

CHARACTERISTICS OF GASEOUS PLASMA IN A LARGE LOW-PRESSURE REACTOR

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Doctoral Dissertation
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ZNAČILNOSTI PLINSKE PLAZME V VELIKEM NIZKOTLAČNEM REAKTORJU

Doktorska disertacija

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Ljubljana, Slovenia, August 2021

Acknowledgments

Žiga Gosar, the author of this thesis, gratefully acknowledges the support provided by colleagues at Elvez company, Department of Surface Engineering at Institute “Jožef Stefan”, University of Maribor and Jožef Stefan International Postgraduate School. In particular, I acknowledge the support provided by the supervisor, prof. Dr. Miran Mozetič, and co-supervisor, doc. Dr. Rok Zaplotnik. The supervisors introduced me to the scientific niche of plasma science and technology and gave me useful hints for my work. They encouraged me to perform systematic experiments that led to numerous scientific results as well as practical applications. The project team working with me in this scientific field helped me understand different aspects of plasma technologies and surface science. I also express sincere gratitude to other members of the Department of Surface Engineering (Department F4), particularly to prof. Janez Kovač, prof. Alenka Vesel, doc. Gregor Primc, Janez Trtnik and Tatjana Filipič. Many thanks to the Laboratory for Electro-optical and Sensor Systems staff at Faculty of Electrotechnique, Computer Sciences, and Informatics, particularly to the head of the lab, prof. ddr. Denis Donlagić. Support from the owner and general manager of Elvez company, Ms. Simona Petrič, and her staff is gratefully acknowledged. A part of this research was funded by Slovenian Research Agency, grant L2-8179: “Evaluation of the range of plasma parameters suitable for nanostructuring of polymers on an industrial scale” (2017 – 2020).

Abstract

The scientific backgrounds of technologies involved in the production of headlamps for the automotive industry are elaborated in this thesis. The experimental work was performed using an industrial plasma reactor with a volume of approximately 5 m³. The reactor enables three different operations, i.e., plasma pretreatment of workpieces made from polymers, deposition of a thin metal film by evaporation, and deposition of a protective coating resembling poly(dimethylsiloxane) by plasma polymerization. The pretreatment removes any surface impurities and functionalises the polymer surfaces with polar functional groups. The surface finish is a result of the interaction of radicals with organic material, in particular, OH and O. Pretreatment enables the good adhesion of metal film on the polymer substrate due to the interface between the layers. The properties of the interface were determined by XPS and SIMS depth profiling. The metallisation is performed in ultrahigh vacuum conditions by evaporation of liquid metal. An appropriate range of parameters enables the deposition of aluminum films with a thickness of approximately 100 nm that are almost completely free from impurities as revealed by depth profiles. The aluminum film is then coated with a protective layer. Plasma polymerisation was used as the deposition technique using hexamethyl disiloxane (HMDSO) as the precursor at a pressure of several Pa, the residual atmosphere was composed predominantly of water vapor. Both XPS and SIMS depth profiling showed an appropriate interface between the metal film and protective coating as well as the composition and structure of the coating. The plasma parameters during deposition of the protective coating were measured systematically at various processing parameters by residual gas analysis (RGA) and optical emission spectroscopy (OES). The results of these complementary techniques enabled the determination of key reactions leading to the formation of coatings with the desired properties. Fragmentation of the precursor in plasma conditions was found rather insufficient as explained by an extremely low plasma density, in the order of 10¹⁴ m⁻³, which was elaborated from measured discharge parameters. A predominant reaction in plasma conditions was the subtraction of H atoms from the HMDSO and partial association of these atoms to hydrogen molecules by heterogeneous surface recombination. Fragmentation also caused the formation of CH radicals as determined by OES. The radicals recombined into stable molecules either in the plasma reactor or on the walls between the reactor and differentially pumped RGA. The major products of the CH association were light hydrocarbons as determined by RGA. The association was explained by surface reactions between adsorbed CH radicals and hydrogen atoms rather than by gas-phase reactions. The collision frequency in the range of investigated pressures was found to be too low to enable significant association in the gas phase. The association was probability rather large since neither XPS nor SIMS showed a measurable amount of pure hydrocarbons or hydrogenated carbon in the deposited films. The results of experimental work enabled faster deposition without reducing the performance of the protective coatings.

Povzetek

V doktorski nalogi sem obravnaval znanstvena ozadja tehnologij, ki se uporabljajo pri proizvodnji žarometov za avtomobilsko industrijo. Eksperimente sem opravljal v industrijskem plazemskem reaktorju s prostornino približno 5 m³. Reaktor omogoča tri različne operacije: predhodno plazemsko obdelavo obdelovancev iz polimerov za aktivacijo površin, nanašanje tankega kovinskega filma z naparevanjem in nanašanje zaščitne prevleke (polidimetilsiloksan) s plazemsko polimerizacijo. Predhodna obdelava odstrani vse površinske nečistoče in funkcionalizira polimerne površine s polarnimi funkcionalnimi skupinami. Površinska obdelava je posledica interakcije radikalov z organskimi snovmi, zlasti radikalov OH in O. Predhodna obdelava aktivira vmesno plast med polimerno podlago in kovinskim nanosom ter s tem omogoča dober oprijem kovinskega filma. Lastnosti vmesne plasti smo določili z merjenjem globinskega profila z uporabo tehnik XPS in SIMS. Metalizacijo smo izvedli v pogojih ultravisokega vakuumu z naparevanjem kovinskih atomov iz tekoče kovine. Ustrezen obseg parametrov omogoča nanos aluminijevih filmov debeline približno 100 nm, skoraj brez nečistoč, kar je razvidno iz globinskih profilov. Tanko plast aluminija nato prevlečemo z zaščitno plastjo. Za tehniko nanašanja zaščitne plasti smo uporabili plazemsko polimerizacijo z uporabo heksametil disiloksana (HMDSO) kot monomera pri tlačnem območju nekaj Pa, residualna atmosfera pa je bila pretežno vodna para. Globinsko profiliranje z metodama XPS in SIMS je pokazalo nastanek primerne vmesne plasti med kovinskim nanosom in zaščitno prevleko, obenem pa tudi ustrezno sestavo in strukturo zaščitne plasti. Parametre plazme med nanašanjem zaščitnega premaza smo sistematično merili z analizo residualne atmosfere (RGA) in optično emisijsko spektroskopijo (OES) pri različnih razelektritvenih parametrih. Rezultati teh komplementarnih tehnik so omogočili določitev ključnih reakcij, ki vodijo do nastanka tankih plasti zelenih lastnosti. Fragmentacija prekursorja pri različnih plazemskih razmerah je bila razmeroma majhna, kar smo razložili z izredno nizko gostoto plazme reda 10¹⁴ m⁻³. Gostoto nabitih delcev smo ocenili iz rezultatov meritev razelektritvenih parametrov. Prevladujoča reakcija v plinski fazi je bila disociacija, ki je vodila k nastanku atomov vodika. Atomarni vodik se je na površinah združil v molekularnega preko heterogene površinske rekombinacije. Disociativni trki elektronov s prekursorjem so povzročili tudi nastanek CH radikalov, kar je bilo razvidno iz optičnih spektrov. Radikali so se rekombinirali v stabilne molekule bodisi v plinski fazi v plazemskem reaktorju bodisi na stenah med reaktorjem in diferencialno črpanim RGA-jem. Glavni produkti združenja CH radikalov so lahki ogljikovodiki, ki smo jih določili z RGA-jem. Njihov nastanek smo razložili s površinskimi reakcijami med adsorbiranimi CH radikali in vodikovimi atomi. Ugotovili smo tudi, da je pogostost trkov v območju raziskanih tlakov prenizka, da bi omogočila pomembno sintezo ogljikovodikov v plinski fazi. Veliko koncentracijo ogljikovodikov smo potrdili tudi iz analiz nanosenih filmov. Rezultati znanstvenega dela so solidna osnova za razvoj postopka za hitrejše nanašanje zaščitnih prevlek ne da bi bistveno spremenili lastnosti zaščitnih plasti plazemsko nanesenega polimera.

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Abbreviations

AFM	... Atomic force microscope
CCP	... Capacitively coupled plasma
CVD	... Chemical vapor deposition
HMDSO	... Hexamethyl disiloxane
OES	... Optical emission spectroscopy
PDMS	... Polydimethylsiloxane
PECVD	... Plasma enhanced chemical vapor deposition
RF	... Radiofrequency
RGA	... Residual gas analysis
ToF-SIMS	... Time-of-flight secondary ion mass spectrometry
UHV	... Ultra-high vacuum
UV	... Ultra violet
VUV	... Vacuum ultra violet
XPS	... X-ray photoelectron spectroscopy

Chapter 1

Introduction

1.1 Thesis Structure

This Ph.D. thesis is a result of scientific work performed during the past four years on the properties of gaseous plasma in a large low-pressure reactor which is routinely used in the production of various components for the automotive and electro industry. The aim of the thesis is to gain knowledge of complex gas-phase and surface phenomena that take place during the deposition of thin protective coatings on the surface of polymer samples using Plasma Enhanced Chemical Vapour Deposition (PECVD) at low pressures. The thesis starts with a comprehensive introduction to the plasma methods used for surface activation and coating deposition. The basic phenomena of gaseous plasma are presented along with the peculiarities of the plasma reactor and the technology. The main body of the thesis contains copies of four scientific papers published in renowned journals specialised in plasma chemistry, material sciences, and the science of surfaces and thin films: Plasma Chemistry and Plasma processing (current impact factor 2.768), Materials (IF 2.972) and Coatings (IF 2.330). The author of this thesis is the first author of all four papers. Žiga Gosar performed experiments with the help of other scientists, selected the experimental results, contributed to the interpretation, and wrote the drafts of the papers. The co-authors helped with experiments and interpretation of the result, and performed the final scientific editing of the manuscripts. The co-authors also helped to improve the manuscripts according to the referees' suggestions. References to the literature used during the preparation of experiments, for the interpretation of results, and while writing the papers are listed at the end of this thesis.

1.2 The Technological Challenge

The author of this thesis is employed by the company that manufactures automotive lamps. The lamps are made from plastic with some metalised surfaces, and the metalisation must be protected against corrosion with a thin protective polymer-like coating. Metallisation is performed by evaporation of molten metal. The metal vapor diffuses inside the vacuum chamber and condenses on the polymer surface forming a thin film. The adhesion of such metallic films is inadequate because of the unbalanced surface energies as well as internal stresses. Adhesion may be improved by briefly treating the plastic components with a plasma containing oxidising species such as O and OH radicals. A technological challenge is the development of plasma methods that enable a reliable surface finish of the plastic components. The methods should be as fast as possible, enable moderate or high surface energy, and not modify other properties of the treated products. During metallisation, a thin aluminum film is deposited by a processes of vacuum evaporation to obtain a suitable

reflectance of the lamp. Vacuum metallisation is fast and was elaborated decades ago, and is regarded as a routine method. The freshly deposited metal film oxidises quickly in harsh environments, and so must be protected with a coating. The protective coating is deposited using the PECVD process with a HMDSO precursor in plasma conditions. The technological challenge is to assure the optimal protective properties irrespective of the type of product to be treated. A further technological challenge is the accomplishment of deposition in as short a time as possible. The requirements are contradictory, so compromises are made. The technological challenges could only be appropriately addressed by an experimental approach. That is why a detailed study of the plasma was performed in our reactor to understand both plasma techniques, i.e., surface activation of plastic substrates and the deposition of polymer-like coatings by plasma polymerisation. Both processes are performed in batch mode in the same plasma reactor. The reactor used for this thesis is described in detail in the scientific literature. A photograph of the reactor is shown in Figure 1.1. The vacuum chamber has two doors allowing for the assembly of the components to be treated on planetaria on one door while the other door is closed so that the plasma processing takes place in the reactor.



Figure 1.1: The plasma reactor used for experiments performed in the frame of this thesis.

1.3 Surface Energy and Activation of Polymer Substrates

The surface energy dictates the wettability of solid materials. Materials with low surface energy will be wetted only by non-polar liquids. Increasing the surface energy will increase the types of liquid with which the surface of a solid material will be wetted. Solid materials with a very high surface energy will be wetted by all liquids. Adequate wetting is essential in many technological processes in which good adhesion of a coating to the substrate is desired, for example, when gluing, printing, metallising, or depositing a protective coating. In some other applications, however, wetting is not preferred, such as with self-cleaning materials, kitchenware, etc. Materials with high surface energy are referred to as hydrophilic, while those of low surface energy are hydrophobic. Wetting of the solid materials by polar or non-polar liquids (water and oil, respectively) is illustrated in Figure 1.2.

Materials with very low surface energy will cause a water droplet to retain its near-spherical shape (Figure 1.2 (a)). Such a material is called “super-hydrophobic”. Good examples are some types of fluorinated polymers like expanded or knitted polytetrafluoroethylene. In nature, the lotus leaf is a well-known example of an almost super-hydrophobic surface. Super-hydrophobic materials may or may not be oleophobic, which means that even a liquid with low surface energy like oil will not spread over the surface. However, few materials exhibit super-hydrophobic properties.

Pastics (different polymers, polymer blends, and polymer composites) are moderately hydrophobic. The water and oil droplets on the surface of such materials are shown in Figure 1.2 (b). The contact angle of a water droplet on a moderately hydrophobic material is close to 90° , while the contact angle of a non-polar liquid, like oil, is very low.

Some materials are moderately hydrophilic. The list of such materials includes many types of glass, ceramic, and metal oxides. Since most metals exhibit a thin natural oxide film, metals are sometimes regarded as moderately hydrophilic, although the surface energy of pure metals is extremely large. Droplets of water and oil on moderately hydrophilic materials are illustrated in Figure 1.2 (c). The water contact angle is often approximately 45° for moderately hydrophilic surfaces, but the oil contact angle is usually very low or immeasurable since the oil droplet will spread across a large surface.

Any liquid will wet a super-hydrophilic material. The water and oil contact angles are immeasurably low for such materials. Super-hydrophilic materials do not exist in nature but can be synthesised in laboratories. For example, pure metals will exhibit such high surface energy that a water droplet will wet a large surface area. The spreading of the water and oil droplets on such materials is shown in Figure 1.2 (d). Details about super-hydrophilic surface finishes have been published in a review paper [1].

