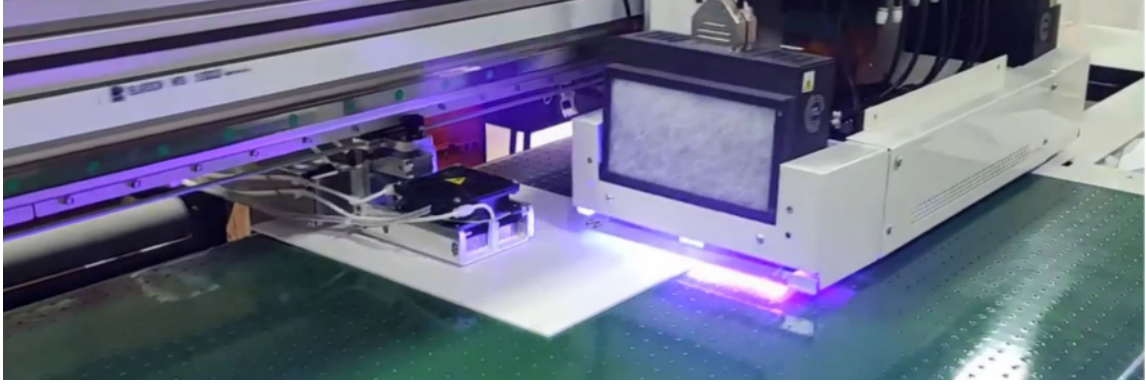


Figure 2.11: The photograph of UV-digital printer prototype with HDCSBD technology. (Image is taken from and legally protected by outcomes listed in Section 5 of [11].)

2.4.4 Chemical Characterization

The chemical changes on the surface of the material were analysed to further understand results of plasma treatment. For this analyzes we used a method called X-ray photoelectron spectroscopy (XPS). XPS is a surface-sensitive quantitative technique that is based on photoelectric effect, emission of electrons caused by x-rays. XPS is a powerful measurement technique that can identify the elements that exist on the surface of the material, binding states of these elements, or by using the ion-beam, we can also etch the surface and analyze the inside of the material. Using photoelectric effect:

$$E_b = E_p - (E_k + \Phi), \quad (2.15)$$

Where E_b is the binding energy of the electron, E_p is known energy of the photon, E_k is the kinetic energy of emitted electrons from the surface of material and Φ is a work function specific for the material. The work function can be thought of as an adjustable instrumental correction factor that specifies energy needed for electron to be removed from the material. Electrons emitted by x-rays are then transferred to the energy analyser and detector. Energy analyser further measures the kinetic energy while detector will determine the amount of electrons. Due to the sensitivity of the technique, all measurements are performed under high vacuum. The outcome of measurement is an electron spectrum with the electron count dependence on the binding energy of electrons. From the spectrum we can determine the percentage representation of elements in observed part of the material by equation:

$$X_p = \frac{I_p/S_p}{\sum_j I_j/S_j} \quad (2.16)$$

where I_p is an area under the spectral peak and S_p is a relative sensitive factor.

Experimental Setup

The XPS analyzes was performed by the spectrometer Axis Supra (Kratos Analytical Ltd., Manchester, UK) using monochromated ALK α radiation with energy of 1486.6 eV. The conditions used in this paper are same as in [2]. Collected electrons that were emitted from a sample area of size $300 \times 700 \mu\text{m}^2$ perpendicular to the surface of the sample. The samples used in this paper are polymers, therefore a charge neutralizer in the form of argon ions and electrons of small energy was used to compensate the sample charging. Due to the usage of charge neutralizer energy calibration had to be performed by shifting the spectra. Survey spectra used in this thesis are high-resolution spectra using an analyzer pass energy of 2 eV and spectra of 80 eV. The step size for the high-resolution spectra was 0.1 eV. All of the digital processes such as needed calibration of the spectra, processing of the measured data, analyzes and standard fitting of the spectral peaks were conducted by CASA software (trial version CasaXPS 2.3.16, CASA international nv, Olen, Belgium). Used spectrometer can be seen in fig. 2.12.



Figure 2.12: Photograph of Axis Supra used for XPS analysis [48].

2.5 Morphological Characterisation

Plasma treatment can alter the surface properties of variety of materials to either make them bond or paint easily. That is being done by cleaning the material and activating the surface adhesive properties. Unfortunately, usage of incorrect type of plasma for a certain material can also lead to damaging the material either by etching mentioned before or creating unwanted changes in morphology of the surface. Due to the risk of extreme and unwanted morphological changes, the samples are further analyzed by Atomic force microscopy. The samples also underwent scanning electron microscopy analysis and con-

focal microscope analysis.

2.5.1 Atomic Force Microscopy

Atomic force microscopy (AFM) is a high-resolution, non-optical imaging method to analyze surface of the material. With different types of setups, the AFM allows us to do accurate and non-destructive measurements of not just topography. The basic principle of standard AFM involves an probe with a very sharp AFM tip. The tip is moving over a sample surface connected to the flexible cantilever, which movements are controlled by piezoelectric ceramic scanners. The tip moving over the surface reacts to changes of heights by deflecting the cantilever. These deflections are tracked by laser beam reflected on a thin, reflective layer at top of the cantilever. After the reflection, the beam is directed to the photosensitive detector. This records the movements of the tip, which are used to generate topographic image of the surface. This process is shown on fig. 2.13.

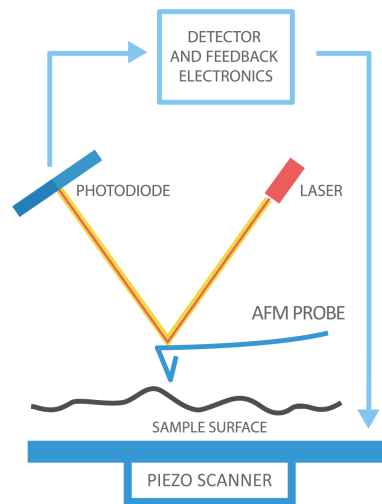


Figure 2.13: AFM schematic. [49]

Furthermore, we can use the AFM in different modes to measure topography of the material. The most common mode is **Contact Mode**, which consist of the AFM tip being in contact with the surface of the material. The feedback system aims to maintain constant interaction force. For this usage, Soft cantilevers are used to minimize AFM tip wear and surface damage of the material.

Tapping Mode consist of cantilever oscillations created by piezoelectric actuator. The AFM tip is lowered to the sample surface so that it slightly touches the surface at the end of oscillation. The amplitude is then recorded. In this case, the feedback system is trying to maintain a constant cantilever amplitude. This mode is considered to be less invasive and as in the contact mode, the forces that dominate in this interaction are repulsive. This interaction is shown in figure 2.14.

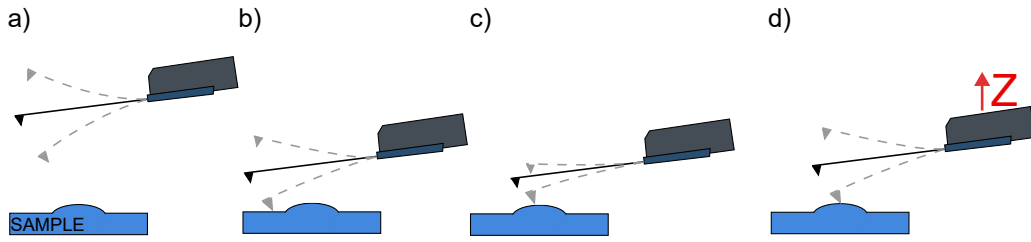


Figure 2.14: **a)** the cantilever is oscillating in air at maximum amplitude. **b)** Cantilever taps on the surface, setpoint amplitude. **c)** Tip gets to the higher surface, the amplitude of oscillation drops. **d)** Feedback system either lowers the sample, or lift ups the cantilever, returning to the setpoint amplitude.

Non-Contact Mode is the only mode that is not in direct contact with sample at any point of measurement and therefore provides the lowest possible chance of damaging either the tip or surface of the sample. The cantilever again oscillates at resonance frequency but the AFM tip is kept at a small distance (several nanometers) from the surface. The material then interact with AFM tip due to attractive forces and the changes of cantilever amplitude are noticed. The feedback then again maintains a constant oscillation frequency. The main disadvantage is the difficulty of the method.

After the image acquisition, we can convert the data into the height map, where each pixel initially corresponds to the height value collected from image. To better understand the roughness of the material, the mean height is calculated for the surface:

$$\bar{h} = \frac{1}{N} \sum_{i=1}^N h_i \quad (2.17)$$

Where N is the number of data points and h_i is the value of height for a given data point. By knowing the deviation of each point, we can calculate Root Mean Square (RMS), overall roughness of the surface, with equation:

$$\text{RMS} = \sqrt{\frac{1}{N} \sum_{i=1}^N h_i^2} \quad (2.18)$$

Where h_i^d is a height deviation of certain data point.

Experimental Setup

The changes in the roughness of the material before and after plasma treatment were measured using the atomic force microscope AFM NTEGRA Prima (NT-MDT, Moscow, Russia) in tapping mode called "semi-contact mode". The AFM probes used in the measurements were golden-silicon probes AN-NSG10 (Applied NanoStructures Inc., Mountain View, CA, USA) with a typical resonant frequency of 240 kHz with a typical force constant of 11.8 N/m. To measure a Root Mean Square (RMS) and average roughness, we used 100-400 μm^2 with a resolution of $512 \times 512 \text{ px}^2$. The scanning frequency during the measurements was up to 1 Hz.

2.5.2 Scanning Electron Microscopy

Scanning electron microscope is using a focused electron beam to scan a surface of observed sample. As electron interacts with the sample a wide spectrum of signals is created which are furthermore detected by a different kind of detectors. A simple image showing different interactions of electrons with atom of the sample can be seen in Fig. 2.15.

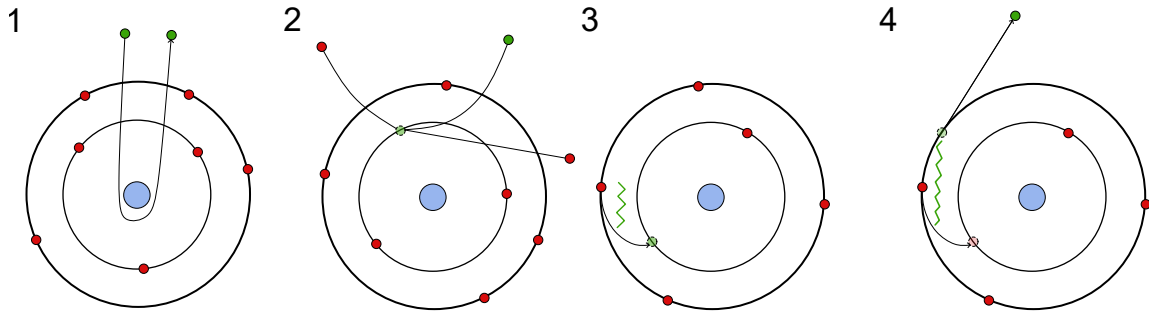


Figure 2.15: An figure showing a different interaction of electrons with atoms: **1)** Backscattered electrons, **2)** secondary electrons, **3)** x-ray emission, **4)** Auger's electrons.

On the fig. 2.15 are shown 4 sources of signal in scanning electron microscopy. The interaction shown in 2.15(1) is for creation of backscattered electrons (BSE). When an electron beam hits the sample, the initial electrons can interact with the nucleus of atoms, therefore deviating the trajectory. Under the right circumstances, the electron can emerge back to the surface, keeping its high energy. The most common source of signal for scanning electron microscope (SEM) are secondary electrons whose interaction is shown in 2.15(2). In contrast with backscattered electrons, interaction between initial electron and atom is inelastic, therefore the secondary electron originates from atom of the sample. These two are the main signals in SEM.

Another useful signal that can be detected during scanning with an electron beam is x-rays (whose interaction can be seen in 2.15(3)). The creation of x-rays is a process with two steps. In the first step, the electron beam brings energy to the atom. This energy can then be used by an electron to move to the higher energy shell or completely leave the atom, leaving a hole behind. The second step is the attraction of a negative electron from a higher-energy shell by a positive hole, leading to release of energy in the form of x-rays. An honorable mention, is the 4th source of signal, Auger's electrons shown in 2.15(4). If an electron moves from higher energy shell to the lower, the energy that could be released as an x-ray can be caught by electron inside the atom, leading to the release of that electron to the surface.

Electrons emitted from the material are then detected by detectors. The most common way to obtain an image is through secondary electrons (SE). The reason is their low energy, which means that they are emitted from the surface of the material or a depth of a few nanometers. After emerging from the sample, they are commonly collected by the Everhart-Thornley detector (ETD). ETD is the most commonly used device for SE detection. The detector is positioned close to the sample, and it consists of a scintillator and a photomultiplier. Not all SE need to emerge into the detector. For this reason, the scintillator is inside the Faraday cage with high positive voltage to attract electrons. Electrons that reach the scintillator are turned into photons that reach the photomultiplier,

which amplifies the signal, which changes to digital form and creates an image. Signals from secondary electrons are useful for topography measurements.

Although signal from BSE can also be used for imaging, we will not achieve a resolution higher than SE. BSE are mostly used for their dependency on the material composition. Since heavier elements are much better scatterers than lighter elements, we can expect a higher intensity of the BSE signal for large atoms. The number of BSE reaching the detector is dependent on atomic number of the component. Common detectors for BSE are "donut" like shaped around the beam and above the sample to collect most of the scattered electrons. These detectors are mostly made out of doped semiconductor material, typically silicon. BSE electrons have higher energies; therefore, materials such as semiconductors that are sensitive only to higher energies collect mainly BSE. We detect the BSE using the electron-hole pair created by the impact of the initial electron which excites electrons in silicon. The number of pairs is proportional to the energy of the initial electron.

Last detected signals in this section are x-rays. Method to detect x-rays is called energy-dispersive x-rays (EDX or EDS). Unlike electrons, x-rays are electromagnetic radiation consisting of photons. These photons are collected by the silicon-drift detectors. These detectors are placed close to the sample at an angle and can measure the energy of x-rays with high precision. X-ray emitted from material due to process explained earlier transfers energy which is characteristic to the difference between two shells. The software can then categorize this energy to the element, creating a spectra with peaks corresponding to the components in the sample. This method can be used not to just find the amount of elements inside the sample but with the correct measurement, we can also get the percentage of the concentration for found elements.

Experimental Setup

Changes in the morphology of the sample were observed using the Mira3 scanning electron microscope (Tescan, Brno, Czech Republic) shown in the figure 2.16. To prevent charging of the samples, substrates were coated with 20 nm of the Au/Pd layer by sputter coater Quorum Q150R-ES (Quorum Technologies, Lewes, UK). Due to the usage of XPS for element detection, the SEM method was used only to observe morphological damage on the surface. Detector for secondary electrons was used with the accelerating voltage of 7-10 kV. The photos were taken with 50 000 MAG.



Figure 2.16: Photograph of used scanning electron microscope Mira3 [50].

Chapter 3

Results of experiments and discussion

Results present in this section should compare and prove the compatibility of used plasma sources. Due to the extensive nature of the experiment, only a subset of the data was selected to present the results. Notably, the results incorporated in this thesis have been partially published [[11](#)].

3.1 Power efficiency

3.1.1 DCSBD

The power efficiency for DCSBD was calculated using the method mentioned above. The power efficiency is meant to be percentage ratio between the power inside the plasma (P_p) and the power provided by the generator (P_s) connected to the discharge. To measure current and voltage, schematic shown in figure 3.1 was used. The electrodes are in a special oil that travels between the electrode and a cooling system to keep the ceramic from overheating and at the same time insulating to prevent sparking inside the plasma unit. A closer look at the calculated voltage and measured current can be seen in figure 3.2. The vibrating structures on the current curve are micro filaments. All the measurements were acquired after 5-10 minutes to ensure stabilization of temperature and the discharge. The power efficiency is shown in figure 3.3. The DCSBD efficiency at 200 W is 81% and increases to 90 % at 350 W. Power loss is expected and can occur in the electrical circuit (transformer, power generator, or cable connections) or dielectric losses that play a role in DBD. The differences are probably due to the technical incompatibility of the transformers and generator used. A sudden drop at 400 W is probably due to maximum coverage of ceramic with micro-discharges. We also calculated the power over the area of the ceramic at maximum input power for a 15 kHz transformer, which is mostly used for any application. With an input of 400 W and power in unit calculated as 333 W, we calculated the power per area unit with value of 2,08 W/cm². The standard error for the use of 4 GSa/s sampling is 2.7 % according to the lecroly datasheet. This error was used for measured points on channels of lecroly. The errors for efficiency as well as for P_p were calculated from propagation of uncertainties.