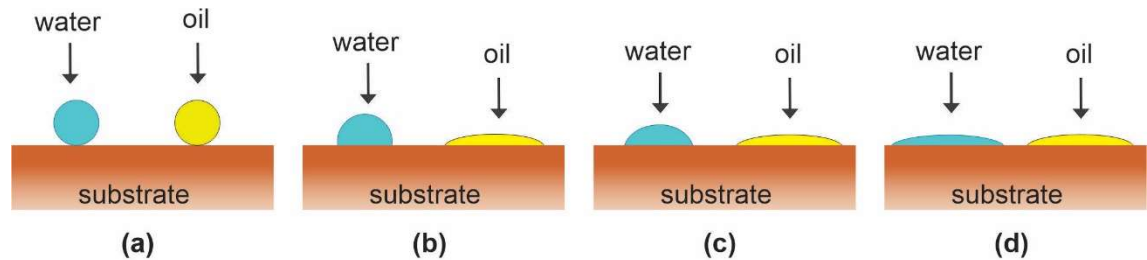


Figure 1.2: Water and oil droplets on different materials a) super-hydrophobic and oleophobic, b) moderately hydrophobic, c) moderately hydrophilic, d) highly hydrophilic.

Let us now consider the wetting of polymer materials by metals. As explained above, a pure metal has a high surface energy, while polymers are usually moderately hydrophobic. Metal vapor arriving at the surface of a polymer will not form a uniform film but thermodynamically favoured clusters, because a three-dimensional geometry enables the minimisation of surface energy. In fact, it had been theorised that a monolayer of any material, even a material of very low surface energy, could not exist. This belief was falsified by the discovery of graphene – two-dimensional graphite comprising a monolayer of carbon atoms arranged in a hexagonal structure [2]. The discovery won a Nobel prize [3].

Metals are far from graphene, and they do not form a self-standing two-dimensional structure. When metal vapor arrives at the surface of a polymer, the condensed atoms form clusters rather than a uniform film. The effect is illustrated in Figure 1.3. Prolonged deposition will cause the formation of a porous metallic structure. Porous metals do not satisfy the required properties, so such a coating will not meet industrial standards. Furthermore, since the wetting is inadequate, the adhesion of the metallic film to a substrate of low or moderate surface energy will be poor. Namely, as shown in Figure 1.3,

the contact area between the metallic clusters and the polymer substrate is much smaller than the geometric dimensions of the polymer surface.

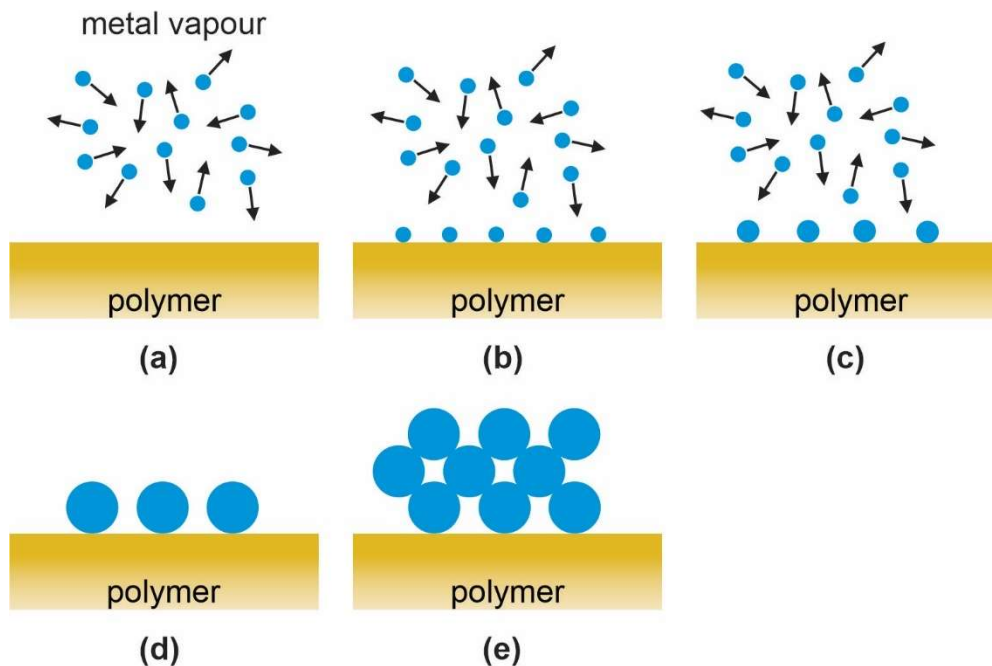


Figure 1.3: The condensation of metal atoms on a polymer surface. The initial surface is free from metal atoms (a). When condensation starts, the surface is covered with sparsely distributed atoms (b). Further deposition will cause the formation of clusters of metal atoms (c). The clusters will grow in size (d), and eventually, several layers of clusters will form (e) to make a porous metal film that does not meet the desired properties.

The problem of clustering is efficiently overcome by surface activation of the polymer. As explained above, polymers exhibit low surface energy. The surface energy is increased by grafting polar functional groups on the surface of the polymer [4]. The grafting is performed by plasma treatment, which causes the formation of polar oxygen-containing functional groups on the polymer's surface, as shown schematically in Figure 1.4. Such a surface finish is beneficial for the binding of metal vapors arriving at the site and thus immobilisation of metal atoms as soon as they touch the surface. The immobilisation prevents (or at least suppresses) the formation of metallic clusters. Once the surface is covered with a monolayer of metallic atoms, the surface properties change. As explained above, pure metals exhibit high surface energy, so additional metal atoms arriving at the substrate that is already covered with a monolayer of chemically bonded metal will form a compact film and not clusters. The kinetics of metal atoms on the surface of polymers are illustrated in Figure 1.5.

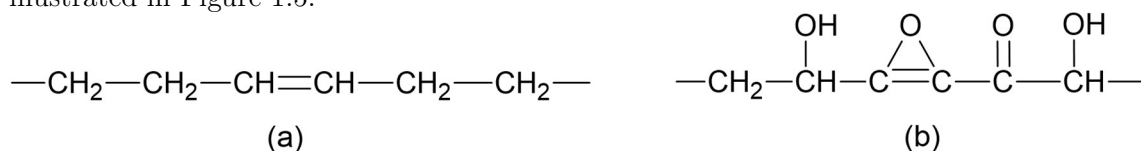


Figure 1.4: Schematic of the surface of a pristine polymer (a) and plasma-treated polymer (b). The surface carbon atoms of a pristine polymer are terminated by hydrogen atoms, the bond is non-polar and thus inert. The plasma treatment causes the formation of various

functional groups which are polar and serve as binding sites for metal atoms arriving at the polymer surface during metalisation.

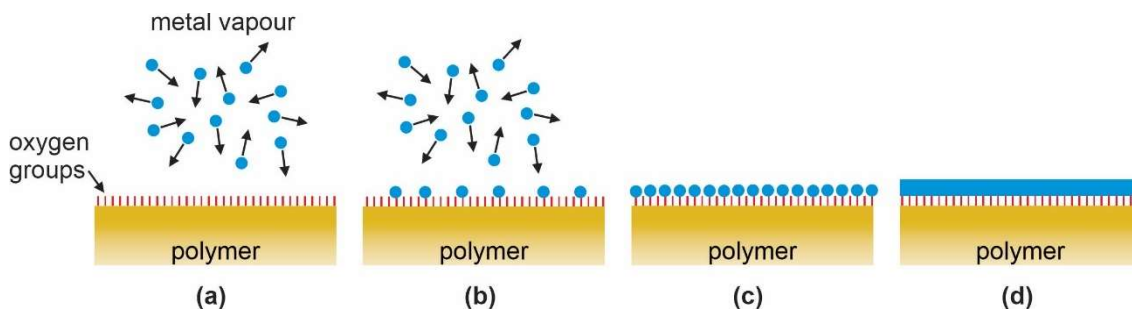


Figure 1.5: The condensation of metal atoms on a plasma-activated polymer surface. The initial surface is free of metal atoms (a) but rich in polar functional groups. When condensation starts, the surface is covered with sparsely distributed metal atoms, which will be chemically bonded to the polar functional groups at the surface (b). Further deposition will cause uniform distribution of metal atoms chemically bonded to polar functional groups (c). Still further deposition will result in the formation of a compact, thin metal film since the surface energy of freshly-deposited metal is large (d).

1.4 Formation of Polar Functional Groups on Polymer Surfaces

Pristine polymers do not exhibit polar surface functional groups due to their chemical structure. The addition of oxygen-containing polymers in the polymer blend will not influence the surface properties since a high concentration of polar surface groups is against the rules of thermodynamics. The thermodynamics dictates the minimisation of free energy, so any polar group that might appear on the surface will be either re-oriented toward the inside of the polymer or covered with a third molecule, usually a gaseous impurity such as a hydrocarbon, which are always present in minute quantities in ambient air. The surface may be grafted with polar groups only by using a thermodynamically non-equilibrium treatment. The grafted groups will not be stable unless the treated polymer is kept in a very inert atmosphere at a very low temperature. Still, the shelf-time of grafted polar groups may be long enough, providing they are stabilised by the deposition of a coating of high surface energy material, for example, metal.

As shown schematically in Figure 1.4 (b), the surface finish is realised by treatment of the pristine polymer with a non-equilibrium oxygen-containing plasma. The treatment should be performed when the polymer material is at low temperature, preferably room temperature, to avoid rapid re-orientation of functional groups at the surface.

Non-equilibrium oxygen plasma consists of O_2 molecules at the ground state, molecules in electronically excited states, and molecules in vibrationally and rotationally excited states. Furthermore, a significant fraction of oxygen molecules are dissociated, so nascent (atomic) oxygen is present in non-equilibrium plasma. Some molecules are even ionised to form positively charged molecular ions (O_2^+). Negatively charged ions (O_2^-) are also formed because of the attachment of slow electrons, but they do not play an important role in polymer functionalisation. The ionisation fraction of oxygen molecules is often orders of magnitude smaller than the dissociation fraction, so the density of O atoms is orders of magnitude larger than the density of charged particles. Atomic oxygen is among the oxidants of highest oxidation potential, and will thus react with the polymer surface even

at room temperature. The reaction will typically lead to the substitution of the C – H bond on the polymer surface with the hydroxylic group (C – OH). This reaction is exothermic, and the potential barrier is minimal [5], so the substitution is likely to occur. The illustration of the formation of hydroxylic groups on the polymer surface upon interaction with O atoms is shown in Figure 1.6. The OH radicals exhibit about the same oxidation potential to enable a similar surface finish as oxygen atoms.

The surface of the polymer upon exposure to oxygen plasma will soon be saturated with hydroxyl groups. Further treatment will cause the formation of various functional groups. The kinetics of surface functionalisation are complex and remain a subject of scientific research. It involves the substitution of atoms or molecular groups, breaking bonds in the polymer chain, formation of volatile molecules, diffusion of oxygen from the surface to the subsurface film, etching, and nanostructuring. The evolution of functional groups is usually monitored by X-ray photoelectron spectroscopy. Figure 1.7 reproduces the concentration of various polar functional groups on the surface of polystyrene. The evolution is represented versus the fluence of O atoms.

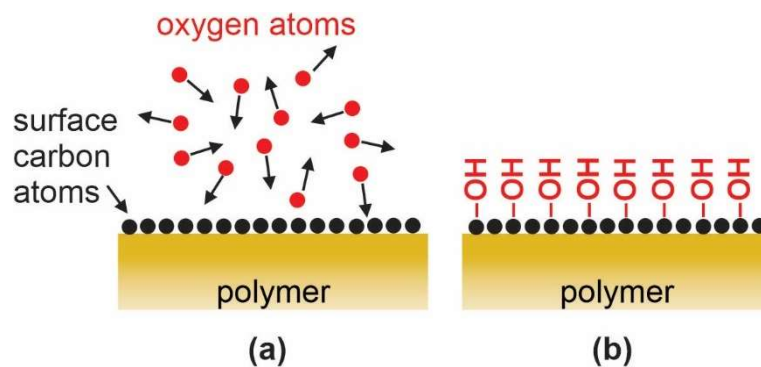


Figure 1.6: Schematic of the surface functionalisation with polar hydroxylic groups. (a) pristine polymer exposed to gaseous plasma is subjected to a random flux of O atoms, (b) the O atoms interact with the C – H surface bond to form hydroxyl groups.

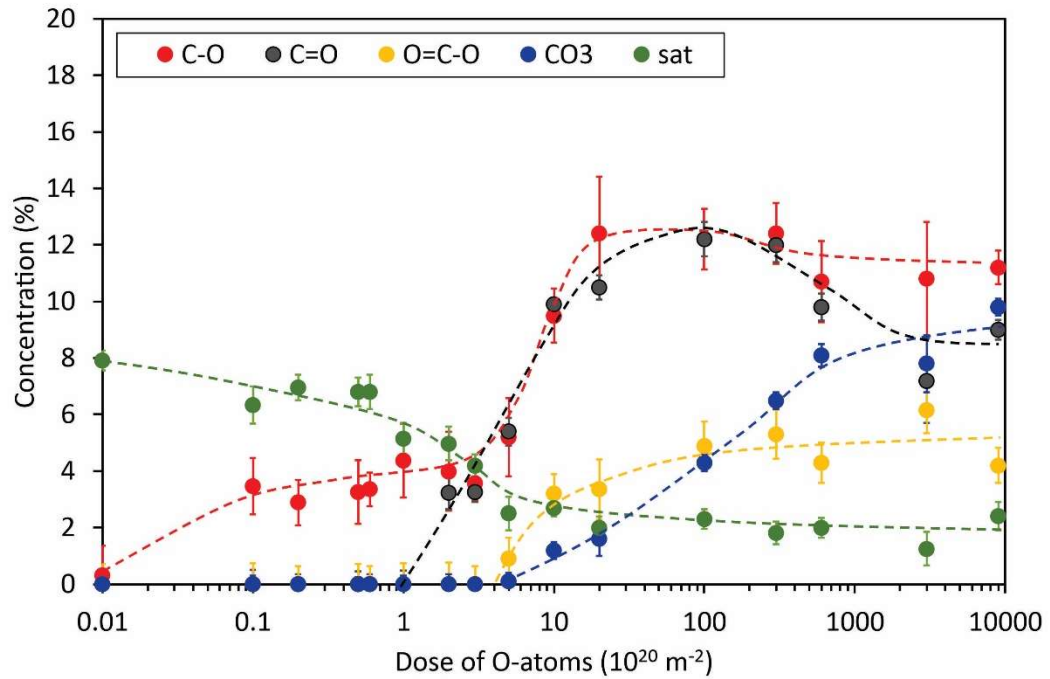


Figure 1.7: The concentration of polar groups on the surface of polystyrene versus the fluence of O atoms. Reproduced from [6].

1.5 Plasma Polymerisation

Although studied in detail by numerous authors, the kinetics of reactive species formed in oxygen plasma is complex and not well understood. Much more complex, however, is the science of plasma polymerisation. The basic principle is as follows:

1. A vacuum chamber is evacuated to low pressure;
2. A gaseous precursor, typically a monomer or oligomer, is introduced into the vacuum chamber;
3. Plasma is ignited so that the precursor is partially dissociated to form fragments;
4. The fragments condense and chemically bond to any surface facing the plasma.

In reality, the plasma polymerisation process is extremely complex due to the large number of precursor fragments. Hexamethyl disiloxane (HMDSO) is often used as an appropriate monomer to provide building blocks for the surface film of a polymer. The structural formula of this monomer is shown in Figure 1.8. The three methyl radicals are bonded to silicon atoms, which are bonded via an oxygen bridge. Dissociation of this molecule in plasma conditions occurs at any bond between atoms in this molecule, so numerous radicals (over 100 different species) may be formed. The dissociation is due to the interaction of energetic electrons upon inelastic collisions. Electrons in the plasma assume a Maxwellian distribution over the kinetic energy. The relatively low-energy electrons that abound in plasma will preferentially break bonds between hydrogen and carbon and will also be capable of breaking bonds between methyl groups and silicon atoms. They are not capable of breaking bonds between oxygen and silicon because this bond is stronger. The electrons in the high-energy tail of the distribution function, however, will also be capable of breaking these Si – O bonds. As a result, the plasma sustained in HMDSO will be rich in hydrogen and methyl radicals, will have a significant concentration of siloxane radicals ($\text{SiO}_2\text{C}_x\text{H}_y$), as well as containing some other radicals. The siloxane radicals will adhere to the substrate

and form a layer resembling the most stable form of polymerised siloxane, i.e., polydimethylsiloxane. The structural formula of polydimethylsiloxane is shown in Figure 1.9. The backbone of this polymer is a chain of Si-O-Si-O-Si, with a couple of methyl groups chemically bonded to each silicon atom. Polydimethylsiloxane is often used in industry as an inert material, typically in the form of foils. It is also hydrophobic and moderately oleophobic, so it is among the best materials to protect the surface of any material against corrosion. The plasma-deposited film is not a completely stoichiometric polymer as shown in Figure 1.9 but has many defects due to the peculiarities of its deposition. Still, it keeps the properties of PDMS as prepared by chemical methods. A depth profile of an aluminum sample coated by plasma polymerisation is presented in Figure 1.10.

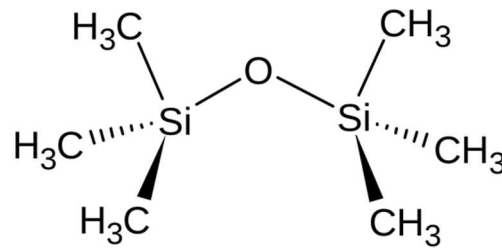


Figure 1.8: Hexamethyl disiloxane (HMDSO)

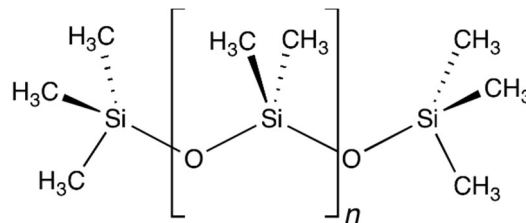


Figure 1.9: Polydimethylsiloxane (PDMS)

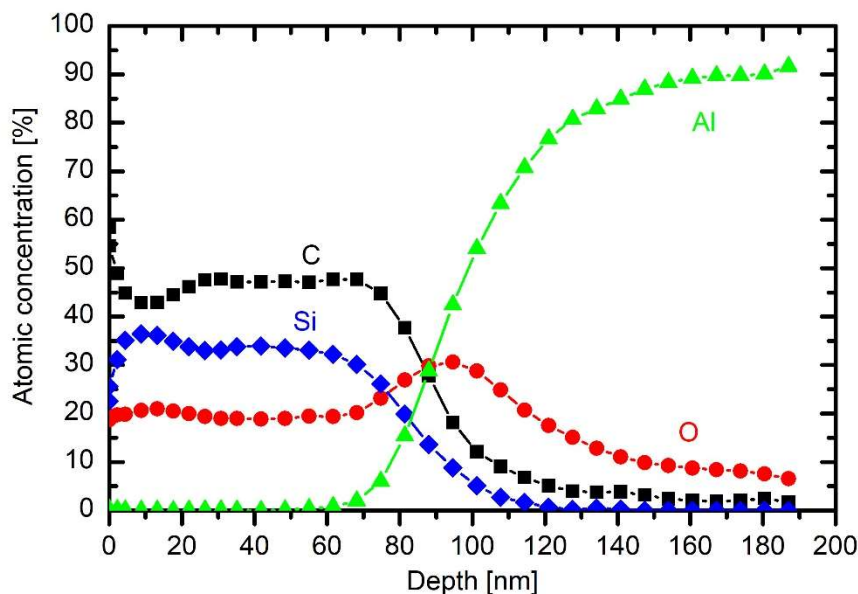


Figure 1.10: XPS depth profile of a thin film resembling polydimethylsiloxane on an aluminum substrate deposited by plasma polymerisation.

As explained above, the most likely dissociation event in HMDSO plasma is the subtraction of a hydrogen atom from the precursor molecule. Hydrogen atoms will be associated by forming H_2 molecules at heterogeneous surface recombination, and molecular hydrogen will not interact with any material since it is a stable molecule but will be pumped away from the plasma reactor. The methyl radicals will partially adhere to the surface but will preferentially interact with H atoms (and form methane that is pumped away from the vacuum chamber) or interact with another CH_x radical to form light hydrocarbons like ethane. All stable light hydrocarbons will be pumped away from the plasma reactor since they will not bond to surfaces due to their chemical inertness. Both molecular hydrogen and light hydrocarbons were detected in our system, as shown in Figure 1.1, and their kinetics are explained in the main part of this thesis (scientific papers).

The upper description is a simple guide to the complex reactions that occur during plasma polymerisation. In practice, however, the detailed description is still a subject of extensive research due to the lack of probes for measuring the concentrations of various radicals in plasma of the HMDSO precursor. A further complication is oligomerisation in the gas phase. Simple radicals like H or O atoms will not form molecules (H_2 or O_2) in the gas phase due to restrictions on total energy and momentum conservation. They will recombine on surfaces to form stable molecules, and the excess energy will result in heating the solid material. On the other hand, more complex radicals may interact in the gas phase and form molecular complexes. The excessive energy (association energy, because the reaction is exothermic) during this type of gas-phase reaction transforms into the internal energy of the newly formed molecule, such as vibrational and rotational states. This effect may lead to the formation of macromolecules in the gas phase, and finally, molecular clusters. Slow electrons may attach to the clusters to form negatively charged clusters. Since the surface of any macroscopic object in contact with gaseous plasma assumes a negative surface charge, the charged clusters cannot reach the surface, so they remain in the gas phase. This effect causes the formation of dusty plasma, which is regarded as detrimental to plasma polymerisation. Namely, the dust particles in the plasma act as a sink of radicals. These should be used as building blocks for thin films of plasma polymer on the surface of components installed into the plasma reactor. Finally, the dust particles become so large that gravitation overcomes electrostatic repulsion, and the large dust particles attach to the surface of materials as defects. Oligomerisation and clustering are illustrated in Figure 1.11. The forces on large clusters of different sizes close to the surface of a macroscopic object are shown in Figure 1.12. The electrostatic force increases with increasing negative charge, but gravitation increases with mass, which increases with the size of the cluster diameter. Therefore, large enough clusters will always sediment on the surface of an object placed in the plasma reactor, irrespective of electrostatic forces. A feasible solution to overcome this problem is occasional termination and re-ignition of the gaseous plasma. This solution is applied in our production.

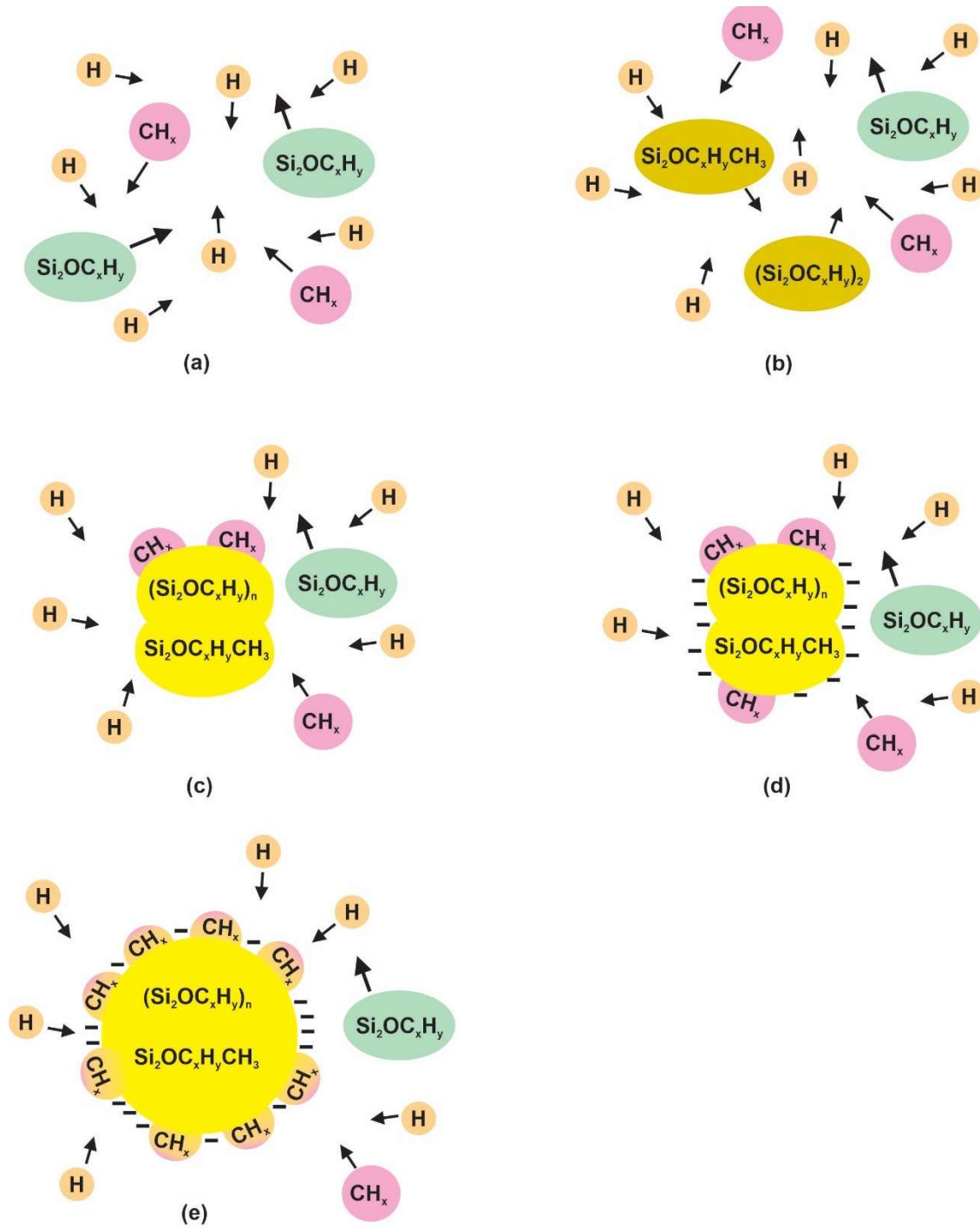


Figure 1.11: Oligomerisation, clustering, and formation of dusty plasma. Initially, only the fragments of the original precursor are present (a). Complexes or initial radicals soon form (b). Neutral complexes and radicals form clusters (c). The clusters charge negatively (d) and grow in size (e).

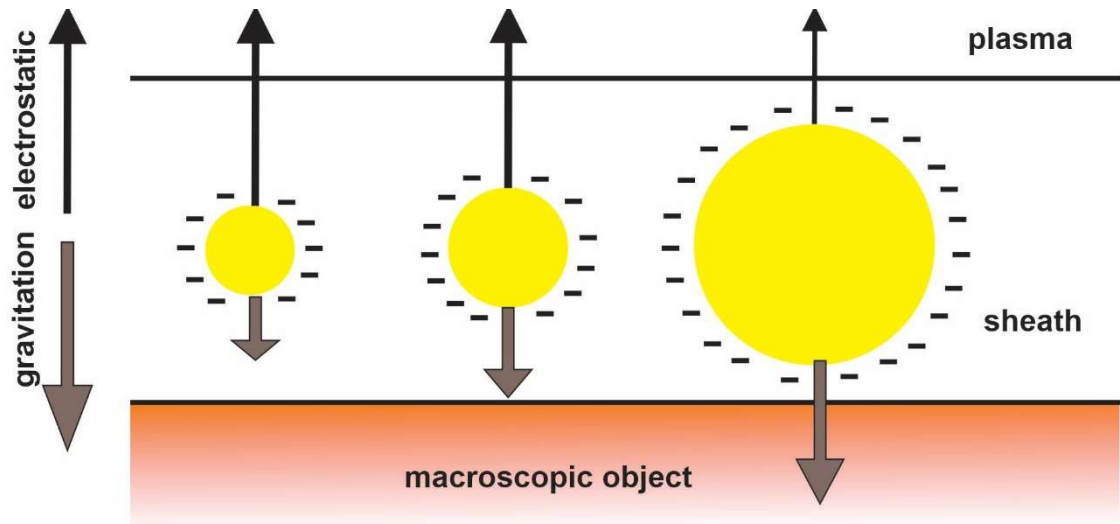


Figure 1.12: The electrostatic and gravitational forces of clusters in the sheath between the surface of a macroscopic object and the non-perturbed plasma. Both the macroscopic object and the clusters are negatively charged, so the electrostatic force is repulsive. Gravitation overcomes the electrostatic force for large clusters.