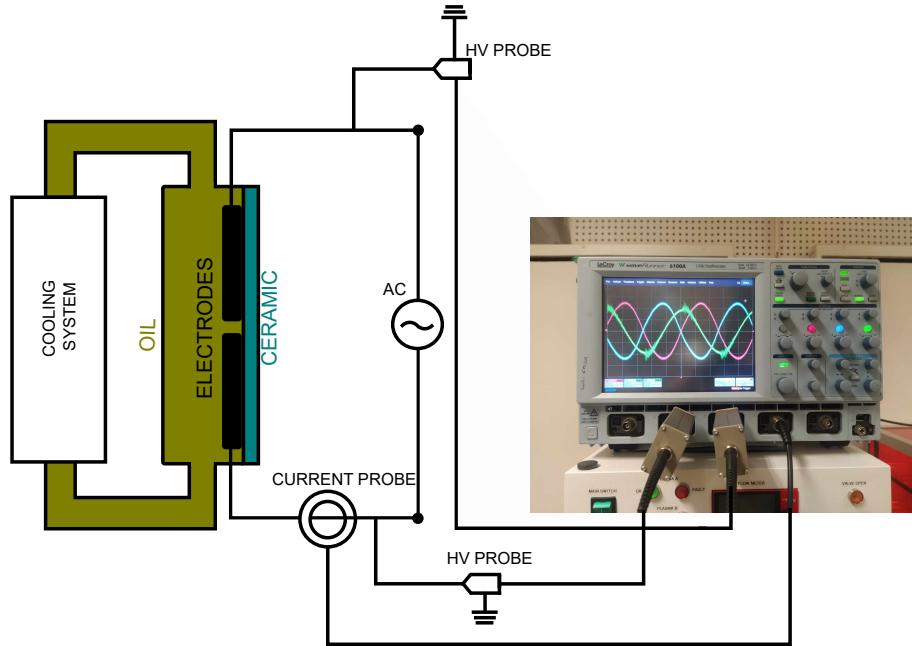


Figure 3.1: Schematic of HV electric circuit used for measurements of power efficiency for DCSBD.

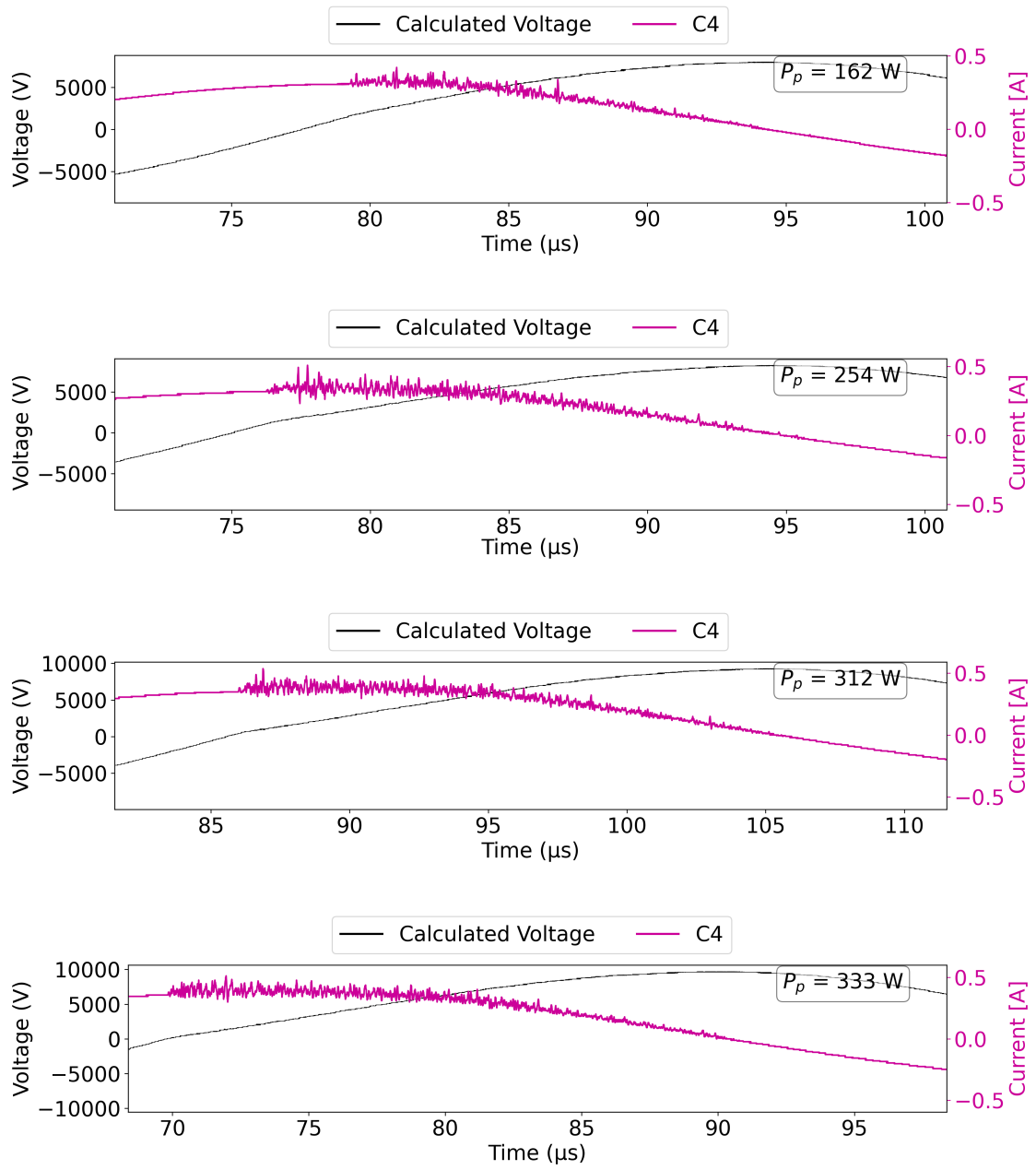


Figure 3.2: Closer look at waveform of current (C4) and calculated voltage and with calculated power inside of plasma for conditions: **a)** 200 W, **b)** 300 W, **c)** 350 W and **d)** 400 W. All measurements were done with a 15 kHz transformer.

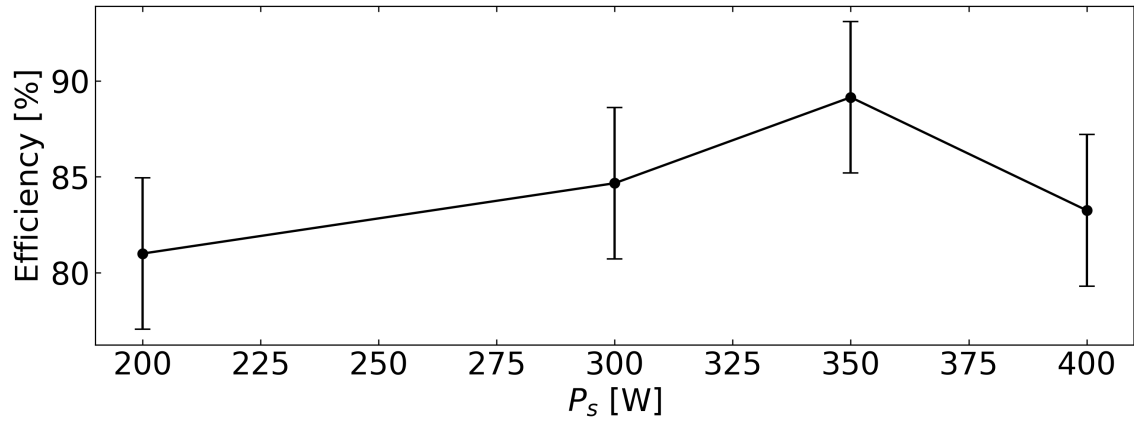


Figure 3.3: Power efficiency calculated as a ratio of power in plasma and power supplied by generator for DCSBD.

If we look at the figure 3.4 and 3.5, we can see dependency of voltage amplitude on power supplied to the discharge with a relation to power in plasma and efficiency respectively. On both figures we see a moment of saturation between 300 and 350 W. This could mean, that it's a zone where the amount of micro-discharges grows rapidly, leading to the almost maximum coverage of the discharge zone. This could explain the rapid drop in the efficiency [9].

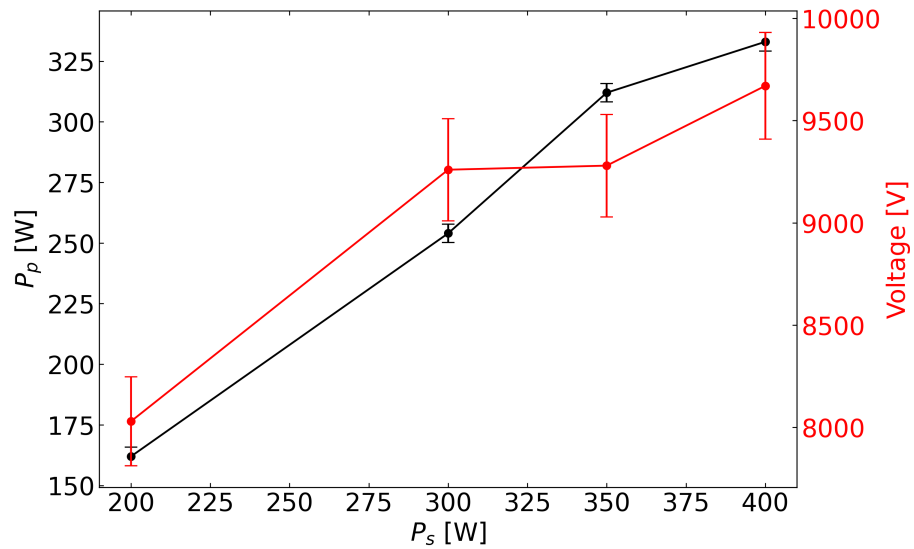


Figure 3.4: Dependency of power in plasma and voltage amplitude on input power for DCSBD.

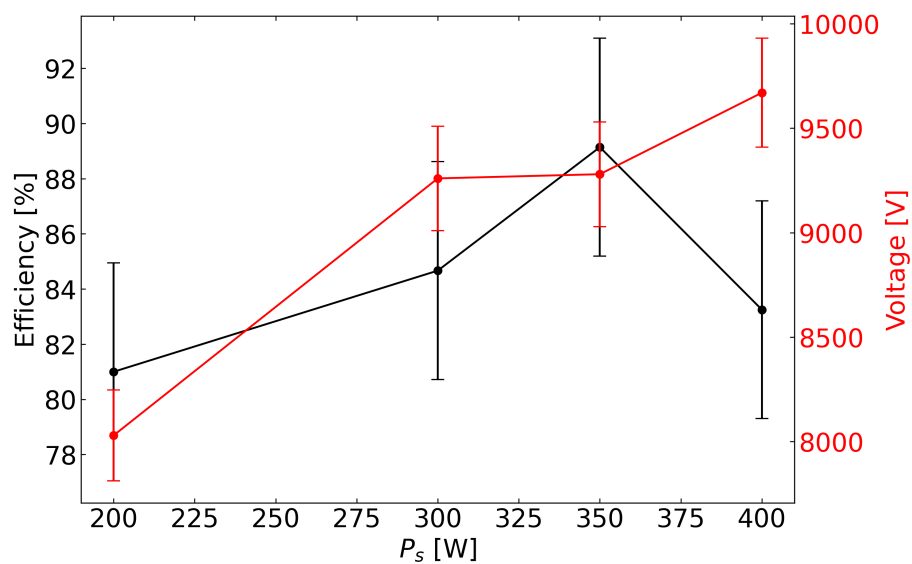


Figure 3.5: Dependency of power efficiency and voltage amplitude on input power for DCSBD.

3.1.2 HDCSBD

The power efficiency for HDCSBD was calculated the same way as for DCSBD. Measurements were done using the schematic shown in figure 3.6. In this schematic, we used the generator with adjustable voltage (0-24 V) as a power supply for the fan used to cool the aluminum heater. The generator was also connected to a temperature sensitive probe located between the aluminum sink and the ceramics to monitor and control temperature. This added component worked as a temperature regulator to provide a stable temperature of ceramic for measurement. Figure 3.7 shows closer look at the current and calculated voltage. We can see characteristics peaks for micro filaments appearing close to the maximum of voltage signal. Measurement shown in the figure were conducted at a temperature of approximately 70 °C. This temperature is similar to the temperature of ceramic using DCSBD at the commonly used power 400 W. The temperature couldn't be set to exactly 70 °C due to the hysteresis behavior of the aluminum heater. Temperature fluctuations were maintained at around 2 to 3 °C. Furthermore, all the measurements were acquired after 5-10 minutes of stabilization. The power efficiency is shown at figure 3.8. The power efficiency appears to be moving from 80% to 95% within error. The power per unit of area at 250 W (231 W in plasma) is 2.9 W/cm². Furthermore, if we look at area power 200 W (194 W in plasma) the efficiency at the half of power commonly used for DCSBD is 2.14 W/cm². The standard error was calculated same way as mentioned in section 3.1.1.

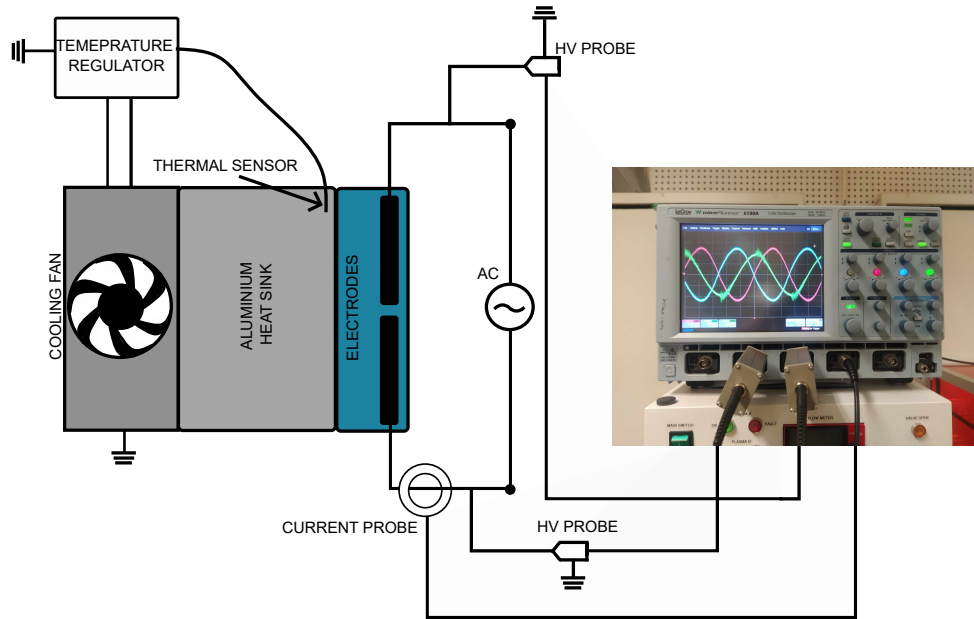


Figure 3.6: Schematic of HV electric circuit used for measurements of power efficiency for HDCSBD.

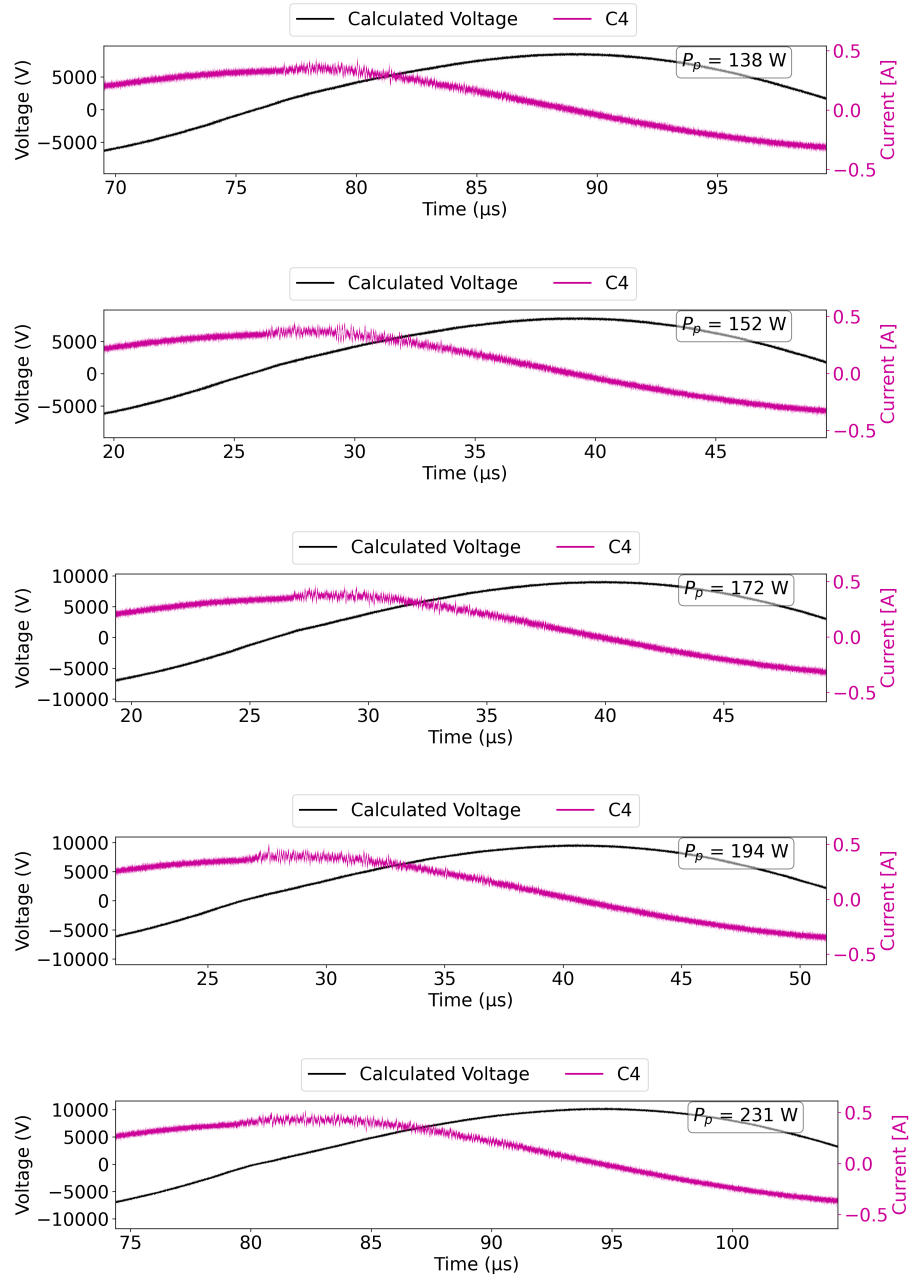


Figure 3.7: Closer look at course of current and calculated voltage with calculated power inside of plasma for conditions: **a)** 150 W and 19.824 kHz, **b)** 175 W and 19.536 kHz, **c)** 200 W and 19.248 kHz, **d)** 225 W and 18.944 kHz, **e)** 250 W and 18.720 kHz.

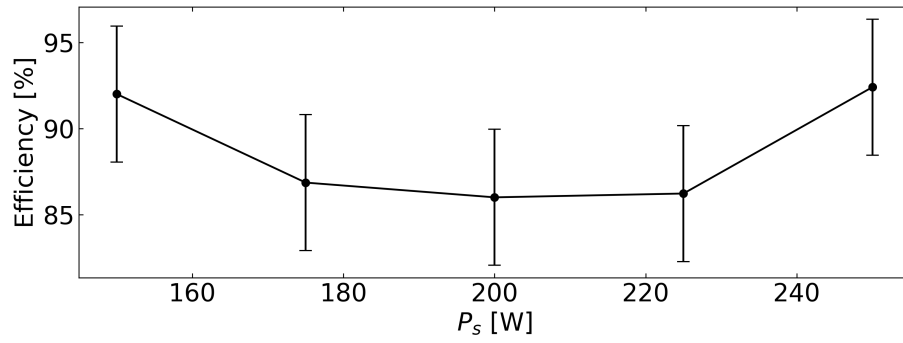


Figure 3.8: Power efficiency calculated as a ratio of power in plasma (P_p) and power (P_s) supplied by generator for HDCSBD with ceramic at temperature of approx. 70° C.

When it comes to the HDCSBD, if we look at dependency of measured voltage amplitude on power supplied from the generator and its relation with the power in plasma, we won't see any saturation and the growth is linear. The decline that we can see between 175 W to 225 W seems to be irrelevant to the amplitude of measured voltage, although the slope when it comes to the amplitude of voltage is higher after 200 W. This could mean that at 150 W, we reached the maximum of efficiency due to the maximum amount of micro discharges but doesn't explain the maximum at 250 W. Due to the error of the measurement we are unable to tell if the decline in 175 W to 225 W region is of any kind of device nature. Mention dependencies are shown in figures 3.9 and 3.10. In the future it would be advised to secure more accurate measurement and increase the range of the measurements to confirm these findings.

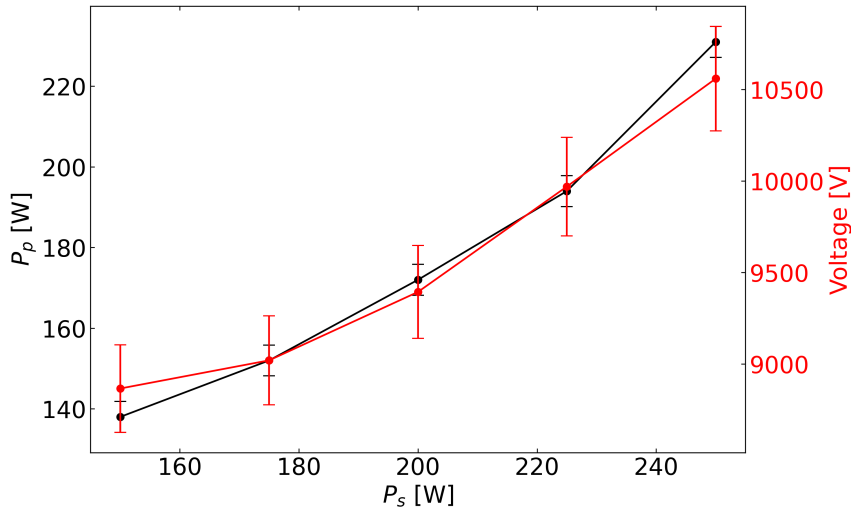


Figure 3.9: Dependency of power in plasma and voltage amplitude on input power.

Fan that was used to cool the aluminium heat sink can be supplied by generator in range of 0-24 V. This generator acts like a temperature controller as its connected to the thermocouple built in the heat sink. Since to achieve 70 °C, we needed only an input of 10 V on maximum power load (250 W) we decided to measure efficiency on lower temperatures of ceramic for two highest power loads. The dependency of power efficiency on temperature

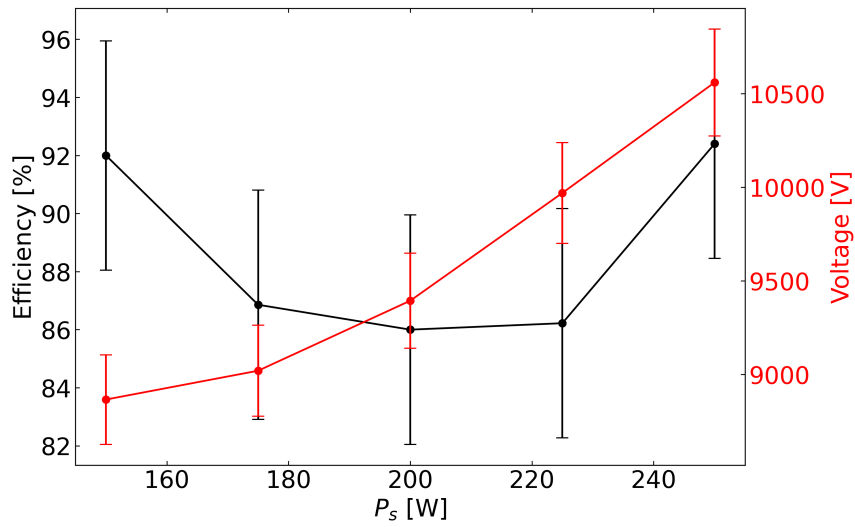


Figure 3.10: Dependency of power efficiency and voltage amplitude on input power.

with input power of 225 and 250 can be seen in figure 3.11. Since we expected no changes of efficiency, we measured down to 50 °C in two steps for both power inputs. As we can see on figure, there is a small change in efficiency which is within standard error of used oscilloscope. By neglecting the error, according to the measurement, the optimal temperature of ceramic for usage of HDCSBD is 60 °C. In the future work, the measurement could be improved by widening the range of temperatures and using more stable supply of power or more accurate measurement method.

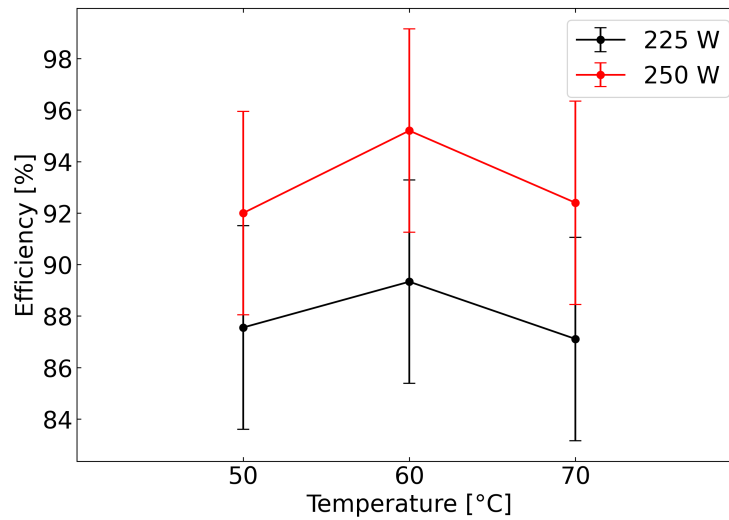


Figure 3.11: Dependency of efficiency on temperature of HDCSBD's Kyocera ceramic with input of 225 and 250 W.

3.2 Optical emission spectroscopy of plasma sources

Optical emission spectroscopy (OES) was used to observe HDCSBD with input power in range of 150-250 W powered by adjustable generator with internal 20 kHz transformer. OES was also used to observe DSCBD with input power of 400 W mostly used in applications and 15 kHz transformer. The measurements were focusing on nitrogen vibrational bands spectrum in range of 366 to 382 nm. The optical fiber was placed approx. 7 cm above the plasma which means we monitored around 5 mm of surface. The results were calculated by already mentioned SpectrumAnalyzer 1.7. which stated the error bars from pyrometric line.

Vibrational and rotational temperature was a point of different studies considering material treatment and the changes of the material surface [51]. In [52] authors show the dependency of vibrational temperature on adhesion properties in a way, that higher vibrational temperatures lead to the better results. Graph in Figure 3.12 shows vibrational temperature calculated from above mentioned region and its dependence of input power. The results are also seen in Table 3.1.

Input Power [W]	Vibrational Temperature [K]
150	2430 ± 330
175	2540 ± 270
200	2530 ± 270
225	2400 ± 310
250	2400 ± 330

Table 3.1: Calculated vibrational temperatures from N₂ 0-2 region for different input power on HDCSBD.

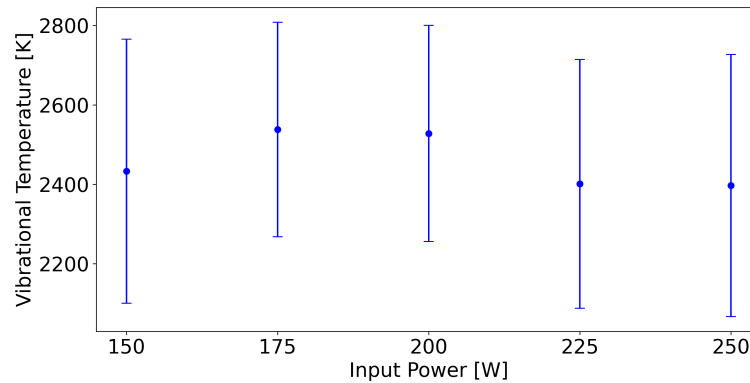


Figure 3.12: Measurement of vibrational temperature from N₂ 0-2 region for different input power on HDCSBD.

Calculated values show almost identical results. A small difference within the error can be noticed at input power of 175 W and 200 W. OES measurement was also done on DCSBD powered by generator with input power of 400 W and 15 kHz transformer. These conditions

are the most common used conditions for LTP treatment by DCSBD. The measurement was also done for N_2 0-2 vibrational bond:

$$T_v = 2300 \pm 270K \quad f = 15kHz$$

As HDCSBD is powered by different generator with approx. 20 kHz transformer, we looked at the difference of vibrational temperature for DCSBD powered by generator with 30 kHz transformer. The results are from thesis of Dr. Kelar [9]:

$$T_v = 2100 \pm 150K \quad f = 30kHz$$

HDCSBD shows slightly higher values of vibrational temperature but the results are within the error. HDCSBD should then be suitable for surface treatment by providing the same results as more industrially used DCSBD [9]. Since the temperature of ceramic on HDCSBD can be regulated by a heat sink connected to the fan, we also lowered the temperature while providing the power of 225 W and 250 W. Temperature of ceramic was controlled by a fan connected to the generator with adjustable input voltage. Generator has built-in thermal controller that is connected to the thermocouple inside the aluminium heat sink of HDCSBD. Measurements were done in the range of 50 °C to 70 °C. The results are shown in Figure 3.13. The results are also shown in Table 3.2. The measurements of vibrational temperature are affected by a large statistical error, therefore we cannot confirm or deny any dependence on the changing parameters.

Temperature [°C]	Vibrational Temperature [K]	
-	225 W	250 W
50	2460 ± 310	2500 ± 300
60	2350 ± 370	2420 ± 320
70	2400 ± 310	2400 ± 330

Table 3.2: Calculated vibrational temperatures from N_2 0-2 region for different temperatures of ceramic.

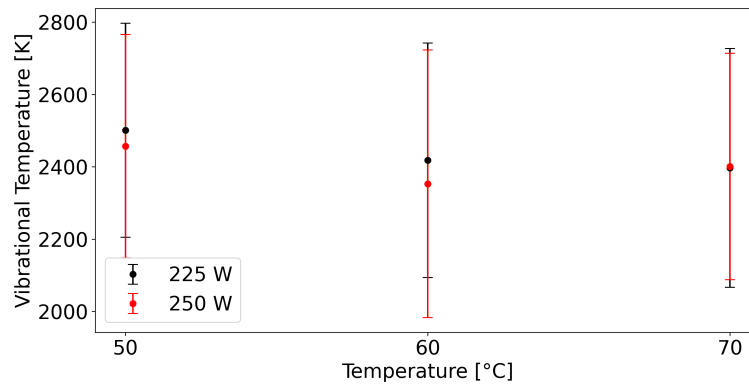


Figure 3.13: Measurement of vibrational temperature from N_2 0-2 region in dependence of temperature of ceramic.

Vibrational temperature and rotational temperature contributes synergistically during the treatment process. We investigated rotational temperature of HDCSBD at different input powers and temperatures. Knowledge of rotational temperature is important due to its significant input for different plasmachemical processes. Since the temperature of neutral particles in plasma can be determined by rotational temperature, results can help us during treatment of temperature sensitive materials. Experiment was focused on OES measurement in range of 306 to 312 nm. In this range, we can look at OH^- rotational lines and calculate the rotational temperature with used software. Due to the quenching effect, the listed temperatures are overestimated and do not represent the temperature of heavier particles and neutral gas within the plasma. Results of spectroscopy are shown in Figure 3.14. The Table 3.3 shows numerical values of the calculations.

Input Power [W]	Rotational Temperature [K]
150	560 ± 80
175	560 ± 80
200	550 ± 50
225	560 ± 80
250	560 ± 90

Table 3.3: Calculated rotational temperatures from OH^- region for different input power on HDCSBD.

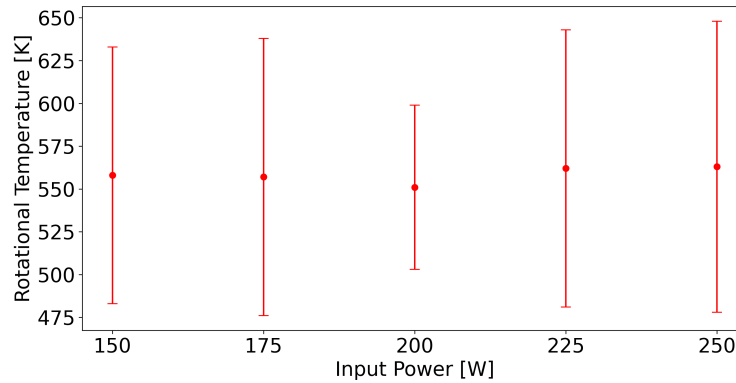


Figure 3.14: Measurement of rotational temperature from OH^- region for different input power on HDCSBD.

Although the error intervals are smaller as in case of vibrational temperature, the differences in temperatures are very small, leading to no noticeable difference in changing of power parameter. Similar measurement was done on DCSBD at commonly used input power of 400 W with 15 kHz transformer for OH^- . We also looked at the rotational temperature of DCSBD powered by generator with 30 kHz transformer [9]:

$$T_r = 510 \pm 80\text{K} \quad f = 15\text{kHz}$$

$$T_r = 540 \pm 80\text{K} \quad f = 30\text{kHz}$$

DCSBD value at it industrially used parameters shows lower rotational temperature. According to the authors of [51] increase in rotational temperatures is unwanted as it leads to worsening of surface treatment. Exposure time to achieve HDCSBD spectrum which could create unwanted noise. Considering the error, the slightly higher temperature should not lead to the damaging of temperature sensitive samples or degrade the effect of plasma treatment.

We also observed OES for the HDCSBD while controlling and changing temperature. Results of the measurement are shown in Figure 3.4 and in Table 3.15. The changes in the rotational temperature in correlation to the changes of ceramic's temperature are insignificant. The measurement of rotational and vibrational temperature for HDCSBD are similar as for DCSBD at it commonly used configuration for different applications. Small deviations of these temperatures in dependence on plasma source are within the error of the used calculation method and therefore should not had any significant effect on plasma treatment. For the future measurement it would be practical to use a systematical error for a set of measurements rather than error from fit of pyrometric line.