1.6 Thesis Objectives

The key objective of this thesis is to understand the behavior of gaseous plasma in an industrial-size plasma reactor. The literature on various aspects of plasma activation of polymer surfaces is abundant, as is the literature on the plasma-enhanced deposition of protective coatings using HMDSO as a precursor. Searching international databases, however, I have not found a single scientific article on the behavior of plasma in large, industrial-size reactors. The vast majority of authors have used small and simple experimental chambers with a volume about 1 liter, in which gaseous plasma is sustained at a rather large power density. The power density in the reactor shown in Figure 1 is solely 1 W/l. I have not found a single scientific document reporting the use of 1 W of power to sustain plasma in a reactor with a volume 1 liter. In fact, I believe it is impossible to sustain plasma at this power in an experimental plasma reactor.

Scientific aspects of plasma technology in the production of automotive lamps were prepared for publication in international scientific journals. I am the first author of four scientific papers which were published in 2019 and 2020. The scientific papers attracted immediate attention from the scientific community. Figure 13 represents the number of abstract and full-text views as reported on the journal homepage [7] for the paper Ž. Gosar et al., “PECVD of Hexamethyldisiloxane Coatings Using Extremely Asymmetric Capacitive RF Discharge”. Other scientific papers, in which I served as the first author, were viewed several hundred times.

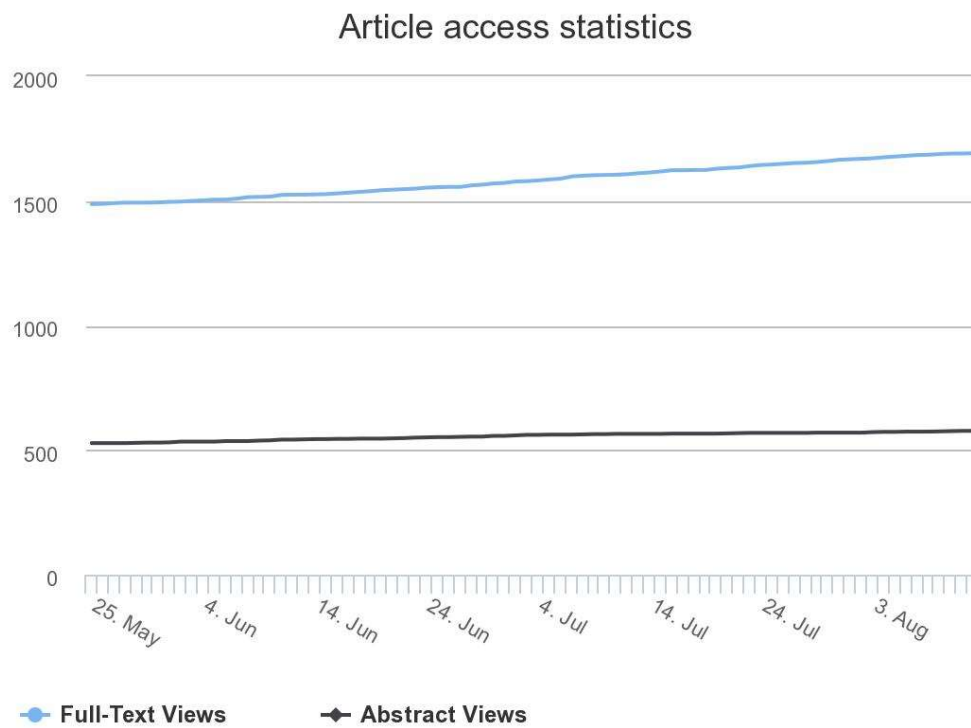


Figure 1.13: The article statistics for my paper [8].

Chapter 2

Deposition of SiO_xCyHz Coatings in an Industrial-Scale PECVD Reactor

This chapter provides an introduction to the deposition of polymer-like coatings in the plasma reactor shown in Figure 1. The plasma reactor is represented schematically using the internationally adopted symbols for vacuum components. The pumping curves are presented and discussed in the view of pumping kinetics, effective pumping speed, and desorption of gases from the surfaces of components installed into the plasma reactor. The composition of gases in different stages of reactor operation was measured by mass spectrometry. This technique will identify stable molecules that are capable of reaching the quadrupole filter of the differentially pumped mass spectrometer. The spectra revealed various molecules in the pre-pumping stage, the plasma activation of the polymer components, the main pumping, the metal film's deposition, and the protective coating's deposition. The permanent gases (in particular nitrogen and oxygen) are quickly removed from the vacuum chamber, so the pressure in the pre-pumping stage is governed by water vapor. The chamber is pumped in this stage by a roots pump backed by a mechanical rotary pump. The atmosphere in this stage does not contain a significant concentration of air, but about 99% is water vapor. Once the prescribed vacuum level is achieved, some argon is introduced into the chamber, and plasma is ignited. Argon gas causes increased electron temperature (as compared to plasma sustained in water vapor), and the argon metastables help distribute the dissociation of water vapor evenly in the entire chamber. After igniting plasma, the water vapor partial pressure increases slowly, although no water was leaked intentionally. The increase of water partial pressure was explained by increased desorption, which is desired to remove the excessive adsorbed water from polymer surfaces prior to deposition of a metal coating. The abundance of OH radicals formed upon plasma condition assured for optimal surface activation of polymer products, i.e., formation of hydroxyl radicals on the surface of originally moderately hydrophobic surface. When surface functionalization is accomplished, the argon valve is closed, and the valve above the diffusion pumps is opened. The diffusion pumps have a large pumping speed, so the pressure starts decreasing until high-vacuum conditions are met. When the pressure drops below about 0.02 Pa, the evaporation of aluminum is performed. The freshly deposited metal layer acts as a getter (a material that captures all gasses except noble gases), so the water vapor partial pressure drops until the aluminum surface is covered with about a monolayer of oxide. The evolution of aluminum oxides within the deposited film was probed by high-resolution XPS depth profiling and explained by the gas composition upon metallization of the polymer products. Simultaneously with the accomplishment of the metallization, the HMDSO precursor is introduced into the chamber at the pressure of a few Pa, and plasma is ignited. The atmosphere in the plasma reactor upon polymerization

consists of numerous stable gases and radicals that cannot be detected by mass spectrometry. The most intensive signal arises from hydrogen molecules, indicating radicalization of the precursor. The water vapor still persisted in the system even after the prolonged deposition of the polymer-like coating, but the concentration was low enough to prevent significant deviation of the surface film from polydimethylsiloxane. The thin films deposited on the surface of polymer products were analyzed by XPS depth profiling. The broad interface between the substrate and the metal film was rich in oxygen, which was explained by a rather high water partial pressure and saturation of the polymer surface with polar functional groups that have interacted with the polymer surface upon plasma activation.

Article

Deposition of $\text{SiO}_x\text{C}_y\text{H}_z$ Protective Coatings on Polymer Substrates in an Industrial-Scale PECVD Reactor

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Received: 6 March 2019; Accepted: 1 April 2019; Published: 3 April 2019



Abstract: The deposition of protective coatings on aluminised polymer substrates by a plasma enhanced chemical vapour deposition PECVD technique in a plasma reactor with a volume of 5 m³ was studied. HMDSO was used as a precursor. Plasma was sustained in a capacitively coupled radiofrequency (RF) discharge powered by an RF generator operating at 40 kHz and having an adjustable output power up to 8 kW. Gaseous plasma was characterised by residual gas mass spectrometry and optical emission spectroscopy. Polymer samples with an average roughness of approximately 5 nm were mounted into the plasma reactor and subjected to a protocol for activation, metallisation and deposition of the protective coating. After depositing the protective coating, the samples were characterised by secondary ion mass spectrometry (SIMS) and X-ray photoelectron spectroscopy (XPS). The combination of various techniques for plasma and coating characterisation provided insight into the complex gas-phase and surface reactions upon deposition of the protective coatings in the industrial-size plasma reactor.

Keywords: plasma-enhanced chemical vapour deposition (PECVD); hexamethyldisiloxane (HMDSO); industrial-size plasma reactor; capacitively coupled radiofrequency (RF) discharge; optical emission spectroscopy (OES); time-of-flight secondary ion mass spectrometry (ToF-SIMS); X-ray photoelectron spectroscopy (XPS)

1. Introduction

Plasma-enhanced chemical vapour deposition (PECVD) is a popular technique for the deposition of thin films, including protective coatings. Over 8000 scientific papers with a keyword PECVD have been published, including 400 papers in 2018. Although the technique was commercialised decades ago, it is still of high scientific importance despite its simple basic concept: a gaseous precursor is introduced into a processing chamber where it is weakly ionised and partially radicalised under plasma conditions, and the resultant reactive species condense on the substrate and thus cause growth of a solid film. Traditionally, the processing takes place in a vacuum chamber, but the current trend is applying atmospheric-pressure discharges [1] due to their obvious advantage: they are much cheaper than their vacuum counterparts.

For the deposition of Si-containing films, various precursors can be used [2–4], one of the most popular of which is hexamethyldisiloxane (HMDSO). It is used for the deposition of various coatings ranging from polymers to almost pure SiO_x films [5,6]. HMDSO is liquid at atmospheric pressure, but

the vapour pressure is rather large (approximately 50 mbar at room temperature); therefore, it is suitable for introduction into a processing chamber via a leak valve or a gas flow controller. Non-equilibrium gaseous plasma is sustained in the processing chamber, and free electrons (whose temperature is on the order of 10,000 K) cause radicalisation and ionisation of the precursor. Plasma is often sustained by high-frequency discharges of rather low power density. In a typical industrial reactor, the power density is on the order of kW/m³. The reactive species diffuse inside the chamber and eventually reach the surface, where they stick at a certain probability. The substrates are often activated prior to deposition to improve the adhesion of the coating. Depending on plasma parameters, coatings of various properties are deposited.

One extreme is a coating resembling polydimethylsiloxane. Such a coating is obtained at a very low power density (to preserve the original composition of HMDSO) and with almost no other gases present. The other extreme is a thin film of silicon dioxide that grows when an oxygen-containing gas is present in the chamber. Water vapour is usually in chambers, and, occasionally, a small amount of oxygen is intentionally added to favour the formation of almost pure SiO_x. In between these two extremes, numerous types of coatings are obtainable depending on the processing parameters. The flux of radicals onto the surface (and thus the deposition rate) obviously increases with increasing pressure and power density. At elevated pressure (more than approximately 10 Pa), the radicals, however, start to agglomerate in the gas phase, so the coating becomes grainy, which is often regarded as detrimental in industrial systems. If the power density is elevated, the dissociation of the precursor is comprehensive; therefore, carbon atoms or even dimers may be incorporated into the SiO_x film, making it less transparent, which is also a major obstacle in such systems. Another obstacle is plasma uniformity—the dissociation and ionisation events are more intensive next to the electrodes, so the SiO_x film is deposited primarily onto the electrodes instead of on the substrates. The tuning of discharge and plasma parameters therefore represents a challenge that has been the focus of scientific study for decades. Only a recent literature survey is presented here.

Mitschker et al recently presented a good summary on the formation of protective coatings (see the references in paper [7]) and stressed the influence of oxygen admixture on the barrier properties of deposited films. He also reported beneficial results using HMDSN instead of HMDSO. Another rather complete paper on coatings prepared by PECVD using HMDSO was published recently by Prykryl et al. [8]. They found an immeasurably low coefficient for oxygen permeation for a polymer foil coated with a SiO₂ layer. They also investigated the brittleness of the glassy coating and stressed that SiO_x must be deposited primarily on a low-swellability polymeric foil and that, due to its brittleness, it must immediately be laminated with another foil to prevent mechanical damage. M. Cavalcante dos Reis [9] reported interesting results on properties of coatings on dental materials. Various discharge parameters were used to obtain coatings with appropriate properties. This paper represents an interesting application in the niche characterised by a high value-added product. An interesting approach to the deposition of SiO_x coatings was adopted by Brochhagen et al. [10]. Instead of using a continuous supply of precursor, they pulsed small doses of HMDSO into the reaction chamber and used oxygen or argon plasma for transformation of the extremely thin polymer film created on the surface at each HMDSO pulse into a silica-like protective coating. This approach led to the formation of SiO_x films free from carbon or Si–OH groups with a very high (for industrial standards) deposition rate of approximately 1 nm/s. Scalability might be questionable since inductively coupled RF plasma in H-mode was applied. Pandiyaraj et al. [11] reported a DC plasma source for the rapid deposition (approximately 1 nm/s) of SiO_x films using a mixture of HMDSO and oxygen at a total pressure of 20 Pa. They found an interesting evolution of the film morphology as a function of discharge parameters. The initial stages in the nucleation and growth of SiO_x films on model substrates were elaborated by a team from Paderborn and Bochum [12]. Unlike most studies, they used oxygen as a major gas with a small admixture of HMDSO. Experiments were performed in a pulsed microwave plasma reactor at 25 Pa. The group also reported a numerical value of the O-atom flux onto the surface in order to explain the surface reactions in a rather quantitative manner. The key observation was a high density

of defects, which was attributed to the incorporation of oxidised aliphatic fragments into the SiO_x network and/or the deterioration of the plasma-induced crosslinking of adsorbed HMDSO fragments.

Atmospheric pressure discharges have also been used for deposition of such coatings from HMDSO. Gas-phase and surface effects were studied both theoretically and experimentally. Among recent papers, D. Loffhagen et al. [13] applied a time-dependent, spatially one-dimensional fluid-Poisson model to analyse the impact of HMDSO admixtures on the discharge characteristics of DBDs in argon at atmospheric pressure. They considered a limited number of collision processes relevant for HMDSO but obtained reasonable consistency with available experimental data. They found that Penning ionisation due to collisions of HMDSO with metastable and resonance argon atoms becomes the main source of electron production already for HMDSO fractions ≥ 5 ppm. Some attempts have also been made to coat materials immersed into liquid HMDSO and apply atmospheric-pressure plasma next to the liquid surface. The most recent paper was published by Pavlinak et al. [14], who created plasma above liquid HMDSO and successfully coated Teflon tubes with a thin film resembling polydimethylsiloxane. Obviously, such treatments cannot be used for the deposition of SiO_x coatings.

Thin films containing Si, O, C and H are suitable for numerous applications. Traditionally, these films have been used as hydrophobic and flexible protective coatings on products exposed to harsh environments. A thin PDMS film is an effective coating to prevent corrosion of metals [15]. It is also a classic textile coating able to ensure the super-hydrophilic properties of textiles [16]. More recently, it has been used as a scaffold for tissue engineering and similar biomedical applications [17–19], including microfluidic systems [20,21]. A comprehensive review of recent applications was reported by Edouk et al. [22].