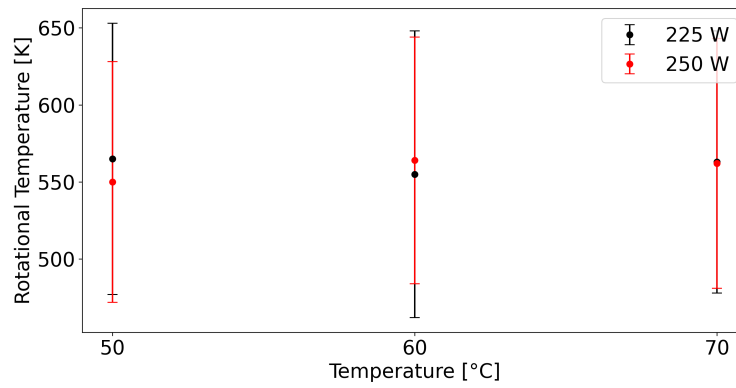


Figure 3.15: Measurement of rotational temperature from OH^- region in dependence of ceramic's temperatures.

Temperature [°C]	Rotational Temperature [K]	
	225 W	250 W
50	550 ± 80	570 ± 90
60	560 ± 80	550 ± 80
70	560 ± 80	560 ± 90

Table 3.4: Calculated rotational temperatures from OH^- region for different ceramic's temperatures.

3.3 Wettability and Adhesion of Treated substrates

The total SFE and adhesion changes for two polymers will be discussed in this thesis. The mentioned polymers are industrial grade polycarbonate (PC) and polyethylene on

aluminum surface (Pe-Al). The core of Pe-Al is made of low-density polyethylene (LD-Pe) covered by aluminum and a thin player of polyethelene on the surface. The scheme of the material is shown in figure 3.16. In this thesis, we use the technical name for Pe-Al, Dibond. Materials were provided by Effetec s.r.o. (Čelechovice na Hané, Czech Republic). Boards with dimensions of $15 \times 10 \times 0.3 \text{ cm}^3$. Experiments were conducted on smaller pieces with dimensions of $1.5 \times 10 \times 0.3 \text{ cm}^3$ that were cut from the boards, maintaining thickness of 3 mm. The surface of the materials was protected by a protective foil that was removed prior to plasma treatment to ensure that the samples were not contaminated. Figure 3.17 shows uncut boards of used Dibond with protective layer.

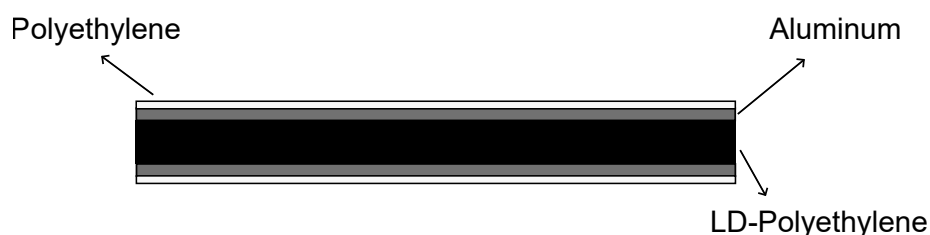


Figure 3.16: Schematic showing structure of Dibond.



Figure 3.17: Used Dibond plates with peeled of protective player.

Materials were treated by low temperature plasma (LTP) generated by both already mentioned plasma sources DCSBD and HDCSBD. The treatment then proceeded at different distances of samples from plasma source. Distances used in this thesis are $225 \mu\text{m}$, $300 \mu\text{m}$ and $450 \mu\text{m}$. Plasma treatment was done by a plasma source moving above the surface keeping set distance. Distance was set by using of kapton tapes of known thickness and then removed from the sample before the plasma treatment. Variations of exposure time were also included. The time of treatment varied from 1 to 5s. Plasma source movement was ensured by adjustable generator. The ageing of the treatment was measured in this thesis. To prevent contamination and ensure controlled ageing, samples were stored in a desiccator cabinet at room temperature (23°C) and constant humidity of 40%. Setup used for the plasma treatment of polymers is shown in figure 3.18.

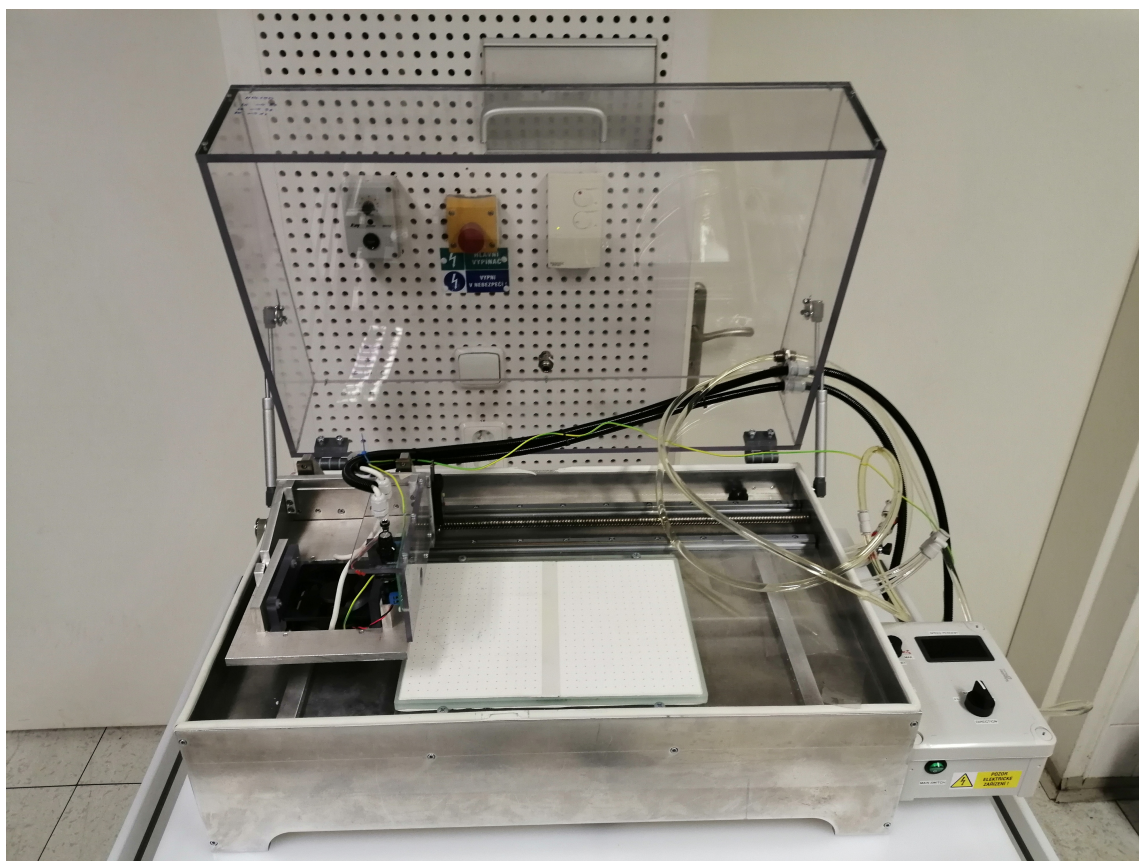
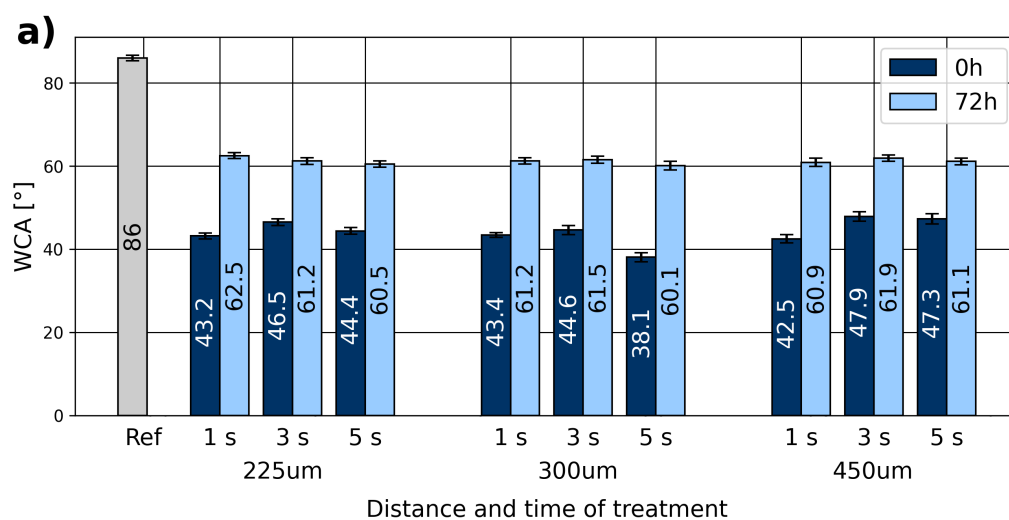
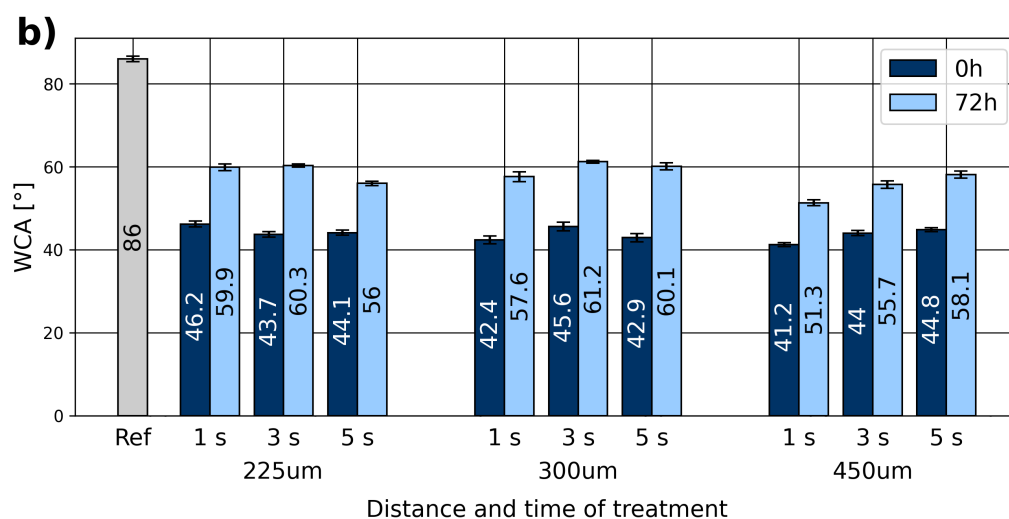


Figure 3.18: Apparatus used for plasma treatment with HDCSBD as a plasma source, exchangeable for DCSBD.

Due to the amount of data, figure 3.19 shows results for reference, values of treated samples immediately after treatment and after 3 days. Wettability of the samples changed due to the LTP treatment. In case of PC right after the treatment the WCA values dropped from the reference value of 86° down to $43\text{--}47^\circ$ depending on the time of the treatment, distance and used source. These fluctuations are very small and considering the mean error and error of used technology, the values seem to be quite consistent. Prolonged ageing of the samples shown no significant increase in WCA values up to 24 hours. Further measurements shown, that after 24 hours values increased mostly for lower treatment times (1-3 s) while 5 s treatment shown no significant changes. After three days, all values stabilized for DCSBD at approx. 61° within the error. For HDCSBD however, we see a different trends depending on the distance from plasma source. For the lowest distance of $225\text{ }\mu\text{m}$ we observe expected results, where WCA values decrease with longer times of treatment down to 56° . For $300\text{ }\mu\text{m}$, the trend reverses, and the lowest time of treatment yields best results. The same trend is repeated for $450\text{ }\mu\text{m}$ where after 72 hours we reach the minimum value of 51° . In [53] authors used DBD reactor with helium-plasma to observe ageing of the PC samples. Although immediately after the treatment they achieved better results of 40° for treatment time of 30 s, after 3 days the value reached 79° . This could be explained by the reactor running on lower power.



(a) DCSBD.

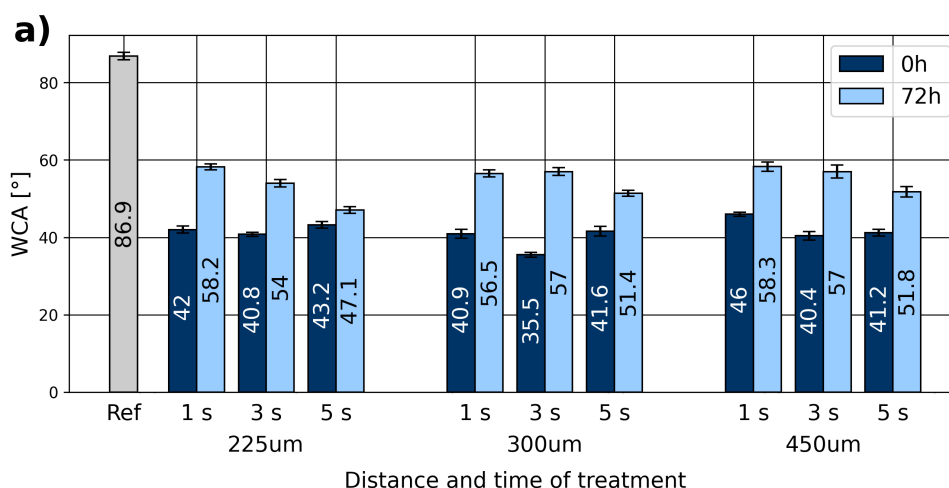


(b) HDCSBD.

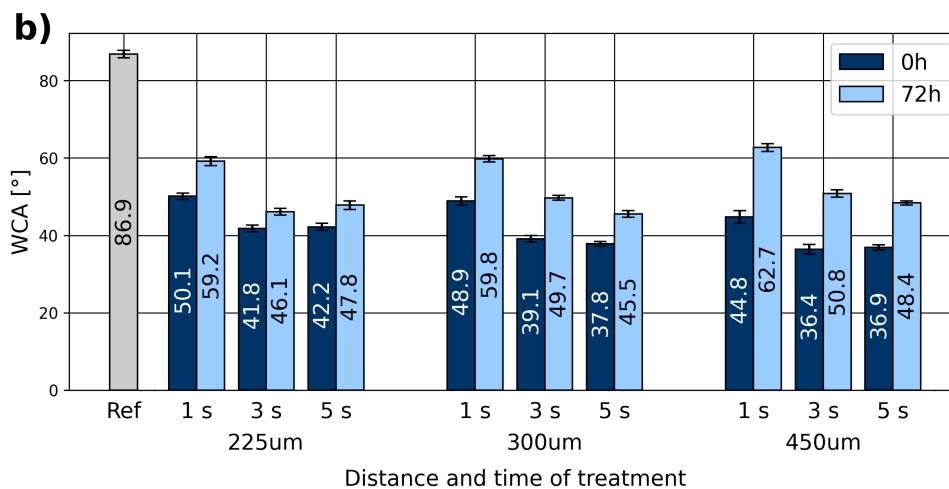
Figure 3.19: The WCA (determined from the average angle of 14 droplets of water) of PC substrates treated by **a)** DCSBD, **b)** HDCSBD.

For Dibond there is a significant improvement of WCA for all treated samples. The results can be seen in figure 3.20. For DCSBD, The initial value of 86.9° for reference dropped to $35\text{--}46^\circ$ in dependence on distance and exposure time. The differences between measurements are quite small and stabilize at approx 41° for most of the measurements considering the difference. The only exceptions are 3 s treatment time with distance of $300\text{ }\mu\text{m}$ that reached the overall minimum of 35.5° and the overall maximum at 1 s and $450\text{ }\mu\text{m}$ where the value reached was 46° . From the measurements it seems that lower times are better immediately after the treatment excluding the $450\text{ }\mu\text{m}$. After 72 hours, we can see opposite trend, where the aging is more pronounced for shorter time of treatment Showcasing that the longer exposure time and smaller distance yield best results. For HDCSBD, we can see the decrease of WCA depending on exposure time. In comparison, using HDCSBD is actually favorable for longer times, while 1 s exposition

although it improves WCA, it is less significant. We can also notice, that bigger distance is more suitable immediately after the treatment. After 72 hours, 1 s exposure time shows significant aging, while 3 and 5 seconds does not change much, depending on distance during treatment. From the results it was established that longer treatment times with the distance of 300 μm yield the best results. Furthermore, immediately after treatment and 72 hours later, the values never reached the reference value.



(a) DCSBD.

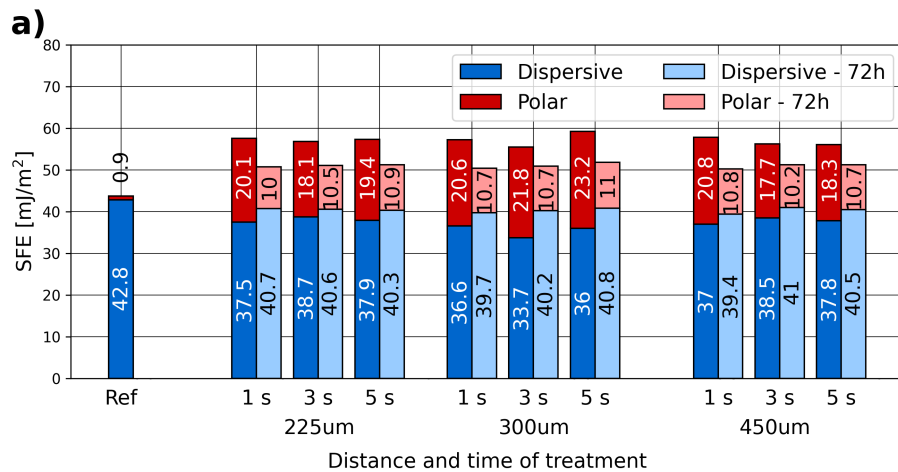


(b) HDCSBD.

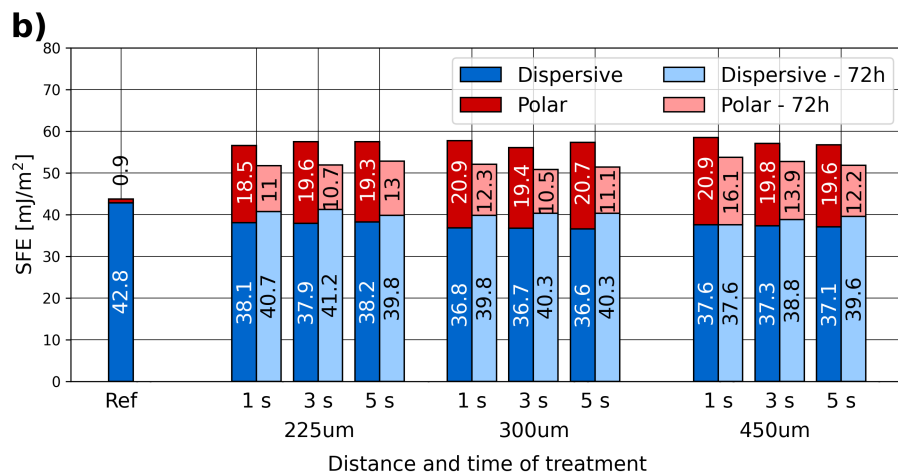
Figure 3.20: The WCA (determined from the average angle of 14 droplets of water) of Dibond substrates treated by **a)** DCSBD, **b)** HDCSBD.

The CA of different liquids (Diiodomethane, Water and Ethylene glycol) were used to calculate dispersion and polar components for a better understanding of changes that occurred during measurements of wettability for plasma-treated substrates. Figure 3.21 shows that the total SFE of PC substrate increased after the plasma treatment, leading to better adhesive properties and enhancement of the polymer surfaces. The standard error of the procedure is approx. 1 mJ/m^2 . In case of PC the polar component increased

significantly as expected. Right after the treatment the polar part of SFE increases from starting 0.9 mJ/m^2 to the value of $18\text{--}23 \text{ mJ/m}^2$. The disperse part decreases by $4\text{--}9 \text{ mJ/m}^2$. The increase of polar component is common in LTP treatment in air due to the surface activation and creation of functional polar groups on its surface due to the reactive oxygen and nitrogen species (known as RONS) [2]. Surface activation can modify SFE through chemical grafting and oxidation. The reason for the drop of values for disperse forces could be due to the cleaning of the surface, polar saturation on the surface and morphological changes. Due to ageing, the polar components start to drop while the disperse part starts to recover. After 3 days of measurement the SFE components did not reach the reference values. We can notice that similar trends that we saw at WCA in 3.19 can be observed in the increase of the polar component at 3.21. Authors in [54] achieve similar results with Air DBD treatment where after 3 days of ageing they reach almost identical values of polar components for PC.



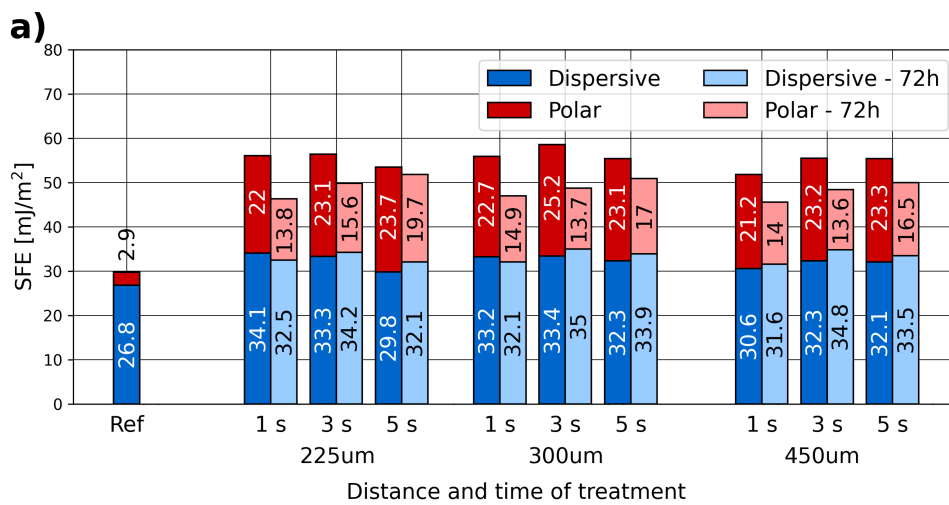
(a) DCSBD.



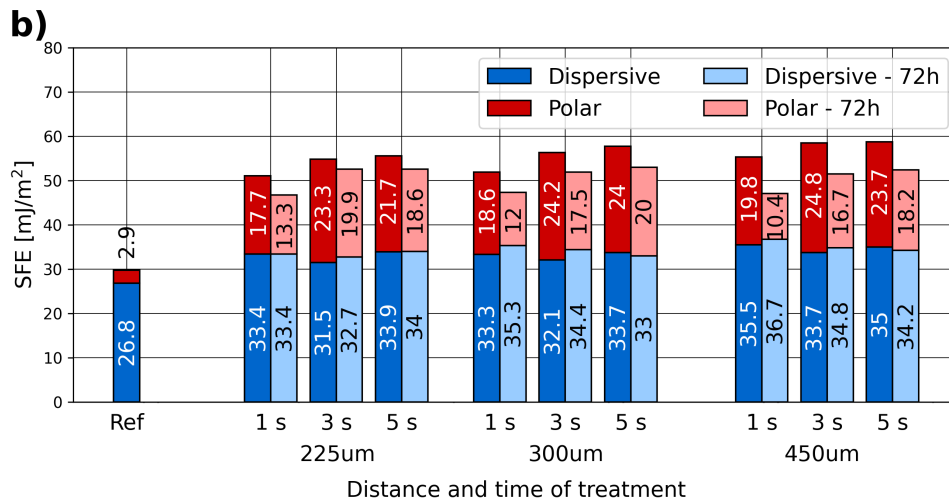
(b) HDCSBD.

Figure 3.21: The SFE (determined from average angle of 14 droplets per liquid) of PC substrate treated by **a)** DCSBD, **b)** HDCSBD.

Figure 3.22 shows the results of the SFE for Dibond immediately after treatment and 72 hours later. The results show an increase in the polar and dispersive part of the SFE for all the observed samples. Right after treatment, we can follow improvement of the polar part in the range of 19 to 22 mJ/m^2 for DCSBD and 15 to 22 mJ/m^2 for HDCSBD. We can see that the total SFE follows the patterns seen in the WCA results (Figure 3.20) that shorter times are better for DCSBD, except the distance of 450 μm where we again follow a slight decrease for 1 s exposure time compared to longer treatment times. After 72 hours, the SFE stabilizes with a smaller drop, again more significant for shorter treatment times, following the trend. In case of HDCSBD, we can see, that the total SFE increases with longer treatment times and the drop after 72 hours is more significant for shorter exposure times.



(a) DCSBD.



(b) HDCSBD.

Figure 3.22: The SFE (determined from average angle of 14 droplets per liquid) of Dibond substrate treated by **a)** DCSBD, **b)** HDCSBD.

Presented results shows increase in polar and dispersive components of the SFE after LTP

treatment. According to [55], changes in surface roughness that occur during plasma treatment as well as formation of polar oxygen-containing functional groups can lead to the improvement in adhesion. Changes in adhesion were observed for PC and Dibond right after the plasma treatment and in 24 hours after the plasma treatment. Samples underwent LTP treatment at different distances and exposure times. Distances were selected unison with WCA and SFE data sets. Exposure time of 1 s was excluded due to the amount of available samples provided by manufacturer. Another reason is fast aging of polymer samples evaluated in previous studies [1]. The ageing effect was observed up to 24 hours. Results of this measurement for PC can be seen in figure 3.23.

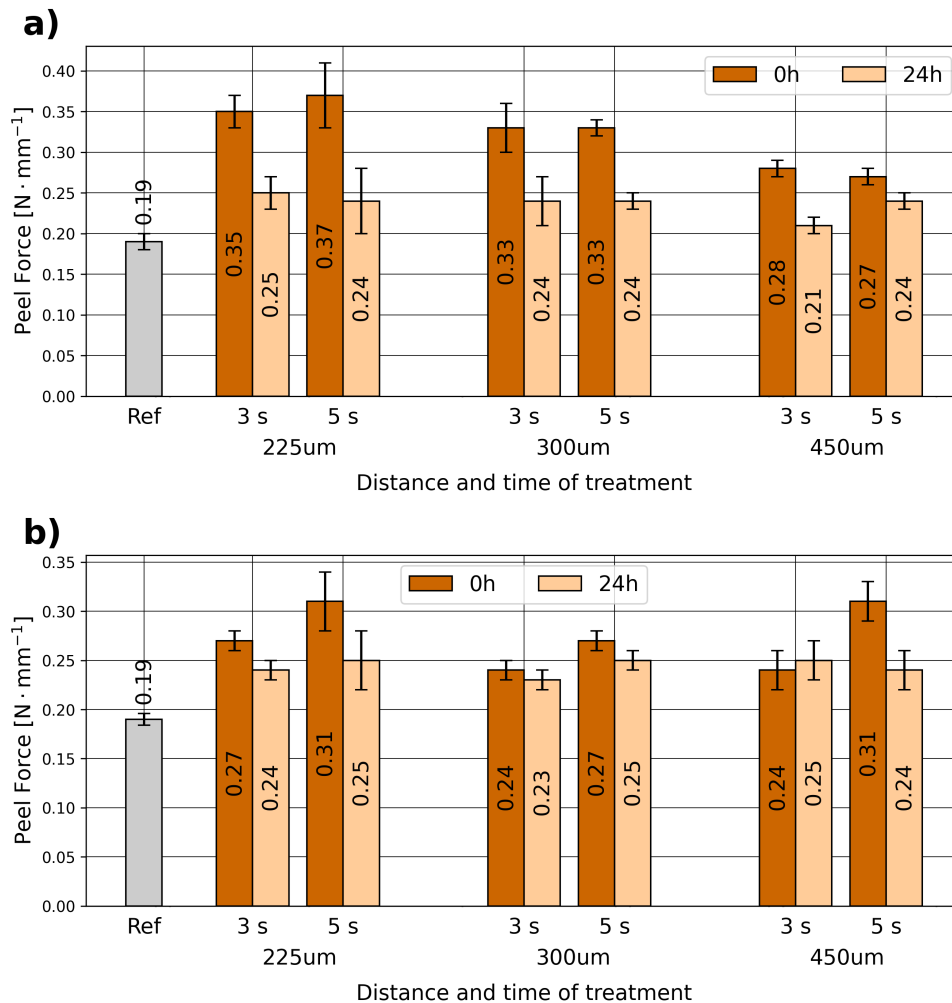


Figure 3.23: Mean peel force of PC substrates treated by a) DCSBD, b) HDCSBD for different distances and exposure time.

Immediately after LTP treatment of PC using DCSBD, adhesion increased compared to reference. At the lowest used distance of 225 μm, the peel force almost doubled after 5 s exposure time. It should be noted, that there is a small difference between 3 s and 5 s treatment which is almost the same within margins of error. Same statement can be applied for further distances. Increasing the distance leads to the decrease of the peel force in comparison to the 225 μm. These results are different for HDCSBD, where the longer

exposure times shows better results. Only exception to the decrease of the peel force with increase of distance is 5 second treatment with HCDSBD at the distance of 450 μm , where the achieved peel force of 31 N/mm is comparable to the 5 second treatment at the distance of 225 μm . All the samples treated by either DCSBD or HCDSBD shown improvement of surface adhesion.

Value of peel force remained higher than the one of reference samples even after 24 hours. The decrease in the peel force was significant for PC as for all the measurements it decreased to the value approx. 0.24 N/mm. As the aging effect we have to consider uptake in WCA or decrease of SFE with time. Same trend can be seen in measurements of adhesion after 24 h due to the possible contamination, chemical reactions, relaxation of the sample or reorientation of functional groups [56]. Although the peel force decreased significantly after 24 hours, the in-line process should diminish the ageing effect, leading to the stable improvement of surface adhesion [11].

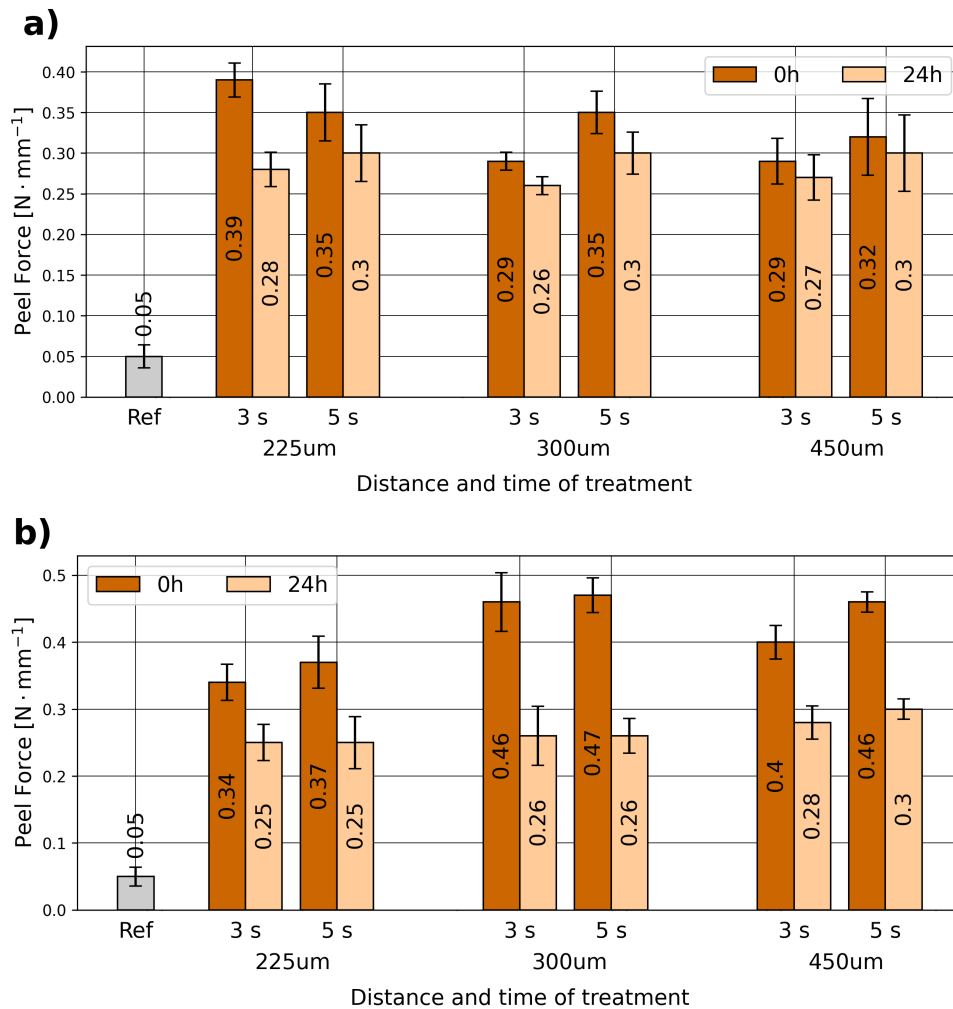


Figure 3.24: Mean peel force of Dibond substrates treated by **a)** DCSBD, **b)** HCDSBD for different distances and exposure time.

Results for the measurement of the peel force in Dibond can be seen in Figure 3.24. The initial value for reference is 0.05 N/mm. After the treatment with DCSBD, we observe

values almost 6 times higher for the lowest reached value of 0.29 N/mm. Overall, we can see increase in range of 0.29 to 0.39 N/mm. Shorter distances yield better results, as the mean peel force decreases with increasing distance. We can observe that the best results are for the shortest observed treatment time at the closest distance of 225 μm . 24 hours after treatment, we observe a slight decrease in the peel force to the lowest 0.26 N/mm and the maximum value of 0.3 N/mm. Distance of the sample in our range doesn't seem to be a factor as the peel force reaches the same value respectively to the exposure time. Higher exposure time seems to bring better results. Although the treatment at a distance of 300 μm appears to have smaller errors and feels more stable, more samples would be needed to confirm this observation.

Treatment by HDCSBD led to greater increase in peel force immediately after treatment up to 0.47 N/mm. Peel force reaches the maximum for treatment distance of 300 μm . The longer treatment time of 5 seconds yields slightly better results. After 24 hours peel force drops to the values in range of 0.25 to 0.3 N/mm. All values reach the same amount within the statistical error, regardless of exposure time. Considering the error of the measurement, the slight increase at 450 μm is negligible.