Only recent achievements have been cited above. The literature on the PECVD deposition of protective coatings is extensive, and various authors have reported results obtained in different experimental setups. Although the technique was commercialised decades ago, the scientific literature on the kinetics of deposition with HMDSO in industrial-scale reactors is very scarce. The present paper fills this niche since we report a thorough investigation of film deposition using PECVD with HMDSO as a precursor in a large-scale reactor that is used for the deposition of protective coatings on car lamps. Unlike most other authors, we performed experiments under conditions typical for industrial reactors. In such reactors, the residual atmosphere always plays an important role due to extensive desorption of gaseous molecules from the surfaces of numerous components mounted inside the system. Nitrogen, oxygen, carbon dioxide and argon (air constituents) are quickly pumped from the system by powerful pumps, but water molecules slowly desorb from the polymer components. The consequence is a rather substantial amount of water vapour in the system throughout the process; therefore, one should always take into account the effect of water vapour when studying processing parameters and explaining the interaction of gaseous plasma with solid materials. Another important difference between experimental systems and large reactors is the power density (discharge power per unit plasma volume). While it is not feasible to operate experimental reactors at powers below few 10 W per litre (few 10 kW/m^{-3}), the industrial reactors suitable for coating components with a thin film resembling polydimethylsiloxane operate at power densities below 1 kW/m^{-3} .

2. Experimental

The plasma reactor used in this study is intended for coating polymer components of rather complex shapes and typical dimensions on the order of 10 cm. The coating procedure is shown in Figure 1. The reactor was first pumped to a pressure of approximately 1 Pa to evacuate air. After pumping for approximately 4 min, argon was introduced upon continuous pumping so that a pressure of approximately 6 Pa was achieved. Plasma was sustained for approximately 3 min to ensure appropriate activation of the polymer components. Argon was then pumped away, and high-vacuum pumps were used to establish high-vacuum conditions. As the pressure dropped to approximately 0.02 Pa, aluminium was evaporated, so the polymer components were coated with a thin metal film.

As soon as evaporation was accomplished, HMDSO was introduced, and the plasma was ignited to deposit a thin film resembling polydimethylsiloxane (PDMS).

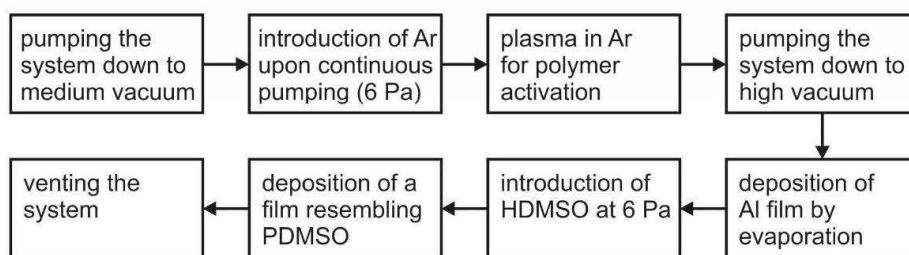


Figure 1. Schematic of the coating procedure.

The experimental system is shown in detail in Figure 2. The plasma reactor was a large chamber of a cylindrical shape made from steel. The diameter of the plasma reactor was 1.9 m, and the height was 1.8 m. The volume of the reactor was thus approximately 5 m³. The reactor was pumped with a couple of diffusion pumps with a total nominal pumping speed of approximately 40 m³/s. The fore-pumps were large one-stage oil rotary pumps with a nominal pumping speed of 1260 m³/h. In between these pumps, there were a couple of roots blowers with a combined nominal pumping speed of 8800 m³/h to ensure pre-compression of gas before entering the large rotary pump and thus enable an appropriately low pressure at the exhaust from the diffusion pumps. A cold trap was cooled down to a temperature of approximately 130 K and represents an extremely powerful pump for pumping water vapour from the plasma reactor. The nominal pumping speed of the cold trap was 140 m³/s. HMDSO was introduced into the plasma reactor via a flow controller. The HMDSO container was kept at a constant temperature of approximately 310 K. There was also an argon flask connected to the plasma reactor via a flow controller. Plasma was ignited and sustained with an RF generator. The generator operated at a frequency of 40 kHz and an adjustable output power up to approximately 10 kW. The generator was connected to the RF electrode, which was placed asymmetrically in the plasma reactor. The dimensions of the electrode were 150 cm × 27 cm, so the electrode area was much smaller than the area of the grounded plasma reactor. The discharge coupling was almost purely capacitive. The asymmetry caused preferential power dissipation in front of the powered electrode. The electrode was subjected to ion bombardment, while the bombardment of the grounded housing was regarded marginal. Samples were mounted on fixtures and kept at floating potential during plasma treatment. Typical samples were polymeric components. There was a holder of small aluminium sheets that were heated under high-vacuum conditions by resistive heating to allow rapid deposition of a thin aluminium film onto the surface of the polymeric samples. Plasma was characterised by a residual atmosphere gas analyser (RGA, PrismaPlus QMG 220, Pfeiffer Vacuum, Asslar, Germany, sometimes referred to as mass spectrometry) and optical spectroscopy. The RGA was differentially pumped using a turbomolecular pump HiPace 700 (Pfeiffer Vacuum, Asslar, Germany) with a nominal pumping speed of 0.7 m³/s backed with a small two-stage rotary pump with a nominal pumping speed of 5 m³/h. There was a glass window on the plasma reactor, which was made from steel. An optical fibre was mounted onto the glass window and connected to an optical spectrometer AvaSpec-3648 (Avantes, Apeldoorn, The Netherlands) to allow the sampling of optical spectra from gaseous plasma in the wavelength range between approximately 200 and 1100 nm. The transmission of the glass window was negligible in both the UV and IR ranges.

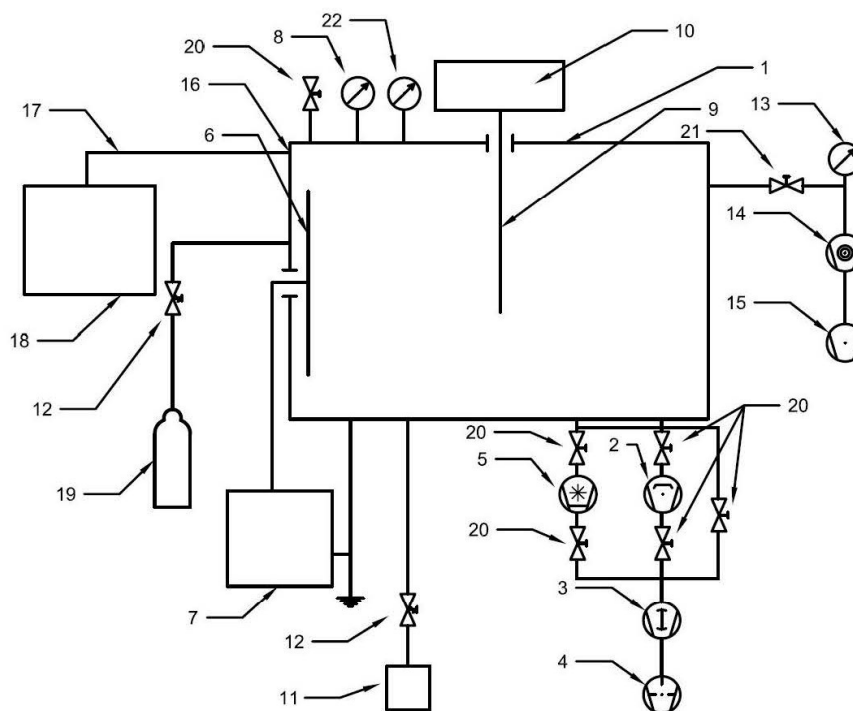


Figure 2. Schematic of the experimental setup: 1, plasma reactor; 2, diffusion pumps; 3, roots pumps; 4, large rotary pumps; 5, cold trap; 6, RF electrode; 7, RF generator; 8, Pirani gauge; 9, Al holder; 10, power supply for Al evaporation; 11, HMDSO container; 12, flow controller; 13, residual gas analyser; 14, turbomolecular pump; 15, small rotary pump; 16, glass window; 17, optical fibre; 18, optical spectrometer; 19, Argon container; 20, valves; 21, dosing valve; 22, Penning gauge.

Samples were commercial plastic components made from polycarbonate. The samples were made by injection moulding, and the surface of each sample was approximately 200 cm². Several samples were cut into small pieces with a surface area of approximately 1–2 cm² to enable characterisation. The samples were taken directly from the production line, so no pre-cleaning was performed. Some samples were first characterised by atomic force microscopy (AFM, Solver PRO, NT-MDT, Moscow, Russia) to determine their roughness. The average roughness (S_a), as determined by AFM, over an area of 20 $\mu\text{m} \times 20 \mu\text{m}$ was approximately 5 nm or, in terms of root-mean-square height, $S_q = 6.5$ nm. An AFM image is presented in Figure S1 in the Supplementary Materials. The samples were then mounted into the plasma reactor. The reactor was pumped to a reasonable pressure using the roots and large rotary pumps. Then, some argon was introduced into the reactor during continuous pumping, and plasma was sustained in the mixture of argon and residual atmosphere for a couple of minutes. This treatment was necessary for surface activation of the polymer samples prior to deposition of any coating. After plasma activation, the valve between the plasma reactor and the diffusion pumps was opened to reach high-vacuum conditions. The final pumping before depositing an aluminium coating was also performed with the cold trap. Once a suitable vacuum level was achieved, a thin film of aluminium was deposited in a short time to prevent significant contamination of the Al film due to the residual atmosphere. As soon as the Al coating was prepared, the cold trap and diffusion pumps were separated from the plasma reactor, HMDSO was introduced through the flow controller, and discharge was turned on to deposit the protective coating. During the introduction of the precursor, the reactor was pumped only with the roots and large rotary pumps. After depositing the protective coating, the pumps were separated, the reactor was vented, and the samples were taken for characterisation.

Samples with protective coatings were characterised by time-of-flight secondary ion mass spectrometry (SIMS) and X-ray photoelectron spectroscopy (XPS). In both cases, we used ion guns for removal of surface layers to obtain depth profiles. We used a ToF-SIMS 5 instrument (ION-TOF, Münster, Germany) equipped with a bismuth liquid metal ion gun with a kinetic energy of 30 keV. SIMS spectra were measured by scanning a Bi_3^+ cluster ion beam over an area of $100 \times 100 \mu\text{m}^2$. The beam current was 0.6 pA and the total measurement time to acquire the SIMS spectra was 30 s. The dose of primary ions during the measurements was in the static regime. The SIMS spectra were processed with the software SurfaceLab 6.3 (ION TOF).

Some samples were also characterised by XPS. We used a PHI-TFA XPS spectrometer produced by Physical Electronics Inc. (Chanhassen, MN, USA). The analysed area was 0.4 mm in diameter, and the analysed depth was approximately 3–5 nm. The sample surface was excited by X-ray radiation from a monochromatic Al source at a photon energy of 1486.6 eV. High-energy resolution spectra were acquired with an energy analyser operating at a resolution of approximately 0.6 eV and a pass energy of 29 eV. During data processing, the spectra acquired from the surface were aligned by setting the C 1s peak at 284.8 eV, characteristic of C–C bonds. Quantification of surface composition was performed on XPS peak intensities taking into account relative sensitivity factors provided by the instrument manufacturer.

3. Results and Discussion

The pressure in the plasma reactor presented schematically in Figure 2 during the entire procedure for deposition of protective coatings is shown in Figure 3. The reactor was first pumped with the large rotary pump. When a pressure of approximately 5000 Pa was reached, the roots pump was turned on, resulting in a knee in the curve at 1 min. The second knee was at approximately 50 Pa when cold trap was turned on, and the third knee was at approximately 5 Pa when valves to the diffusion pumps were opened. When the pressure dropped to approximately 1 Pa, argon was introduced, so the pressure increased to approximately 6 Pa. Gaseous plasma was created in the mixture of Ar and residual atmosphere to ensure appropriate surface activation. This treatment was accomplished in minute 6, as indicated in Figure 3. Then, the reactor was pumped with the cold trap and diffusion pumps for approximately 6 min. When the pressure inside the reactor dropped to a level of approximately 0.02 Pa, the Al heater was turned on (13 min). Once the Al coating was obtained, the cold trap and the diffusion pumps were separated, causing an almost instantaneous increase in pressure. HMDSO was then introduced, so the pressure increased to approximately 6 Pa. After that, the three cycles of the PECVD process were performed.

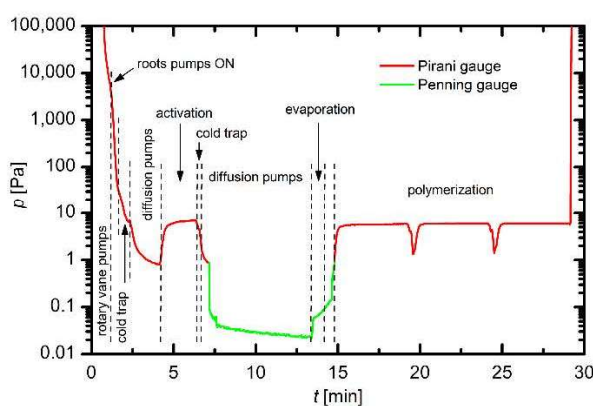


Figure 3. The vacuum levels in the plasma reactor at different stages.

During the upper procedure, mass spectra were measured continuously. Figure 4 presents the behaviour of different masses versus time in terms of the ion currents. The gaseous molecules were partially ionised in the residual gas analyser, and the positively charged ions entered the ion detector and caused ion currents. Comparison of Figures 3 and 4 reveals important observations that were crucial for deposition of the protective coatings. During initial pumping, there were essentially ion currents at only masses 18 and 16. These masses correspond to water and methane, respectively. The absence of currents at masses 28 and 32 indicated the lack of nitrogen and oxygen, respectively, in the vacuum chamber, which was explained by two facts: first, the plasma reactor was hermetically tight, and second, air was pumped much more efficiently than water vapour. The latter was due to extensive release of water vapour from the polymer samples. The intensity of water was considerably larger than that of methane, so the residual atmosphere in the plasma reactor practically consists of water vapour only.