3.4 XPS measurements of treated polymers

Chemical changes and the creation of functional groups on the surface due to the LTP treatment were already mentioned in this thesis. Samples of PC and Dibond that underwent XPS analysis were treated by plasma sources at different distances and exposure times. The distance of 225 μm was excluded due to the large amount of data and processing time. The results of XPS analysis are shown in Tables 3.5 and 3.6. The analysis was focused on the main composing elements such as C and O. Nitrogen is also mentioned, as the plasma treatment in ambient air can lead to its implementation. The trace elements such as Si are not listed as we used pristine samples.

A slight increase of nitrogen was expected, yet the changes due to the distance or exposure time are not obvious as they are within the error. After the treatment there are noticeable changes of C and O elements as expected. The initial O/C ratio of 0.13 increased after plasma treatment for all samples. The increase was more noticeable for a shorter distance of 300 μm , with an increase to 0.18. Longer exposure times were needed for samples treated at a distance of 450 μm to increase oxygen concentration to reach similar values achieved at 300 μm . This could remote reaction of gaseous chemical products and long-living particles.

Distance	Reference	300 [μm]		450 [μm]	
Exposure Time	-	3 s	5 s	3 s	5 s
At. Concentration [%]					
C	88	74	76	81	77
O	11	23	22	17	21
N	-	1.8	1.5	1.0	1.3
O/C Ratio	0.13	0.31	0.29	0.21	0.28

Table 3.5: Atomic concentration estimated from survey spectra for PC.

As it was already mentioned, the increase of oxygen content is most likely due to the creation of functional oxygen groups. Results in Table 3.6 show the concentration of functional groups at the surfaces of the PC samples. The deconvolution of C 1s high-resolution spectra reveals, that after the plasma treatment, a new C=O group is created as well as shake-up-satellite $\pi - \pi^*$. There is also a small but noticeable increase of O-C=O and C=O concentrations which correlates with changes we see at Table 3.5. Slight changes of O - C = O₂ group are insignificant as the standard error is approx. 1%. Similar changes were observed for PC treated by DCSBD [1].

Distance	Reference	300 [um]		450 [um]	
Exposure Time	-	3 s	5 s	3 s	5 s
Functional Group Conc. [%]					
C-C/C-H	71.4	66	65	74	66
C-O	24	24	23.4	20	24
C=O	-	2	4	2	2.4
O-C=O	1	7	4.5	3	3.5
O-C=O ₂	3	2	3	2	3.5
$\pi - \pi^*$	-	-	1	-	2

Table 3.6: Concentration of functional groups estimated by deconvolution of C 1s high-resolution spectra for PC.

Chemical changes were also observed in the case of Dibond. The results of the XPS analysis can be seen in Table 3.7. The samples were treated with DCSBD and HDCSBD at a distance of 300 μm and 450 μm with exposure time of 3 and 5 seconds. As in the case of PC, only the common elements that occur during LTP treatment were analyzed.

Treated samples shown increase of oxygen due to activation of surface and creation of functional groups as well as decrease of carbon. The reference O/C ratio is approx. two-times higher than reference value for all HDCSBD treatments. The difference between PC and Dibond is the higher concentration of nitrogen that increased up to five times the initial value of 3% depending on the distance and exposure time, as well as the plasma source used. It seems that the surface of the dibond is more reactive to the treatment in ambient air than PC. The N implantation could lead to the creation of nitroso, -N=O functional groups.

Plasma Source	Reference	DCSBD				HDCSBD			
Distance	-	300 μm		450 μm		300 μm		450 μm	
Exposure Time	-	3 s	5 s	3 s	5 s	3 s	5 s	3 s	5 s
At. Concentration [%]									
C	79	59	61	60	57	58	57	60	63
O	18	25	26	26	27	26	27	26	29
N	3	15	12	13	15	15	15	13	7
O/C Ratio	0.23	0.43	0.43	0.43	0.47	0.46	0.47	0.44	0.46

Table 3.7: Atomic concentration estimated from survey spectra for Dibond.

Further deconvolution of C 1s and N 1s peaks can be seen in Tables 3.8 and 3.9 [57].

Deconvolution of C 1s shows decrease of C-C/C-H by approx. 20 % and increase in oxygen functional groups. Slight increase of C-OH is insignificant and within the error of measurement. A noticeable increase of C=O/C=N and O-C=O correlates with the changes we see in Table 3.7. Plasma treatment using HDCSBD at distance of 450 μm and exposure time, leads to the smallest elevation of N concentration, which mirrors small improvement of C=O/C=N. Consequently, the observed percentage increases for treatments with different conditions lean towards increase of C=N bond, rather than C=O. N 1s spectra was also observed. LTP treatment of Dibond led to creation of new N = O₂ functional group. The most significant chemical changes can be seen for increasing C – NH₂ group and decreasing C=N-C group after the treatment. According to the results, the plasma treatment with HDCSBD at the distance of 450 μm and 5 s results in creation of higher quantity of nitrate groups at the expense of primary amines such as C – NH₂. These results also helps us to understand increase in atomic concentration of nitrogen. For analysis and deconvolution of N 1s we used informations from following articles [58, 59].

Plasma Source	Reference	DCSBD				HDCSBD			
Distance	-	300 μm		450 μm		300 μm		450 μm	
Exposure Time	-	3 s	5 s	3 s	5 s	3 s	5 s	3 s	5 s
Functional Group Conc. [%]									
C-C/C-H	64	41	45	44	42	44	43	45	48
C-OH/C-O	24	25	24	26	24	24	24	25	25
C=O/C=N	3	13	12	9	9	8	7	10	5
O-C=O	10	21	21	22	25	24	26	21	22

Table 3.8: Concentration of functional groups estimated by deconvolution of C 1s high-resolution spectra for Dibond.

Plasma Source	Reference	DCSBD				HDCSBD			
Distance	-	300 μm		450 μm		300 μm		450 μm	
Exposure Time	-	3 s	5 s	3 s	5 s	3 s	5 s	3 s	5 s
Functional Group Conc. [%]									
C=N-C	41	8	9	8	7	6	7	6	11
C – NH ₂	59	86	83	84	85	85	85	84	78
N = O ₂	-	6	8	7	8	8	8	9	11

Table 3.9: Concetration of functional groups estimated by deconvolution of N 1s high-resolution spectra for Dibond.

3.5 Morphological observations of treated polymer substrates

Plasma treatment of polymers can be damaging to the surface of the material, leading to etching and heat-UV degradation. These interactions however should not appear with such a short LTP treatment. Furthermore, the surface roughness could also play a role in increase of peel force noticed at 3.23. We used AFM and SEM to observe the surface of the material and confirm, that the samples were not damaged due to the plasma treatment and that our plasma source is suitable for these treatments. The same distances and exposure times were used as for XPS analysis. Results of the AFM measurement are shown at Table 3.10 and 3.11. Relative standard error of the measurement is in range of 5 to 10 %. In the case of PC, the changes are minimal. The most pronounced change is for treatment with distance of 300 μm and 5s exposure time, where the RMS is 2.5 times higher with value of 1.40. RMS measured on Dibond substrate shows increase in RMS values for a 3 s exposure time. For both measured treatment distances we observe 1.6 times higher results. These changes doesn't correspond with the changes of peel force nor the SFE or WCA measurements above.

Distance	Reference	300 [μm]		450 [μm]	
Exposure Time	-	3 s	5 s	3 s	5 s
RMS	0.57	0.52	1.40	0.45	0.68

Table 3.10: The roughness of PC after HDCSBD plasma treatment.

Distance	Reference	300 [μm]		450 [μm]	
Exposure Time	-	3 s	5 s	3 s	5 s
RMS	24.22	37.49	23.59	37.93	27.26

Table 3.11: The roughness of Pe-Al after HDCSBD plasma treatment.

Morphological changes of PC were further investigated by SEM. Images acquired by this method can be seen in figure 3.25. Dust particles slightly contaminated the surface due to the static charge created by removing the protective tape. Small cracks that can be seen in the images is due to the interaction of high-energy electrons with conductive Au/Pd coating. PC samples that underwent plasma treatment with exposure time 3 and 5 seconds at a distance of 300 μm show signs of roughness changes. These changes are not see-able for distance of 450 μm . It is also noticeable, that at the distance of 300 μm , there are small "swollen" areas which then join into larger ones after 5s. Small visible particles indicates contamination from the treatment in ambient air. As with XPS, the changes are more pronounced for 300 μm . Considering the previous work using oxidizing plasma [1, 60], we considered the changes of the morphology or roughness as insignificant as they have no contribution to the ink adhesion.

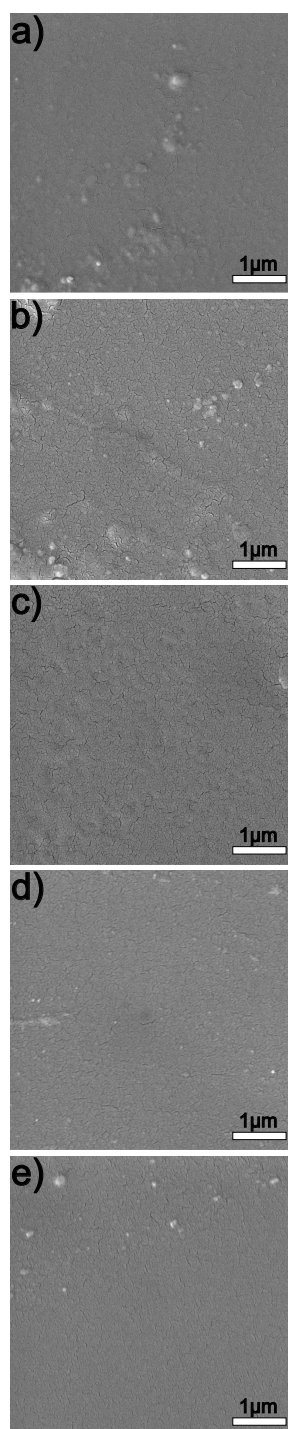


Figure 3.25: SEM images of PC with 50kx magnification; **a)** reference, **b)** 3 s exposure time, distance 300 μm, **c)** 3 s exposure time, distance 450 μm, **d)** 5 s exposure time, distance 300 μm, **e)** 5 s exposure time, distance 450 μm. Scale on images shows 1 μm.

3.6 Cross-Cut test - Ink Adhesion

Samples treated by HDCSBD underwent a Cross-Cut test. To achieve the best result, plasma source had to be implemented into the UV-printing machine. Due to its robust and compact construction, HDCSBD with implemented cooling without the need of oil and vacuum system described in section 1.3 was the appropriate plasma source for the in-line machine. Optimum conditions for testing were set to the exposure times of 1, 3 and 5 seconds at the distance of 300 μm . Figure 3.26 shows the patterns that were printed on polymers. Different colors and templates were used due to the density of pigment. All printed patterns presented proper adhesion. Black and strong red color contain the highest concentration of pigment and according to the printer manufacturer's experience, these colors are challenging when it comes to the adhering to surfaces. Due to these reasons, these colors were main focus of evaluation for the cross-cut test on treated and untreated samples. Cross-cut was done immediately after the UV-digital printing and 24 hours later to observe ink adhesion degradation [61].



Figure 3.26: Photographs of color patterns printed on Dibond after plasma treatment for 1 s and after the crosscut test.

Closer look at the black pattern printed on PC is shown in figure 3.27. In this case, we see the improvement of ink adhesion immediately after 1 s of LTP treatment. The further increase in exposure time leads to visual improvement. These improvements mirror the increase in SFE as the treatment affects the droplets of the ink. The shape and diameter of the droplet can change in time. Detail photographs of samples that were ageing for 24 hours before the cross-cut was done are shown in figure 3.28. It was also established, that roughness changes discussed above have no dominant effect and doesn't affect the UV-ink adhesion. Results showcase a better ink adhesion for samples treated by plasma after and 24 after UV-digital printing.

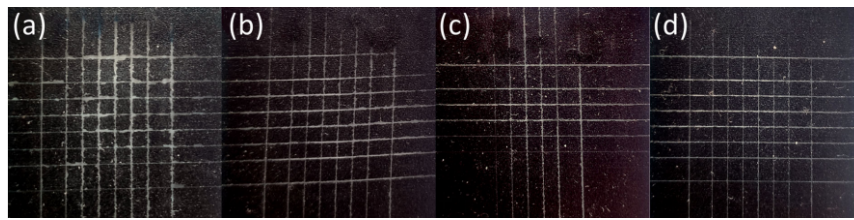


Figure 3.27: Detail photographs of black pattern on PC substrate for (a) reference and immediately after treatment with exposure time of (b) 1 s, (c) 3 s and (d) 5 s. [11]. Photographs have adjusted white color for better contrast.

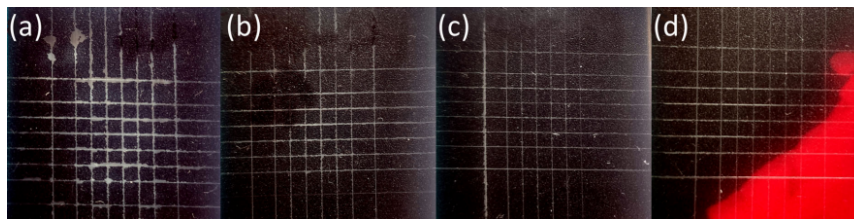


Figure 3.28: Detail photographs of black pattern on PC substrate for (a) reference and 24 hours after treatment with exposure time of (b) 1 s, (c) 3 s and (d) 5 s [11]. Photographs have adjusted white color for better contrast.

Dibond sample proved unique change in contrast after the plasma treatment. A single plate of dibond underwent a partial plasma treatment, treating just the part of the sample for 1 s. This can be observed in Figure 3.29. The wettability of the surface plays role in shape of ink droplets. At beginning of the contact between droplet and substrate, the velocity of the droplet is non-zero. Immediately after the impact, the velocity starts to decrease and reaches zero leading to the final shape of the droplet. The final shape doesn't depend just on the surface properties, but also on the used fluid [61]. Since the Dibond has a metallic conductive layer of aluminium underneath the treated Pe layer. This leads to the creation of VDBD like discharge [3]. Although the treated samples were discharged by conductive rod, there is a chance of small accumulated charge leading to higher speeds of droplets. Photographs using confocal microscope in Figure 3.30 shows, the difference between ink droplets diameter on reference sample and sample treated by HDCSBD for 2 s. Image of ink droplets on surface of treated Dibond shows two layers. One layer are droplets with increased diameter after impact with surface of dibond, that underwent plasma treatment. The diameter greatly increases and the ink fills almost the whole surface. Second layers are droplets, that impacted with already deposited ink. This effect is shown in Figure 3.31 in more detail at white part of the samples that underwent UV-digital printing. This layering is most presumably a reason, why the colors are more saturated after plasma treatment. After conversation with partner from Effetec s.r.o. we came to the conclusion, that saturation is not a problem during the printing since the ink can be premixed, leading to usage of less pigmented ink or less ink in general.

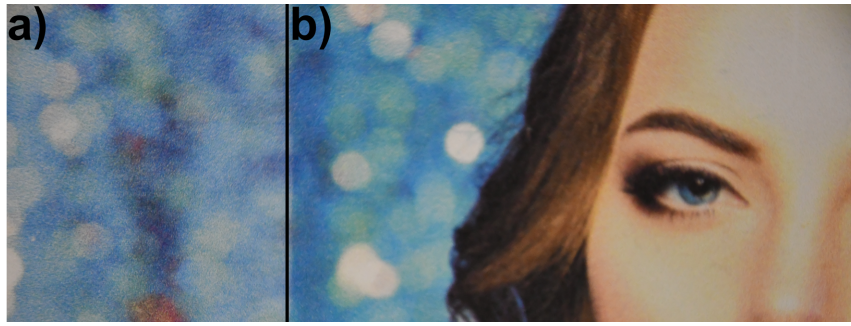


Figure 3.29: Photograph of specific pattern printed on Dibond sample which underwent a partial plasma treatment. **a)** reference, **b)** 1 s plasma treatment. Black line dividing the fragments was added for better orientation.

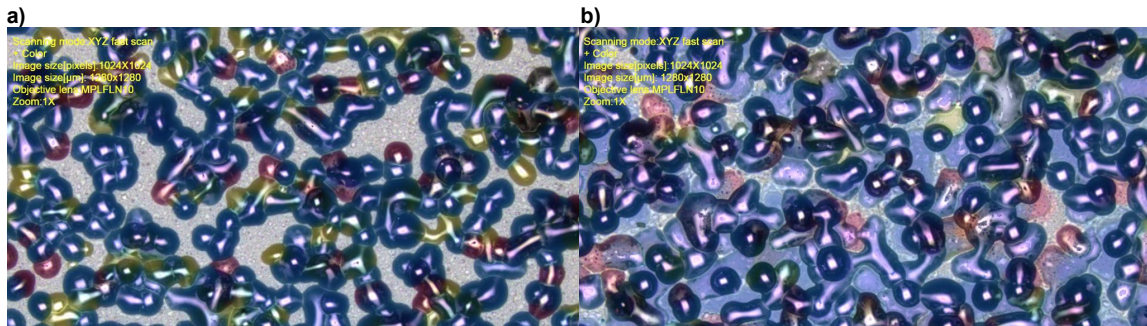


Figure 3.30: Images with 1X magnification made by confocal microscope of ink droplets on Dibond sample: **a)** reference, **b)** 2 s treatment.

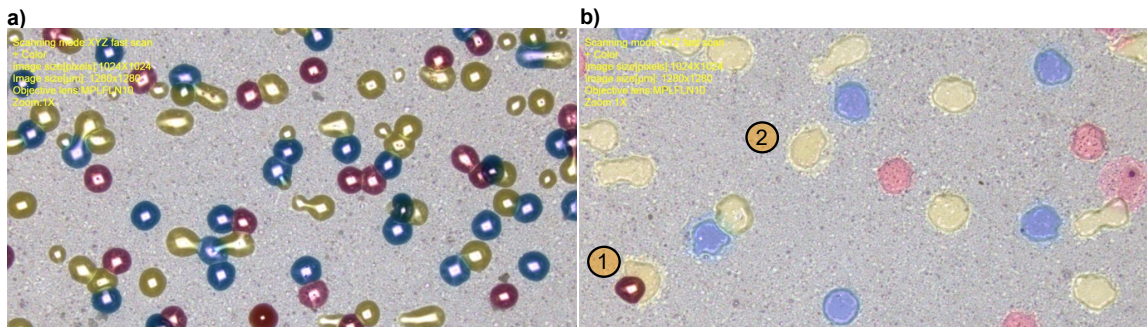


Figure 3.31: Images with 1X magnification made by confocal microscope of ink droplets on Dibond sample for white background: **a)** reference, **b)** 2 s treatment with **1)** impact of droplet on droplet creating second layer and **2)** impact of droplet on surface with wider diameter.

Results of Cross-cut on Dibond samples done immediately after the UV-digital printing can be seen in figure 3.32. Same black pattern was used as in case of PC to showcase the results of LTP treatment. In comparison with PC where the change was slightly less noticeable, the LTP treatment of Dibond had significant impact on ink adhesion. Pattern printed on reference plate of Dibond was completely removed during the cross-cut test. Immediately

after 1 s treatment, we notice great improvement as the ink stays on the sample with a small delamination. These improves after 3 s of plasma treatment and doesn't change with 5 s exposure time. Although we didn't manage to reach a spotless cross-cut, according to the rating shown in Figure 2.10, the scoring went from worst to the best possible. The adhesive properties were preserved even after 24 h after the UV-digital printing, with now slightly better results for longest exposure time of 5 s. Results for cross-cut test after 24 h can be seen in Figure 3.33.

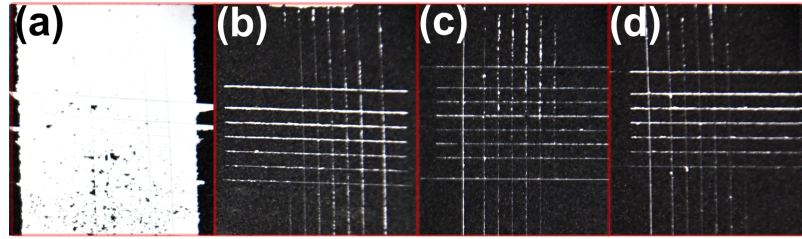


Figure 3.32: Detail photographs of black pattern on Dibond substrate for (a) reference and immediately after treatment with exposure time of (b) 1 s, (c) 3 s and (d) 5 s. Photographs have adjusted white color for better contrast.

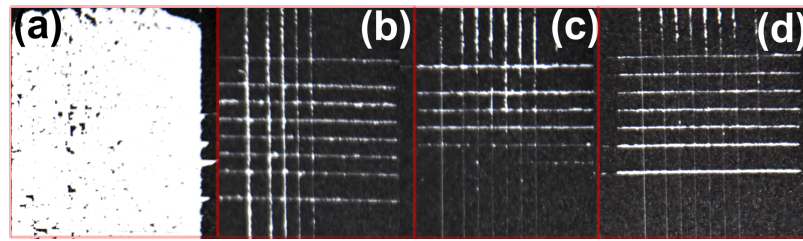


Figure 3.33: Detail photographs of black pattern on PC substrate for (a) reference and 24 hours after treatment with exposure time of (b) 1 s, (c) 3 s and (d) 5 s. Photographs have adjusted white color for better contrast.

Conclusion

The goal of this thesis was to compare properties of standard configuration dielectric coplanar surface barrier discharge (DCSBD) with the special configuration with exchanged cooling system and dielectric barrier for electrodes with technical name half dielectric coplanar surface barrier discharge (HDCSBD). The main focus of this comparison was to prove HDCSBD as a exchangeable and compact unit for DCSBD applications.

We calculated efficiency of power supply for DCSBD commonly used in industrial applications as well as for HDCSBD for the experimental and prototype usage. The efficiency of the power supply for DCSBD is raising between 200 W and 350 W from 81% to 90% with an error of approx. 4%. Power losses are expected and the sudden drop at 400 W shown in Figure 3.3 is due to the maximum coverage of ceramic with micro-discharges, leading to the loss of efficiency. The efficiency of power supply for HDCSBD is in range of 85% to 96% depending on the used voltage. We observe two maximums at 150 W and 250 W seen in Figure 3.8. Furthermore, there is a region with lower efficiency at 175 W to 225 W. Since the measurement is weighted by significant error of used oscilloscope, we cannot prove or disprove that this is a property of the generator. We also measured the dependency of efficiency on temperature of ceramic for HDCSBD in range of 50° to 70° at 225 W and 250 W. According to the results shown in Figure 3.11, the change of temperature is not affecting the efficiency of generator. The power over area for generator powering DCSBD with commonly used power input of 400 W was calculated to approx. 2.08 W/cm², while in case of HDCSBD with power input of 200 W (half of the commonly used DCSBD input power) reached 2.14 W/cm². Furthermore for input power of 250 W (231 W in plasma) that was used for applications in this theses, the power over area is 2.9 W/cm² showing improved power efficiency in HDCSBD configuration. In the future work, the measurement could be improved by widening the range of temperatures and using more stable supply of power or more accurate measurement method, such as repeating measurements with error taken from statistic calculations.

Optical emission spectroscopy (OES) was used to access vibrational and rotational temperature of HDCSBD and DCSBD at its commonly used input power and frequency. For all achieved measurements, we observe no significant changes of vibrational or rotational temperature of molecules in plasma created by HDCSBD. These results are shown in table 3.1 and 3.3 respectfully. In case of DCSBD with an input power of 400 W and frequency of transformer 15 kHz we calculated temperatures:

$$T_v = 2300 \pm 270K \quad T_r = 510 \pm 80K$$

and for 30 kHz [9]:

$$T_v = 2100 \pm 150\text{K} \quad T_r = 540 \pm 80\text{K}$$

Where T_v is vibrational temperature and T_r is rotational temperature. Values of these temperatures for HDCSBD at the half of the DCSBD power input (200W) and approx. 20 kHz transformer,

$$T_v = 2530 \pm 270\text{K} \quad T_r = 550 \pm 50\text{K},$$

are higher especially for vibrational temperature. These differences are minimal and almost within the error in both cases, therefore we don't expect any significant impact of these changes. We also measured T_v and T_r for HDCSBD for two power inputs of 225 W and 250 W in dependence on the temperature of ceramic in range of 50° to 70° C. The results are shown in table 3.4 and 3.2. The measurements of vibrational temperature are affected by a large statistical error, therefore we cannot confirm or deny any dependence on the changing parameters. These analysis confirmed, that plasma created by HDCSBD is similar to the plasma created by DCSBD and therefore suitable as an exchangeable unit. For future tests, the homogeneity of the plasma created by HDCSBD could be observed to prove the efficiency and temperatures at different places of the discharge zone.

Second goal was to introduce both plasma sources for low-temperature plasma (LTP) treatment of polymers, namely polycarbonate (PC) and Polyethylene aluminium (Pe-Al, industrial name Dibond) commonly used in UV-digital printing applications. Distance range of 225-450 µm was chosen to fit in-line industrial printing scale. LTP treatment with chosen exposure time (1-5 s) proved to enhance the surface properties for all process variables. The samples wettability and SFE didn't drop to the reference value even after 72 hours, showing just small hydrophobic recovery. Dibond shows different trend in dependence on plasma source showing higher values of SFE for longer treatment times by HDCSBD. These changes are minimal. Measurements of the peel force also shows improvement for all the treated samples and while aging affect after 24 h is significant, the values never reached back to the reference point.

PC x-ray photoelectron spectroscopy (XPS) shown increase of oxygen-containing polar groups onto the surface, which is indicated by the increase of SFE polar component. No significant increase in dispersive component was observed. Due to the implementation of oxygen and plasma's decontaminating properties, we observe increase of O/C ratio for all the treated PC samples and implementation of oxygen led to creation of C=O group and increase in O-C=O groups.

In case of the Dibond, XPS shows high implementation of O and N after the treatment. The plasma treatment of polyethylene on the surface of the sample led to creation of oxygen polar groups, that lead to increase of polar component. Implementation of O and the cleaning process almost doubled the O/C ratio of all treated samples. Noticeable implementation is for O-C=O group. Nitrogen implementation in such a concentration led to increase of C-NH₂ and creation of N=O₂ group. In deconvolution of C 1s peak, there is a noticeable increase of C=O/C=N peak.

Atomic force microscopy (AFM) was used to observe roughness changes on both treated samples. Although there are noticeable changes depending on the treatment time, especially of Dibond, we consider these changes for minimal and they should have no significant

effect on ink adhesion. Scanning electron microscopy (SEM) was used to visualize a surface of PC after being treated by HDCSBD. Images show to no significant damage of the sample. Photos of ink droplets were taken by confocal microscope for samples of Dibond due to the significant saturation of colors printed on treated materials. From the confocal images, it is noticeable, that the ink droplets form two layers, one with wide diameter of the droplet due to the interaction with treated sample and the second one with smaller, reference like diameter due to the interaction with the first layer of droplets. This behaviour is not unwanted, as the ink can be premixed by manufacturer and prepared upfront.

Crosscut test widely used in industry was used for final tests of the samples. For this purpose, we determined HDCSBD as the only suitable source for in-line printing process due to its compact form and the distance of 300 μm was chosen as optimal for this process. Even after 1 s treatment we observed substantial increase of ink adhesion. This can be most observed at the samples of Dibond, where crosscut test on reference sample leads to complete detachment of black color while after 1 s the color holds almost intact. This adhesive property slightly increases with exposure time up to 5 s. All the samples also shown no degradation of the improved adhesion even after the 24 h after the printing process.

One of the goals of this thesis was to compare HDCSBD with industrially used DCSBD and prove the usability of HDCSBD. Measurements of electrical properties of both plasma unit shown similarity of used power supplies and the power per area comparison shows HDCSBD more efficient. The vibrational and rotational temperature calculations shows small deviations with no significant proving the similarity of the plasma units. Furthermore, application of DCSBD and HDCSBD on surface of polymers PC and Dibond shown very similar result where in both cases LTP treatment led to improvement of the materials surface properties. The HDCSBD shown its advantage in compactness to be implemented into the UV-digital printing unit. As of these reason, HDCSBD was considered to have similar properties as DCSBD and can be used for the same applications.

A subset of results of this thesis was published in impacted journal. The measurement also led to the invention of legally protected and certified technology Czech utility model "A device for plasma modification of large-area planar substrate before UV-digital printing" (no. 35867, PUV2022-39679) and certified technology "Technology for ink adhesion improvement of large-area printing on glass and polymer substrates by atmospheric pressure plasma activation" available at <https://www.isvavai.cz/riv>.

Bibliography

- [1] Jakub Kellar, Masoud Shekargoftar, Richard Krumpolec, and Tomáš Homola. Activation of polycarbonate (pc) surfaces by atmospheric pressure plasma in ambient air. *Polymer Testing*, 67:428–434, 2018.
- [2] Petra Šrámková, Zlata Kellar Tučková, Michal Fleischer, Jakub Kellar, and Dušan Kováčik. Changes in surface characteristics of bopp foil after treatment by ambient air plasma generated by coplanar and volume dielectric barrier discharge. *Polymers*, 13(23), 2021.
- [3] Vlasta Štěpánová, Petra Šrámková, Slavomír Sihelník, Miroslav Zemánek, Jana Jurmanová, Monika Stupavská, and Dušan Kováčik. Adhesion improvement on the inner side of lldpe/pa tubular film exposed to dcsbd roll-to-roll plasma system from the outer side of the film. *Department of Physical Electronics, CEPLANT, Faculty of Science, Masaryk University, Brno, Czech Republic*, 2022.
- [4] Michal Fleischer. Úprava osiva pomocí plazmatu [online], 2020 [cit. 2024-05-01]. SUPERVISOR : Pavel Slavíček.
- [5] Vlasta Štěpánová, Pavel Slavíček, Monika Stupavská, Jana Jurmanová, and Mirko Černák. Surface chemical changes of atmospheric pressure plasma treated rabbit fibres important for felting process. *Applied Surface Science*, 355(November):1037–1043, 2015.
- [6] R. Talviste, O. Galmiz, M. Stupavská, Z. Tučková, K. Kaarna, and D. Kováčik. Effect of dcsbd plasma treatment on surface properties of thermally modified wood. *Surfaces and Interfaces*, 16:8–14, 2019.
- [7] T. Sandanuwan, N. Hendeniya, D. Attygalle, D. A. S. Amarasinghe, S. C. Weragoda, and A. M. P. B. Samarasekara. Atmospheric cold plasma to improve printability of polyethylene terephthalate. In *Proceedings of the 2021 Moratuwa Engineering Research Conference (MERCon)*, pages 654–658, Moratuwa, Sri Lanka, July 27–29 2021.
- [8] D. Pawlak and P. Boruszewski. Digital printing in wood industry. *Ann. Warsaw Univ. Life Sci. For. Wood Technol.*, 109:109–115, 2020.
- [9] Jakub Kellar. Měření parametrů koplanárního bariérového výboje [online]. Diplomová práce, Masarykova univerzita, Přírodovědecká fakulta, Brno, 2015 [cit. 2024-04-23]. SUPERVISOR : Pavel Slavíček.

- [10] Z. Navratil, D. Trunec, R. Smid, and L. Lazar. A software for optical emission spectroscopy - problem formulation and application to plasma diagnostics. *Czechoslovak Journal of Physics*, 56:B944, 2006.
- [11] Michal Fleischer, Zlata Kelar Tučková, Oleksandr Galmiz, Eva Bařková, Tomáš Plšek, Tatiana Kolářová, Dušan Kováčik, and Jakub Kelar. Plasma treatment of large-area polymer substrates for the enhanced adhesion of uv-digital printing. *Nanomaterials*, 14(5), 2024.
- [12] J. A. Bittencourt. *Fundamentals of Plasma Physics*. Fundamentals of Plasma Physics, Third Edition by J.A. Bittencourt. Published by Springer-Verlag, New York, Inc.; 2004. ISBN 0-387-20975-1., third edition, 2004.
- [13] Michael A. Lieberman and Allan J. Lichtenberg. *Principles of Plasma Discharges and Materials Processing*. John Wiley & Sons, Inc., January 2005.
- [14] Francis F. Chen. *Introduction to Plasma Physics and Controlled Fusion*. Springer Cham, 3 edition, December 2016.
- [15] A. Griffin, D. W. Snoke, and S. Stringari. *Bose-Einstein Condensate*. Cambridge University Press, 1996.
- [16] Reece J. Roth. *Industrial Plasma Engineering*. CRC Press, Bristol, UK, 1995.
- [17] Rosalba Gaudiuso. Chapter 7 - laser-induced breakdown spectroscopy in cultural heritage science. In Mieke Adriaens and Mark Dowsett, editors, *Spectroscopy, Diffraction and Tomography in Art and Heritage Science*, pages 209–251. Elsevier, 2021.
- [18] J. M. Anzano, I. B. Gornushkin, B. W. Smith, and J. D. Winefordner. Laser-induced plasma spectroscopy for plastic identification. *Polymer Engineering & Science*, 40(11):2423–2429, 2000.
- [19] L. St-Onge, M. Sabsabi, and P. Cielo. Analysis of solids using laser-induced plasma spectroscopy in double-pulse mode. *Spectrochimica Acta Part B: Atomic Spectroscopy*, 53(3):407–415, 1998.
- [20] Maria Markiewicz-Keszycka, Xavier Cama-Moncunill, Maria P. Casado-Gavaldà, Yash Dixit, Raquel Cama-Moncunill, Patrick J. Cullen, and Carl Sullivan. Laser-induced breakdown spectroscopy (libs) for food analysis: A review. *Trends in Food Science & Technology*, 65:80–93, 2017.
- [21] R. J. Bickerton. Introduction to high temperature plasma physics. *Philosophical Transactions of the Royal Society of London. Series A, Mathematical and Physical Sciences*, 300(1456):475–488, 1981.
- [22] Viktor Martišovits. *Základy Fyziky Plazmy*. UNIVERZITA KOMENSKÉHO, Bratislava, 2004.
- [23] J. H. Malmberg and J. S. deGrassie. Properties of nonneutral plasma. *Physical Review Letters*, 35(9):577–580, 09 1975.