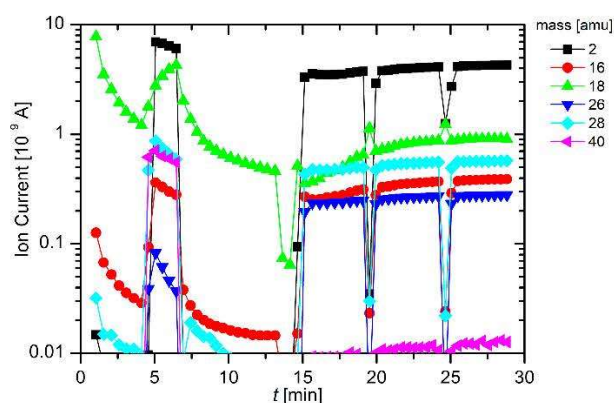


Figure 4. Mass spectrometry of gaseous molecules during all phases of the production process.

When argon was introduced into the reactor, there was an appearance of mass 40 in the spectrum presented in Figure 4. Simultaneously, as the discharge was turned on, one can observe the appearance of mass 2, which was attributed to hydrogen. The water vapour was partially dissociated under plasma conditions to H and OH radicals. H_2 molecules were probably formed by heterogeneous surface recombination of H atoms on the wall of the discharge chamber as well on the polymer samples. Extensive recombination also appeared on the path between plasma and the RGA—this connection was narrow, thus numerous collisions of gaseous species with the surface of the steel tube appeared. The recombination coefficients for polymeric materials were rather low [23], but for H atoms on stainless steel, the probability of surface recombination was close to 0.1 [24]; thus, very few H atoms created in plasma could enter the RGA. As a result, the H_2 signal prevails in Figure 4. Here, it is also worth mentioning that the sensitivity of the RGA for hydrogen was particularly large, thus no quantification of results in terms of partial pressure was possible.

During the activation of polymer substrates with argon plasma, a continuous increase in the intensity of mass 18 (water vapour) was observed (Figure 4). This effect is explained by the heating of all materials facing the plasma and consequent temperature-stimulated desorption of water vapour. All other masses in the time range from minute 5 to minute 7 decreased with time. The masses 16, 26, and 28 were attributed to methane, acetylene and ethylene, respectively, rather than other molecules. As already mentioned, the reactor was tightly sealed, thus mass 28 could not be attributed to N_2 molecules, let alone Si atoms (the vapour pressure of Si was negligible at room or slightly elevated temperature).

Argon was introduced into the plasma reactor for 2 min only. When the Ar valve was closed and the discharge was turned off, mass 40 decreased almost instantly. Features other than mass 18 also vanished. One conclusion that could be drawn on the basis of this observation is that measurable

etching of the polymer samples occurred inside the reactor under plasma conditions. Although the power density was rather small (in the case of Figure 4, the power was 3.5 kW), it was large enough to cause etching and thus formation of molecules that were not observed during pumping down and before the plasma was ignited.

Once the discharge was turned off, the mass spectrum showed only water vapour (mass 18). During operation of the diffusion pumps, the RGA signal of mass 18 decreased by almost an order of magnitude (note the logarithmic scale of the y-axis in Figure 4). Once the cold trap was open, the intensity of the RGA peak decreased by another order of magnitude (at 13 min in Figure 4), which was correlated with the instant pressure drop indicated in Figure 3.

After 14 min, the cold trap and diffusion pumps were hermetically separated from the reactor, HMDSO was introduced, and the discharge was turned on again. As a result, the RGA spectra became extremely rich (Figure S2). There were features corresponding to masses 2, 16, 18, 26, 28, 45, 52, 59, 66, 73, etc. The appearance of the peaks at large masses was attributed to various fragments of the HMDSO molecule. The precursor was thus partially decomposed both in the plasma reactor and in the RGA ionisation chamber. Any detailed analyses of RGA spectra was impossible since any heavy mass could be attributed to various molecules. The richness of the spectrum only indicated complex gas-phase chemistry. The discharge was turned off twice during deposition of the protective coating to prevent formation of dusty plasma. As explained in the Introduction, radicals tended to interact with each other in the gas phase, forming clusters that were negatively charged in plasma, thus could not escape to the surfaces that were also negative against plasma due to differences in mobility between electrons and ions. The net charge flow on the surface of any object facing plasma should be zero under steady conditions, thus the plasma should be positive against the walls to compensate for the very large electron mobility compared to ion mobility.

Mass spectrometry was therefore useful for monitoring the evolution of various molecules that were either created in gaseous plasma and stable enough to enter the RGA or created in the ionisation chamber of the RGA itself. An insight into the rather short-lived radicals that were created in the plasma was, however, obtainable from Figure 5, which presents optical spectra arising from the plasma during deposition.

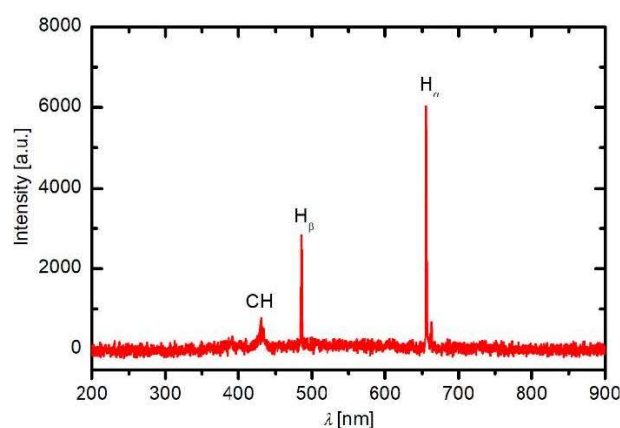


Figure 5. An optical spectrum of gaseous plasma during the deposition phase.

Figure 5 presents a typical optical spectrum during introduction of HMDSO (from minute 15 onward). Unlike the mass spectra in Figure 4, the optical spectrum in Figure 5 is extremely simple. One can observe lines that corresponded to radiative transitions from excited hydrogen atoms to the first excited state—the Balmer series, where the most intensive emission lines were the alpha and beta lines at 656 and 486 nm, respectively. There was also a peak corresponding to the CH radical. This observation was consistent with the mass spectrometry results (Figure 4), which indicate the

presence of a variety of molecular fragments. Optical spectroscopy cannot reveal many-atom molecules since the radiative transitions from such molecules form a continuum. Nevertheless, the appearance of the CH peak at 431 nm revealed fragmentation of the original precursor to CH_x radicals under plasma conditions. This result is consistent with the generally accepted theory that weakly ionised plasma causes decomposition of HMDSO by subtracting methyl radicals. The large intensity of radiation arising from H atoms can be attributed to either dissociation of water vapour or subtraction of H atoms from the original precursor. The oxygen line at 777 nm was absent, which could be explained by either the poor density of O atoms in the deposition phase or low electron temperature. Both explanations are feasible, as became evident by monitoring the properties of the films deposited on sample surfaces upon performing PECVD with HMDSO.

Figure 6 presents a typical XPS depth profile of a polymer sample characterised after completing the entire production cycle, i.e., activation, metallisation and deposition of the protective coating. The substrate was composed of carbon only (XPS is not sensitive to hydrogen). There was a broad interface between pure carbon in the rightmost part of the depth profile and aluminium. The rather large concentration of oxygen at this interface was explained by successful functionalisation of the polymer surface during the activation phase (minute 5 to minute 7 in Figure 4). This functionalisation could not occur due to any interaction of argon or water vapour with the surface of the polymer material. Formation of the oxygen-rich interface between the polymer substrate and aluminium film was obviously due to plasma conditions, but a detailed explanation is not straightforward, as one should take into account various mechanisms.

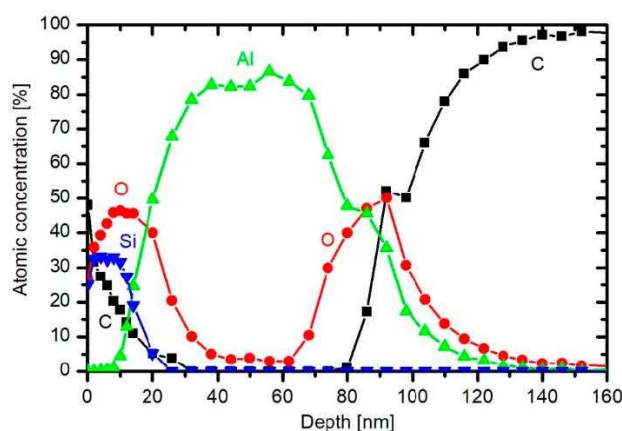


Figure 6. The XPS depth profile of the protective coating on a polymer substrate.

One method for functionalisation of a polymer surface with oxygen functional groups is irradiation with hard UV radiation and subsequent exposition to an oxygen-containing gas. A review of such a method is published recently [25]. Radiation causes bond breaking in the surface layer of the polymer, thus increasing the affinity for oxidation. The radiation in our case arose predominantly from hydrogen. There were two H lines in the optical spectrum marked as H_α and H_β arising from transitions from the second and third excited state, respectively, to the first excited state. The transitions to the ground state (which appear in the hard UV range of spectrum) were not visible, but they were much more intense than the transitions to the first excited state. According to Fanz et al. [26], the transitions to the ground state are at least an order of magnitude more intensive than those to the first excited state. The radiation arising from the transition from the first H-atom excited state to the ground state appeared at a photon energy just over 10 eV, and such photons were effectively absorbed by the surface film of the polymer, thus breaking bonds. The dangling bonds then interacted with the water vapour, which was, according to Figure 4, the major component of the residual atmosphere. The water partial pressure could not be determined accurately from the measured ion currents, but, in a rough

approximation, we could account for the pressure inside the reactor before introducing argon into the system. Figure 3 reveals that the pressure was approximately 1 Pa at this stage of the process. At a pressure of 1 Pa, the density of water molecules in the reactor was as high as 10^{20} m^{-3} , which was calculated using a general gas equation:

$$p = n \times k \times T, \quad (1)$$

where p is the pressure, n is the density of molecules, k is the Boltzmann constant and T is the absolute temperature. The flux of gas molecules onto the surface is

$$j = \frac{1}{4} \times n \times \langle v \rangle, \quad (2)$$

where $\langle v \rangle$ is the average velocity of thermal motion (approximately 600 m/s for H₂O molecules). If all molecules interacted with dangling bonds on the polymer surface, a monolayer of oxygen would form in less than a second. Therefore, there were enough oxidative species to ensure rich functionalisation of the polymer surface prior to deposition of the aluminium film, even though the activation was performed under vacuum condition.

An alternative technique for functionalisation of a polymer surface is dissociation of water molecules into H and OH radicals. This technique is particularly useful for plasma activation of materials that release a large amount of water vapour, for example, textiles [27]. In fact, water vapour is always present in low-pressure reactors and significantly influences the surface finish of plasma-treated polymers [28]. OH radicals are renowned oxidants and interact with the polymer surface to form polar functional groups. Evidence for H₂O dissociation under plasma conditions is shown in Figure 4. The mass spectra were rich in H₂ molecules, and their appearance was attributed to the dissociation of water molecules and subsequent association of H radicals into H₂ molecules. The dissociation may occur by either electron impact or interaction with a metastable Ar atom. Therefore, there were at least two mechanisms that ensured successful formation of oxygen-rich functional groups on the surface of the polymer: (1) formation of dangling bonds on the polymer surface due to irradiation with hard UV radiation and oxidation of this modified polymer with water vapour; and (2) dissociation of water molecules under plasma conditions and interaction of OH radicals with the polymer surface. Unfortunately, the techniques adopted in this study did not allow differentiation between the mechanisms, thus it was not possible to state the prevailing one. Regardless, the high concentration of oxygen at the interface between the polymer substrate and the aluminium film, as evidenced by the XPS depth profile (Figure 6) was explained by the presence of water vapour in the plasma reactor during the activation step.

The broadness of the interface was probably not due to penetration of oxygen deep into the polymer substrate but rather to its roughness. As mentioned above, the industrial polymer samples exhibit a roughness of approximately $S_a = 5 \text{ nm}$ ($S_q = 6.5 \text{ nm}$), which is reflected in Figure 6 as the broad interface. The oxygen-rich layer spans between approximately 70 and 120 nm in Figure 6. On top of this layer, there is a film of aluminium. The aluminium film is almost free from other elements due to the rapid deposition. Nevertheless, one can observe a measurable amount of oxygen (perhaps 5 at.%) in the aluminium film in Figure 6, which was due to the water vapour-rich residual atmosphere. The water molecules absorb on the freshly deposited aluminium and form AlO_x compounds. If the deposition occurred in a very short time or if the water concentration were negligible during aluminium deposition, the Al film would have been free from oxygen. These conditions, however, cannot be ensured in industrial reactors.

On top of the Al film in Figure 6, there is another layer rich in oxygen followed by a thin film of the protective coating. Again, the broad interface was attributed to the sample roughness. The rather large amount of oxygen in this interface was attributed to the fact that the deposition using HMDSO does not start immediately after completing Al deposition, so there is enough time for the formation

of an oxide film on the freshly deposited aluminium surface (see the discussion on molecular fluxes above). Figure 7 shows the stack of Al 2p spectra obtained during XPS depth profiling of the layered structure of the sample. It can be seen that the spectra from the first Al-layer interface had a peak at a binding energy of 74.0 eV, meaning that Al-oxide was formed on the top of the Al-layer. The Al 2p spectra from the central part of the Al layer had a peak at a binding energy 71.8 eV related with Al in its metallic form. At the interface between the metallic Al and the polymer substrate, the Al 2p spectra again had peak at a binding energy of 74.0 eV, indicating that Al-oxide was formed in the first stage of deposition of the Al-film. The results presented in Figure 7 therefore clearly confirm partial oxidation of the Al film at both interfaces. This thin film of oxide on the surface of the aluminium coating was beneficial for adhesion of the protective coating since the surface energy (and thus wettability) of oxides is generally higher than that of pure metals.

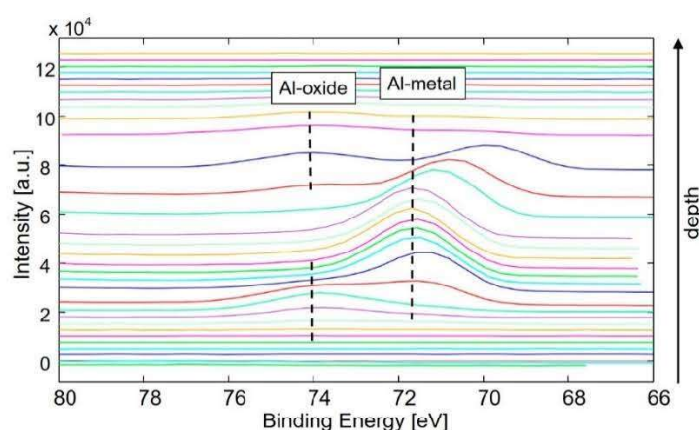


Figure 7. Al 2p spectra obtained during XPS depth profiling of the deposited sample.