- [24] J. J. Bollinger and D. J. Wineland. Strongly coupled nonneutral ion plasma. *Physical Review Letters*, 53(4):348–351, 07 1984.
- [25] W Siemens. Ueber die elektrostatische induction und die varzoegerung des stroms in flaschendraehten. *Poggendorfs Annalen der Physik und Chemie*, 178(9):66–122, 1857.
- [26] On radiant matter: a lecture delivered to the british association for the advancement of science, at sheffield, friday, august 22, 1879, 1879. Archived from the original on 9 July 2006. Retrieved 24 May 2006.
- [27] S. Debnárová, L. Zábranský, P. Souček, V. Buršíková, and P. Vašina. Study of w-b-c thin films prepared by magnetron sputtering using a combinatorial approach. *International Journal of Refractory Metals and Hard Materials*, 85:105066, 2019.
- [28] E. J. Szili, S. Kumar, M. DeNichilod, R. St.C. Smart, et al. Development of surface modification techniques for the covalent attachment of insulin-like growth factor-1 (igf-1) on pecvd silica-coated titanium. *Surface and Coatings Technology*, 205(5):1630–1635, 2010.
- [29] Tetsuji Shimizu, Yukinori Sakiyama, David B Graves, Julia L Zimmermann, and Gregor E Morfill. The dynamics of ozone generation and mode transition in air surface micro-discharge plasma at atmospheric pressure. *New Journal of Physics*, 14(10):103028, 2012.
- [30] TG Klämpfl, G Isbary, T Shimizu, YF Li, JL Zimmermann, W Stolz, J Schlegel, GE Morfill, and HU Schmidt. Cold atmospheric air plasma sterilization against spores and other microorganisms of clinical interest. *Applied and environmental microbiology*, 78(15):5077–5082, 2012.
- [31] C. Campagne F. Leroux, A. Perwuelz and N. Behary. Atmospheric air-plasma treatments of polyester textile structures. *Journal of Adhesion Science and Technology*, 20(9):939–957, 2006.
- [32] K. Salonitis and S. Vatousianos. Experimental investigation of the plasma arc cutting process. *Procedia CIRP*, 3:287–292, 2012. 45th CIRP Conference on Manufacturing Systems 2012.
- [33] C. Berger, M. Dumoux, T. Glen, et al. Plasma fib milling for the determination of structures in situ. *Nature Communications*, 14:629, 2023.
- [34] GJ Pietsch. Properties of dielectric barrier discharges in different arrangements. *Gasentladungstechnik*, 33(1), 2001.
- [35] R Reuter, N Gherardi, and J Benedikt. Effect of n2 dielectric barrier discharge treatment on the composition of very thin sio2-like films deposited from hexamethyl-disiloxane at atmospheric pressure. *Applied Physics Letters*, 101(19), 2012.

- [36] J. P. Boeuf, B. Bernecker, Th. Callegari, and S. Blanco. Generation, annihilation, dynamics and self-organized patterns of filaments in dielectric barrier discharge plasmas. *Applied Physics Letters*, 100(24), 2012.
- [37] C Heuser and G Pietsch. Prebreakdown phenomena between glass–glass and glass–metal electrodes. In *6th International Conference on Gas Discharges and their Applications*, volume 189, pages 98–101, Edinburgh, UK, 1980. IEE Conference Publications.
- [38] Mirko Černák, Jozef Ráheľ, Dusan Kovacik, M. Šimor, A. Brablec, and Pavel Slavicek. Generation of thin surface plasma layers for atmospheric-pressure surface treatments. *Contributions to Plasma Physics*, 44:492 – 495, 09 2004.
- [39] Pavel SLAVÍČEK and Vlasta ŠTĚPÁNOVÁ. Diagnostics of dc-sbd discharge for industrial applications. In *New Trends in Physics - NTF 2012*, pages 135–138, 2012.
- [40] Y. Tang, P. Zhang, M. Zhu, J. Li, Y. Li, Z. Wang, and L. Huang. Temperature effects on the dielectric properties and breakdown performance of h-bn/epoxy composites. *Materials (Basel)*, 12(24):4112, December 2019.
- [41] MA Song, YW Lee, and TH Chung. Characterization of an inductively coupled nitrogen-argon plasma by langmuir probe combined with optical emission spectroscopy. *Physics of Plasmas*, 18(2), 2011.
- [42] Irving P. Herman. Chapter 6 - optical emission spectroscopy. In Irving P. Herman, editor, *Optical Diagnostics for Thin Film Processing*, pages 157–213. Academic Press, San Diego, 1996.
- [43] Andor Technology, Belfast, UK. *Andor Catalog, Digital Camera*, 2006.
- [44] Geoffrey V. Marr. *Plasma Spectroscopy*. Elsevier Scientific Publishing Company, Amsterdam, 1968.
- [45] D. K. Owens and R. C. Wendt. Estimation of the surface free energy of polymers. *Journal of Applied Polymer Science*, 13(8):1741–1747, 1969.
- [46] H. Nakane, M. Kumai, M. Hagi, and K. Nagai. Advanced led uv inks for industrial applications. In *Proceedings of the NIP and Digital Fabrication Conference*, volume 2015, pages 448–451, Portland, OR, USA, 27 September–1 October 2015.
- [47] Sudaxshina Murdan, Laxmi Kerai, and Basma Hossin. To what extent do in vitro tests correctly predict the in vivo residence of nail lacquers on the nail plate? *Journal of Drug Delivery Science and Technology*, 25:23–28, 02 2015.
- [48] CEITEC. X-ray photoelectron spectroscopy (xps) - axis supra. <https://www.ceitec.eu/x-ray-photoelectron-spectroscopy-axis-supra/e1554>, Accessed: 2024-04-24.
- [49] NanoAndMore USA. What is atomic force microscopy (afm). 23.4.2024.

- [50] CEPLANT. Surface analytics. <https://ceplant.cz/equipment-and-services/surface-analytics>. Accessed: April 26, 2024.
- [51] T. Yuji, Y. Suzuki, T. Yamawaki, H. S. Akaue, and H. A. Katsuka. The role of vibrational temperature variations in a pulsed dielectric barrier discharge plasma device. *Jpn. J. Appl. Phys.*, 46:795, 2007.
- [52] F. Nascimento, M. Machida, K. Kostov, et al. Enhanced energy transfer efficiency in a four-electrodes configuration dbd plasma jet. *Eur. Phys. J. D*, 71:274, 2017.
- [53] Rajesh Sharma, Edward Holcomb, Steve Trigwell, and M.K. Mazumder. Stability of atmospheric-pressure plasma induced changes on polycarbonate surfaces. *Journal of Electrostatics*, 65:269–273, 04 2007.
- [54] K.G. Kostov, Y Hamia, Rogério Mota, A. dos Santos, and Pedro Nascente. Treatment of polycarbonate by dielectric barrier discharge (dbd) at atmospheric pressure. *Journal of Physics: Conference Series*, 511:012075, 05 2014.
- [55] Vlasta Štěpánová, Petra Šrámková, Slavomír Sihelník, Monika Stupavská, Jana Jurmanová, and Dušan Kováčik. The effect of ambient air plasma generated by coplanar and volume dielectric barrier discharge on the surface characteristics of polyamide foils. *Vacuum*, 183:109887, 2021.
- [56] F. Awaja, M. Gilbert, G. Kelly, B. Fox, and P.J. Pigram. Adhesion of polymers. *Prog. Polym. Sci.*, 34:948–968, 2009.
- [57] S. Mähl, J. Lachnitt, R. Niemann, M. Neumann, A. Baalmann, A. Kruse, and V. Schlett. Innovative methods for a deconvolution of xps spectra from plasma-oxidized polyethylene. *Surface and Interface Analysis*, 24(6):405–410, 1996.
- [58] Parinaz Saadat Esbah Tabaei, Rouba Ghobeira, Pieter Cools, Fatemeh Rezaei, Anton Nikiforov, Rino Morent, and Nathalie De Geyter. Comparative study between in-plasma and post-plasma chemical processes occurring at the surface of uhmwpe subjected to medium pressure ar and n2 plasma activation. *Polymer*, 193:122383, 2020.
- [59] Changhong Chen, Yiwei Guo, Li Long, Keyan Chen, Xiaolan Hu, and Yingwen Xue. Biodegradable chitosan-ethylene glycol hydrogel effectively adsorbs nitrate in water. *Environmental Science and Pollution Research*, 27, 09 2020.
- [60] A. Vesel and M. Mozetic. New developments in surface functionalization of polymers using controlled plasma treatments. *J. Phys. D Appl. Phys.*, 50:293001, 2017.
- [61] Tim Tofan and Raimondas Jasevičius. Modelling of the motion and interaction of a droplet of an inkjet printing process with physically treated polymers substrates. *Applied Sciences*, 11(23), 2021.

Publication activity

Article in a impacted journal

- “Plasma Treatment of Large-Area Polymer Substrates for the Enhanced Adhesion of UV–Digital Printing”, FLEISCHER, Michal, et al. *Nanomaterials*. MDPI, 2024, roč. 14, č. 5, s. 1-14. ISSN 2079-4991. Dostupné z: <https://dx.doi.org/10.3390/nano14050426>.
- “The Multi-Hollow Surface Dielectric Barrier Discharge Usage for the Seeds’ Treatment Aimed to the Dustiness Decrease of Free-Floating Particles from Agrochemicals”, SLAVÍČEK, Pavel, et al. *Plasma Chemistry and Plasma Processing*. Springer, 2023, roč. 43, č. 6, s. 1887-1906. ISSN 0272-4324. Dostupné z: <https://dx.doi.org/10.1007/s11090-023-10396-x>.
- “Changes in Surface Characteristics of BOPP Foil after Treatment by Ambient Air Plasma Generated by Coplanar and Volume Dielectric Barrier Discharge”, ŠRÁMKOVÁ, Petra, et al. *Polymers*. MDPI, 2021, roč. 13, č. 23, s. 4173-4184. ISSN 2073-4360. Dostupné z: <https://dx.doi.org/10.3390/polym13234173>.

Conference abstract

- “SURFACE TREATMENT OF GLASS AND ITS INFLUENCE ON THE RELIABILITY OF ADHESIVE BONDING”, KELAR, Jakub, et al. In *The 3rd Plasma Nanotechnologies and Bioapplications Workshop*. 2023. ISBN 978-80-280-0387-6.
- “High quality UV digital printing on various materials with plasma enhanced surface”, KELAR, Jakub, et al. In *17th High Pressure Low Temperature Plasma Chemistry Symposium*. 2022.
- “In-line plasma pre- and post-treatment as parts of technology for manufacturing of nanofiber-based filters with the improved performance properties”, KOVÁČIK, Dušan, et al. In *9th Central European Symposium on Plasma Chemistry (CESPC-9) joint with COST Action CA19110 Plasma Applications for Smart and Sustainable Agriculture (PIAgri)*. 2022. ISBN 978-80-8147-115-5.
- “BOPP foil surface treatment by ambient air volume and coplanar dielectric barrier discharge in roll-to-roll configuration”, KELAR TUČEKOVÁ, Zlata, et al. In *2nd Plasma Nanotechnologies and Bioapplications Workshop*. 2021. ISBN 978-80-210-9946-3.

- “Measurements of the nanofibers adhesion to the carrier substrates”, GALMIZ, Oleksandr, et al. In 2nd Plasma Nanotechnologies and Bioapplications Workshop. 2021. ISBN 978-80-210-9946-3.
- “Plasma activation of various industrially used materials for UV-digital printing applications”, KELAR, Jakub, et al. 2021. ISBN 978-80-210-9946-3.
- “Study of the effect of plasma on the efficiency of nanofiber filters”, PAVLIŇÁK, David, et al. In 13th International Conference on Nanomaterials - Research & Application, 2021. 2021. ISBN 978-80-88365-00-6.
- “The effect of plasma on the efficiency of nanofiber filters”, PAVLIŇÁK, David, et al. In 2nd Plasma Nanotechnologies and Bioapplications Workshop. 2021. ISBN 978-80-210-9946-3.
- “Effect of plasma treatment on seeds before coating with agrochemicals and its influence on seeds dustiness”, ŠTĚPÁNOVÁ, Vlasta, et al. In 1st Plasma for Nanotechnology and Bioapplications Workshop, Scientific Program & Book of Abstracts. 2019. ISBN 978-80-210-9487-1.
- “Effect of various types of surface dielectric barrier discharge on seeds of maize and pea”, KELAR TUČEKOVÁ, Zlata, et al. In The Eight Central European Symposium on Plasma Chemistry - CESPC-8 Proceedings. 2019. ISBN 978-961-94716-0-9.
- “Flexible Ceramic Substrates for Use as Dielectric Barrier Layer”, KELAR, Jakub, et al. In 1st Plasma for Nanotechnology and Bioapplications Workshop. 2019. ISBN 978-80-210-9487-1.
- “HV Generators for DCSBD Discharges and Their Properties” ZEMÁNEK, Miroslav, et al. In 1st Plasma for Nanotechnology and Bioapplications Workshop. 2019. ISBN 978-80-210-9487-1.

Research Reports

- “Souhrnná zpráva - Zvýšení kvality velkoplošného UV digitálního tisku atmosférickým plazmatem (FV40114)”, KELAR, Jakub, et al. Brno: Neuveden, 2022, 34 s. Souhrnná zpráva k ukončení projektu FV40114.
- “Výzkumná zpráva z třetí etapy řešení projektu FV40114 - Zvýšení kvality velkoplošného UV digitálního tisku atmosférickým plazmatem (PE-Al)”, KELAR, Jakub, et al. Brno: Neuveden, 2021, 22 s. Souhrnná výzkumná zpráva 2 z projektu FV40114.
- “Výzkumná zpráva z první etapy řešení projektu FV40114 - Zlepšení adheze UV digitálního tisku na povrchu velkoplošného skla s využitím atmosférického plazmatu”, KELAR, Jakub, et al. Brno: Neuveden, 2020, 16 s. Souhrnná výzkumná zpráva 1 z projektu FV40114.
- “Souhrnná výzkumná zpráva zabývající se použitím plazmového zdroje na předúpravu osiva”, ŠTĚPÁNOVÁ, Vlasta, et al. Brno: MU, 2019, 14 s.

Legally Protected Results

- “Zařízení pro plazmovou modifikaci velkoplošného rovinného substrátu před potiskem”, KELAR TUČEKOVÁ, Zlata, et al. 2022.

Conference Presentations

- “Diffuse coplanar surface barrier discharge (DCSBD) plasma treatment as a part of technology for manufacturing of nanofiber-based filters”, GALMIZ, Oleksandr, et al. In 13th International Conference on Nanomaterials - Research & Application. 2021. ISBN 978-80-88365-00-6.
- “TECHNOLOGY FOR NANOFIBER’S SUBSTRATES ATMOSPHERIC PRESSURE PLASMA TREATMENT”, GALMIZ, Oleksandr, et al. In 8th Plasma Science & Entrepreneurship Workshop. 2021.

Contributions in Proceedings

- “DIFFUSE COPLANAR SURFACE BARRIER DISCHARGE PLASMA TREATMENT AS A PART OF TECHNOLOGY FOR MANUFACTURING OF NANOFIBER-BASED FILTERS”, GALMIZ, Oleksandr, et al. In Proceedings 13th International Conference on Nanomaterials - Research & Application. Ostrava: TANGER Ltd., 2021, s. 92 - 97. ISBN 978-80-88365-00-6. Dostupné z: <https://dx.doi.org/10.37904/nanocon.2021.4311>.
- “Atmospheric pressure plasma treatment of wheat seeds in ambient air” ŠTĚPÁNOVÁ, Vlasta, et al. In XXXIV ICPIG & ICRP-10. Sapporo: Neuveden, 2019, s. 1-2. ISBN 978-4-900986-19-0.

Technically Implemented Results (Prototype, Functional Sample)

- “Nanofibers layer deposited on the hydrophobic fiberglass mesh and polypropylene non-woven textile for air filters production with the enhanced properties due to potential implementation of plasma technology to the manufacturing process”, GALMIZ, Oleksandr, et al. 2021.
- “Nanofibers layer deposited on the polypropylene non-woven textile for water filters production with the enhanced properties due to potential implementation of plasma technology to the manufacturing process”, GALMIZ, Oleksandr, et al. 2021.
- “Plazmový zdroj pro předúpravu osiva před mořením”, SLAVÍČEK, Pavel, et al. 2019.

Pilot Operation, Verified Technology, Variety, Breed

- “Technologie zvýšení adheze barev velkoplošného UV digitálního tisku ke kovovým substrátům s polymerní vrstvou aktivací atmosférickým plazmatem”, KOVÁČIK, Dušan, et al. 2021.

- “Verified technology for the optimized plasma treatment of fiberglass and polyester meshes to enhance the adhesion of electrospun nanofibers”, GALMIZ, Oleksandr, et al. 2021.
- “Verified technology for the optimized plasma treatment of non-woven substrate to enhance the adhesion of electrospun nanofibers”, GALMIZ, Oleksandr, et al. 2021.