The uppermost protective coating in Figure 6 contains silicon, oxygen and carbon. This observation was explained by partial dissociation of HMDSO under plasma conditions. Radicals were formed from the precursor, and the molecular fragments adsorbed onto the substrates, forming a layer composed of Si, C, H and O. The radicalisation led to formation of the CH_x and H radicals, which was evident from the optical spectrum shown in Figure 5. The mass spectra (Figure 4), however, revealed very rich plasma chemistry upon depositing the protective coating on freshly metallised polymer substrates. Since water vapour was present during the PECVD process (see Figure 4), the OH radicals might interact chemically with the freshly adsorbed layer of precursor radicals, forming SiO_x , as explained above for the case of surface activation of the polymer substrate and oxidation of the topmost aluminium film.

The depth profile in Figure 6 shows only a rough composition of the silicon-rich film and does not reveal much about the structure. To obtain insight into the structure of the protective coating, we also acquired high-resolution XPS spectra and performed SIMS characterisation. Figure 8 shows high-resolution spectra acquired on the surface of a sample coated with the protective coating. The selected range of binding energies corresponded to silicon, oxygen and carbon. The silicon XPS peaks were at a binding energy of 102.3 eV. This binding energy was representative of C–Si–O bonds. The absence of a peak at 103.5 eV revealed that there was practically no SiO_2 molecules; rather, the topmost layer was a plasma-polymerised film of C–Si–O, which should offer good corrosion protection to the Al-metallisation layer [29]. As mentioned above and elaborated by Prykriil et al. [8], the carbon-free coating obtained by PECVD using HMDSO was extremely fragile and tended to crack. The polymer-like coating with an appropriate structure, as revealed in this work, was more flexible than the carbon-free coating and is thus useful in many applications. Figure 8 also shows the high-resolution oxygen O 1s spectrum with peaks at 532.7 eV. This binding energy is often related to C–Si–O bonds, thus the result is consistent with the position of the Si peak. Finally, the carbon C 1s XPS spectrum is

also shown in Figure 8. The binding energy of this peak was at 284.8 eV, which was assigned to carbon bonded with hydrogen, silicon or another carbon rather than to oxidised carbon such as $\text{O}-\text{C}=\text{O}$, $\text{C}=\text{O}$, or $\text{C}-\text{O}$. The high-resolution XPS spectra therefore indicated a structure practically free from silica and carbon atoms bonded to silicon rather than oxygen.

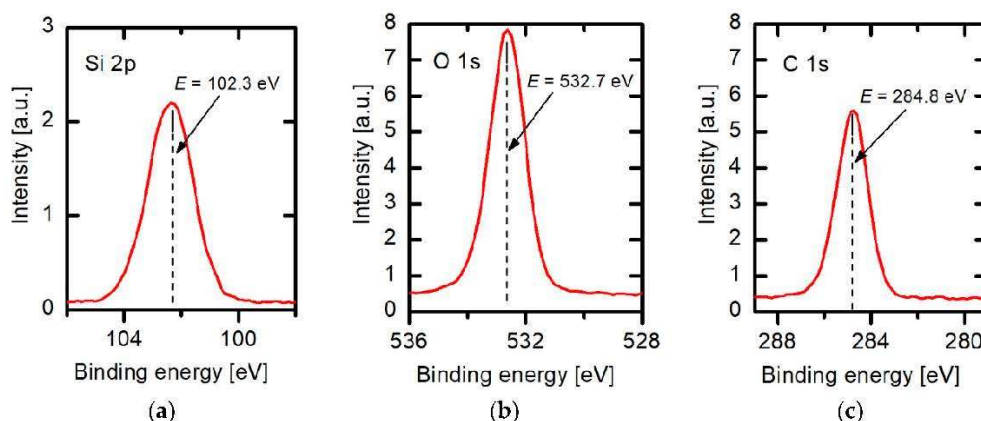


Figure 8. High energy resolution XPS spectra obtained on the surface of the deposited sample of: (a) Si 2p; (b) O 1s; and (c) C 1s.

Additional information about the structure of the deposited protective coating is available from an alternative technique for surface characterisation-ToF-SIMS. The spectrum of positively charged secondary ions emitted from the surface of a sample irradiated with energetic bismuth clusters is shown in Figure 9 in the mass range of 1–200 amu. The main peaks in this spectrum were at 27.97 (Si^+), 42.99 (SiCH_3^+), 59.03 (SiC_2H_7^+), 73.05 (SiC_3H_9^+) and 147.05 amu ($\text{Si}_2\text{C}_5\text{H}_{15}\text{O}^+$). These peaks were actually clusters of the Si–C–H–O compound that forms the uppermost protective layer. The peaks were typical of polydimethylsiloxane [30]. The SIMS spectrum shown in Figure 9 is therefore consistent with the XPS spectra shown in Figure 8. The high concentration of hydrogen in the secondary ion clusters also indicated the polymer-like structure of the deposited protective coating.

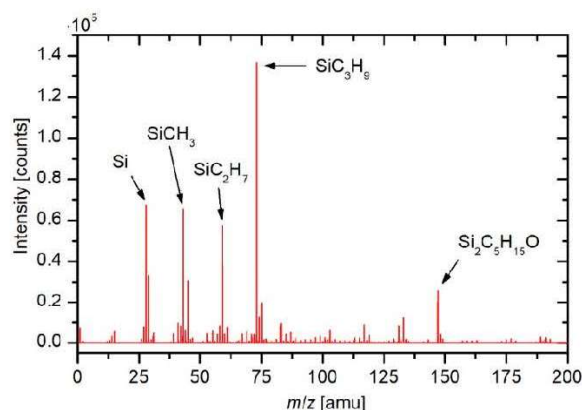


Figure 9. ToF-SIMS spectrum of positive secondary ions emitted from the surface of the deposited sample.

A fundamental discrepancy between the processes of plasma activation and deposition of the protective coating might be observed. As explained above, the gaseous plasma was suitable for formation of oxygen-rich functional groups on the polymer surface during the activation process (5–7 min in Figures 3 and 4), however no measurable oxidation of the protective polymer coating

was revealed from the XPS and SIMS results, as shown in Figures 6–9. This fundamental discrepancy was explained by the various gas-phase and surface reactions involved. The activation process was performed using argon plasma and taking advantage of the presence of water vapour to ensure appropriate surface activation of the polymer substrate. Although the power density was low, the irradiation with bond-breaking UV radiation and oxidation with OH or H₂O molecules were sufficient to functionalise the substrate with polar groups rich in oxygen. During the plasma polymerisation step, however, HMDSO molecules were the predominant gaseous species. Compared to Ar molecules, HMDSO molecules had numerous channels for the loss of electron energy upon collision. The numerous dissociative collisions effectively lowered the electron temperature in HMDSO compared to Ar, thus the electrons were not energetic enough to atomise the molecules. The majority of the available electron energy in the HMDSO plasma was therefore spent on only partial radicalisation of these molecules. As a result, the main backbone of HMDSO was preserved, thus the protective coating grew from molecular fragments rather than atoms. Silicon in HMDSO therefore remained bonded to oxygen and carbon, and this material exhibited much less affinity for oxidation by OH radicals than the polymer substrate, let alone freshly deposited aluminium. Furthermore, as the electron energy was spent preferentially on radicalisation of HMDSO, the water vapour was not dissociated to reactive OH radicals as much as it was in argon plasma, thus the available flux of this highly oxidative radical was not large enough to cause complete oxidation of the Si–C–H–O coating and formation of SiO_x within the protective coating.

4. Conclusions

The combination of various techniques for plasma and surface characterisation adopted in this work provided insight into the mechanisms involved both in the gas phase and on the surfaces of materials facing plasma upon deposition of an appropriate protective coating onto polymer substrates in a large industrial plasma reactor. The reactor configuration enabled appropriate gas composition during all three production steps: surface functionalisation, aluminization and deposition of a protective coating resembling polydimethylsiloxane. The activation process was performed with argon plasma. The lack of electron energy loss mechanisms in argon plasma resulted in preferential dissociation of water vapour molecules present in the residual atmosphere. The resultant H atoms were excited to radiative states, providing UV radiation that caused bond breaking in the polymer surface. The OH radicals enhanced the oxidation of the polymer surface and thus the formation of oxygen-rich functional groups that endowed the polymer substrates with appropriate surface energy to ensure good adhesion of the aluminium coating. In the phase of plasma polymerisation of the protective coating, however, the electron energy was spent preferentially on partial dissociation of the HMDSO precursor. The nature of the deposited film and lack of highly reactive oxygen-containing radicals enabled preservation of the C–Si–O bonds and thus formation of a coating resembling polydimethylsiloxane rather than more extensive oxidation of the protective coating and consequent formation of SiO_x clusters in the film, which was observed by several other authors upon intentionally adding oxygen to HMDSO upon plasma deposition of protective coatings [6,8,10–12].

Supplementary Materials: The following are available online at <http://www.mdpi.com/2079-6412/9/4/234/s1>, Figure S1: One of the AFM images of the untreated sample. Measurements with AFM were performed on 3 samples at different places. The average roughness was around $S_a = 5$ nm ($S_q = 6.5$ nm), Figure S2: Mass spectrometry of gaseous molecules of higher masses during all phases of the production process.

Author Contributions: Conceptualisation, Ž.G., M.M. and R.Z.; Methodology, A.V. and J.K.; Validation, G.P. and A.V.; Formal Analysis, R.Z. and J.K.; Investigation, R.Z., J.K. and Ž.G.; Resources, Ž.G., R.Z. and J.K.; Data Curation, J.K., R.Z. and G.P.; Writing—Original Draft Preparation, Ž.G. and M.M.; Writing—Review and Editing, Ž.G., M.M., A.V. and R.Z.; Visualisation, R.Z.; Supervision, Ž.G. and M.M.; Project Administration, A.V. and G.P.; Funding Acquisition, M.M.

Funding: This research was funded by the Slovenian Research Agency (research core funding No. P2-0082-Thin film structures and plasma surface engineering, as well as project No. L2-8179-Evaluation of the range of plasma parameters suitable for nanostructuring of polymers on industrial scale).

Acknowledgments: The authors thank the Elvez Company for allowing them to use one of their large industrial plasma reactor.

Conflicts of Interest: The authors declare no conflict of interest.

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Supplementary Materials: Deposition of SiO_xC_yH_z Protective Coatings on Polymer Substrates in an Industrial-Scale PECVD Reactor

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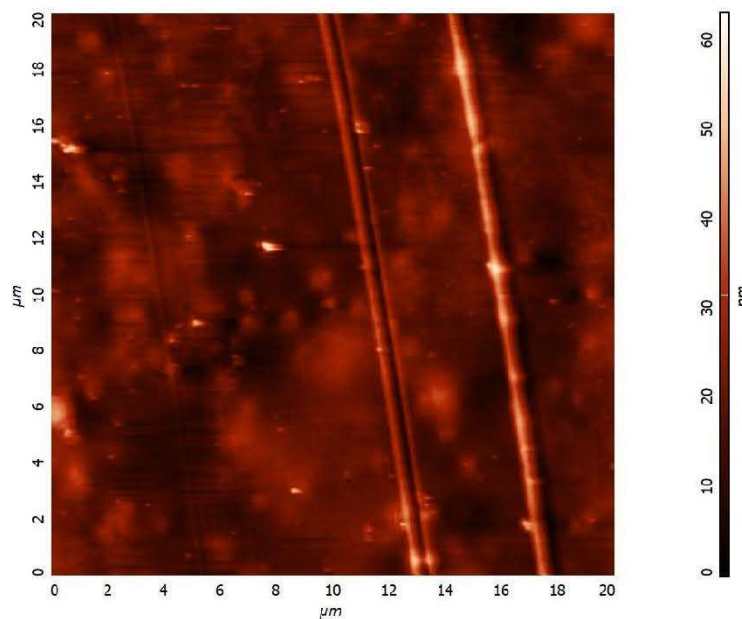


Figure S1. One of the AFM images of the untreated sample. Measurements with AFM were performed on 3 samples at different places. The average roughness was around $S_a = 5$ nm ($S_q = 6.5$ nm).

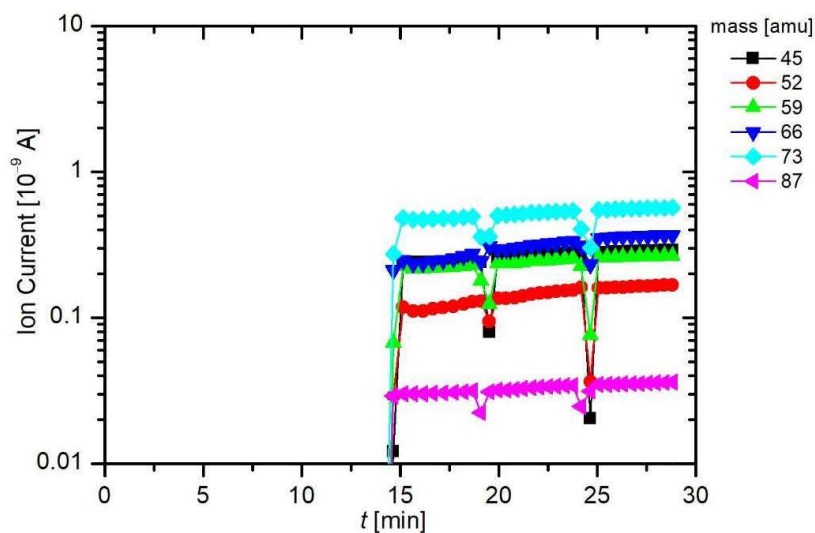


Figure S2. Mass spectrometry of gaseous molecules of higher masses during all phases of the production process.



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Chapter 3

Characterization of HMDSO+O₂ Plasma in an Industrial-Scale Reactor

The processes involved in the plasma treatment of polymer compounds can be understood if plasma properties are known. In this article, we reported the results of plasma characterization. Gaseous plasma was sustained in the industrial reactor shown in Figure 1. We presented the electrode configuration and details about the gas inlet, which is important for proper interpretation of the signals obtained by probes for plasma diagnostics. In this paper, we used optical spectroscopy and mass spectrometry. While the first method is qualitative, it turned out very useful in combination with mass spectrometry, which is semi-quantitative. None technique is absolute. Optical spectroscopy measures the signal of photoelectrode at different wavelengths of the radiation (between about 200 and 1000 nm). We have calibrated the spectral response prior to measurements and measured the “dark spectrum” in order to assure reliable results. Mass spectrometry measures the ion currents at different adjustments of the quadrupole filter. The ions are created in the ionization chamber of the mass spectrometer by inelastic collisions with quasi-monoenergetic electrons, which also lead to dissociation of gaseous molecules, so the interpretation of the ion current spectra should be taken with precautions. The discharge characteristics are also reported in this paper. The voltage and current of the low-frequency RF generator were measured. On the basis of a simple but useful model, we calculated the ion density in gaseous plasma and discussed the reasons for the density, which is at least an order of magnitude smaller than in common experimental systems. Unlike in the previous paper, the plasma was ignited and sustained in a mixture of oxygen and HMDSO. Optical spectra in such mixtures were measured and discussed. Spectra were first measured in the reactor at the base pressure. Apart from a weak oxygen line at 777 nm, the spectra were rich in H-atom transitions belonging to the Balmer series. Rather weak molecular transitions indicated a small concentration of H₂ molecules, which was explained by incomplete dissociation of H₂O molecules and a poor association of H-atoms to H₂ molecules. When oxygen only was introduced, the rather intensive band arising from the transition of ionized oxygen molecules was observed and explained by the presence of fast electrons in the oscillating sheath next to the powered electrode. As long as plasma is sustained in pure HMDSO, the only distinguished spectral features were the hydrogen atom Balmer series and the CH band with the measurable intensity of the transitions from the ground vibrational state. However, the spectrum in the mixture of HMDSO and oxygen was rich in various features, including the CO bands. A continuum was also observed but could not be related to any specific species because several CO, CO⁺, O₂⁺, and CH bands were overlapping. Poor emission from oxygen atoms indicated a rather low dissociation

fraction of oxygen molecules what was explained by various mechanisms. Systematic measurements of ion currents using the mass spectrometer are also presented in this rather extensive article. The results clearly showed different behaviors of various molecules. The ion currents of low-mass fragments of HMDSO increased with increasing discharge power, but the high-mass radicals intensity decreased. The mass spectrometry, therefore, showed clearly the evolution of the fragmentation of the precursor molecules upon plasma conditions, in particular the influence of the discharge power. The article is recommended literature for a broad community of scientists and users of PECVD technique for deposition of polymer-like films since it is the first report about the behavior of plasma parameters in an industrial-scale reactor.



Characterization of Gaseous Plasma Sustained in Mixtures of HMDSO and O₂ in an Industrial-Scale Reactor

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Received: 15 April 2019 / Accepted: 1 September 2019 / Published online: 4 September 2019
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Abstract

Optical emission spectroscopy and mass spectrometry was used to characterize gaseous plasma in an industrial reactor of volume 5 m³ during deposition of protective coatings. Plasma was created in mixtures of hexamethyldisiloxane (HMDSO) and oxygen at the powers between 1 and 8 kW. The plasma density was somehow below 10¹⁴ m⁻³. The flows of both gases were varied up to 200 sccm while the effective pumping speed was adjusted by changing the roots pump rotation speed between 250 and 4000 rpm. At such conditions the HMDSO was only partially dissociated to fragments. The behaviour of optical emission lines and mass ion currents was well correlated indicating that even one single technique was sufficient to monitor the behaviour of plasma at various discharge conditions. The optical emission spectroscopy as a simple and economic method is therefore suitable for controlling key processing parameters in such a plasma reactor.

Keywords Optical emission spectroscopy (OES) · Industrial-scale low pressure plasma · Hexamethyldisiloxane (HMDSO) · Residual gas analyser (RGA)

Introduction

Plasma created in HMDSO or mixtures with other gases, in particular water vapor and oxygen, is a suitable medium for deposition of thin films containing silicon, oxygen, carbon and hydrogen. The properties of such thin films depend on numerous parameters such as the size and geometry of the plasma reactor, the type of discharge and particularities of discharge coupling, the discharge power, the flow rates of gases, the pressure in the plasma reactor and the effective pumping speed, the composition of the residual atmosphere, and

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the properties of materials mounted inside the plasma reactor. The number of parameters is by far too large to predict the behavior of gaseous plasma at different conditions, so the best processing parameters in industrial-scale plasma reactors are often determined according to the quality of the deposited films. Such an approach enables routine use of the reactor as long as the processing parameters remain in the prescribed ranges. In many cases, however, some parameters may vary unintentionally so it is useful to adopt a technique for plasma characterization as a tool for controlling the production process.

The rough estimation of useful processing parameters in industrial reactors is based on detailed study of plasma parameters in small experimental reactors, and characterization of deposited films. Numerous authors reported the influence of processing parameters on the quality of deposited films using small, often flexible experimental reactors of typical volume few liters. Pandiyaraj et al. [1] used plasma created in a mixture of Ar, HMDSO and O₂ by a magnetized DC discharge to deposit high quality SiO_x films on a polymer substrate. The ultimate pressure as estimated with a Pirani gauge was about 0.1 Pa, while the pressure upon depositing the coating was about 20 Pa. In spite of using a rather high ratio between oxygen and HMDSO flow rates the resultant films contained substantial amount of carbon. A similar magnetized discharge was used also by Bian et al. [2], where they managed to estimate some plasma parameters using optical emission spectroscopy. The powerful discharge enabled the electron density exceeding 10^{21} m^{-3} . At such conditions the precursor was highly dissociated resulting in interesting properties of the coatings. Farag et al. [3] used a metallic chamber of volume 50 l to deposit coatings of various properties. They applied an asymmetric capacitively coupled RF discharge at the frequency 13.56 MHz and adjustable power up to 140 W. Plasma was created at various mixtures of HMDSO and oxygen. In this particular system, the concentration of carbon in the deposited films remained measurable even for very large O₂ to HMDSO flow ratio. The O/C ratio was determined by XPS, but the high-resolution C1s spectra didn't show remarkable carbon concentration at the HMDSO to O₂ flow ratio 1:12. At the flow ratio 1:1 the O/C ratio was already about 15, revealing very low carbon concentration. Begou et al. [4] used a helicon-type discharge to create plasma suitable for deposition of coatings using HMDSO and oxygen at various mixtures. The coil was powered with an RF generator of frequency 13.56 MHz and power 300 W. The gas pressure was varied by adjusting the gas flow rates, but a typical pressure was around 1 Pa. At that particular conditions, silica-like coatings were obtained at HMDSO to O₂ flow ratio 1:3, while at larger ratios in favor to HMDSO, polymer-like coatings were observed. Hoppe et al. [5], on the other hand, used a glass reactor with a volume of 6 l and a diameter of 140 mm, powered with a microwave discharge. They used oxygen with a small admixture of HMDSO in order to synthesize silica-like films. They report measurements of the O atom density in such a plasma and the resultant flux of atomic oxygen onto the substrates was about $7 \times 10^{22} \text{ m}^{-2} \text{ s}^{-1}$. An interesting paper was published by Ricci et al. [6]. They used in situ real time resolved Fourier transform infrared spectroscopy (FTIR) [7] for characterization of HMDSO–O₂ plasma sustained in a small reactor powered with an RF generator at powers of few 10 W. Numerous monomer fragments were detected as well as some products of their interaction with oxygen. Formation of dust particles was elaborated as well. At that particular experimental conditions the formation of measurable amount of dust particles was observed after about half a minute of plasma time. The size of dust particles increased with increasing time. Addition of argon was found an effective method to suppress dust formation.

The formation of dust particles was elaborated recently by the group from Laplace laboratory [8]. In this comprehensive paper the authors report results of rather thorough plasma characterization and propose mechanisms of radicals' kinetics. A small reactor powered

with a 13.56 MHz capacitively coupled RF generator was adopted. The authors reported self-biasing of the powered electrode to -600 V at the discharge power of 30 W. Plasma was sustained in argon and HMDSO was introduced into the plasma reactor in pulses. Such experimental conditions enabled detailed study of dust particle formation and disappearance. The experiments were almost perfectly repeatable. The dust cloud filled the plasma reactor in about a minute, and collapsed due to ion drag forces after 2 or 3 min. The $\alpha \rightarrow \gamma$ transition began at the stage of dust formation whereas the reverse transition occurred when dust disappeared from the plasma. Mass spectrometry showed solid fragmentation which proceeded with plasma time, similar to what was observed by Ricci using FTIR [6] and early works on characterization of such plasma by mass spectrometry [9]. Sputtering of organosilicon coating might have also occurred due to large self-biasing of the substrate. The authors reported substantial draining of the slow plasma electrons by attachment to the dust particles, what was already suggested in [10]. Optical emission spectroscopy was applied to monitor the evolution of atomic hydrogen. The H-atoms inhibited dust formation by delaying the nucleation stage.

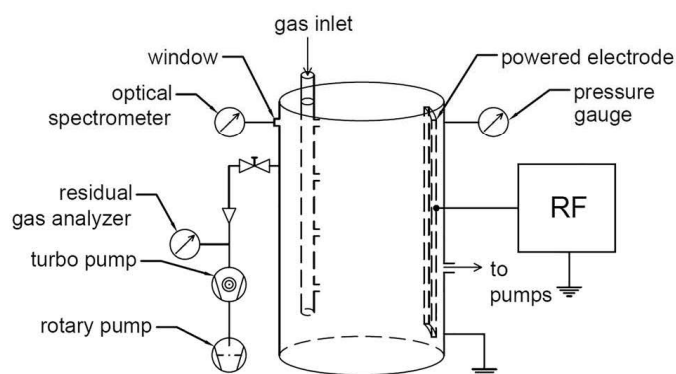
All these papers reveal details about gaseous plasma created in HMDSO at low pressure where the dust formation is either suppressed or at least controlled. Recently, atmospheric-pressure discharges became attractive for deposition of similar coatings and some authors recommend them as a future solution in industrial systems [11] but at present such high-pressure treatments are limited to coating of one- or two-dimensional materials such as textiles or foils [12]. Namely, the uniformity of three-dimensional plasma is increasingly difficult to achieve as the pressure increases and the dust formation also increases with increasing pressure.

Despite the fact that the plasma-enhanced chemical vapor deposition of thin films containing Si, O, C and H has been commercialized years ago there is very little literature on characterization of such a gaseous plasma in reactors measuring several m^3 . Among them, the papers by Corbella et al. [13, 14] reported methods for upscaling from 0.1 to 1 m^3 reactor, but no details about plasma parameters have been revealed.

Experimental

Gaseous plasma was characterized in an industrial system. Schematic of the reactor is shown in Fig. 1. The reactor is of cylindrical shape with 1.9 m diameter and height 1.8 m. The volume is therefore about 5 m^3 . The reactor is pumped with several vacuum pumps

Fig. 1 Schematic of the plasma reactor

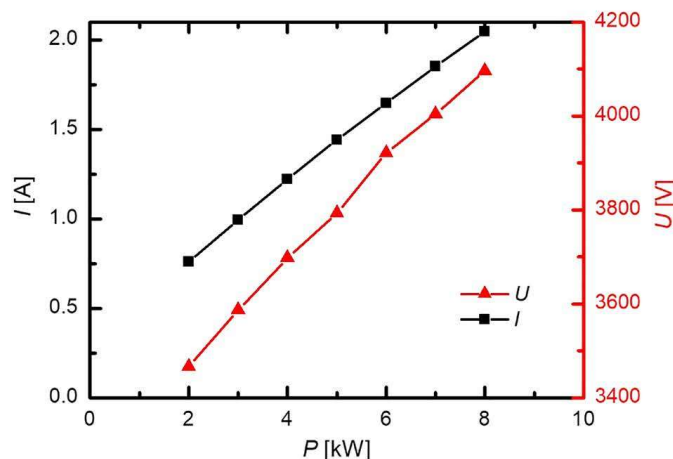


including a cold trap and a couple of diffusion pumps backed by roots and rotary pumps. The pumps are used for pumping the reactor in reasonable time down to the pressure in the range of 10^{-2} Pa. When the reactor is filled with selected gases and plasma is sustained, the reactor is only pumped with the roots and rotary pumps. The nominal pumping speed of the roots pumps is 8800 m³/h at the rotational speed of 4000 rpm. At lower rotational speeds the pumping speed is correspondingly suppressed thus allowing for larger pressure at a given flow rate and longer residence time of gases in the plasma reactor. Gases are fed through a perforated tube to assure rather even distribution of gas inlet into the plasma reactor. The gases are introduced through flow controllers calibrated for HMDSO and oxygen. Plasma is sustained by an asymmetric capacitively coupled RF discharge. Two powered electrodes of area about 0.5 m² each are located few cm from the grounded housing as shown schematically in Fig. 1. The total surface of the grounded housing is almost 17 m². The electrode is connected to an RF generator of adjustable output power up to 8 kW which operates at the frequency of 40 kHz. Pressure in the plasma reactor is estimated with a Pirani gauge, which was previously calibrated for dry air, and Penning gauge for pressures under 1 Pa. An optical spectrometer was connected to an optical fiber, which was fixed onto a small optically transparent window to enable sampling of any radiation in the range of wavelengths from 200 to 1000 nm. The window was not transparent for wavelengths below about 340 nm so UV radiation was not detectable. We used a low-resolution (0.5 nm) spectrometer Avantes AvaSpec-3648 with a 3648 pixels CCD linear array and a 16-bit AD (analog-to-digital) converter. The integration time for all measurements presented in this work was 5 s. A differentially pumped residual gas analyzer (Pfeiffer Prisma-Plus QMG 220) was also mounted onto the plasma reactor as shown in Fig. 1. The range of detectable ion masses was up to 100 Da. There was a small orifice between the reactor and the gas analyzer so most condensable molecules were effectively adsorbed on the surfaces before reaching the spectrometer. Both optical and mass spectra were acquired versus the flows of HMDSO and oxygen for different powers and rotational speeds of the roots pump.

Results and Discussion

The RF generator allowed for adjustment of either voltage, current or power. At the experiments reported in this paper we selected different powers. The corresponding voltages and currents depended slightly on the pressure and gas composition in the plasma reactor, but a typical behavior is presented in Fig. 2. The curves were measured in a gas mixture with the HMDSO flow of 10 sccm and 200 sccm of oxygen. The corresponding pressure as indicated by the Pirani gauge was around 2.5 Pa. The voltage and current increased monotonously with increasing discharge power. The voltage was between approximately 3400 and 4100 V and the current between about 0.7 and 2 A. Taking into account the fact that the voltage on both powered and grounded electrode distribute unevenly in an RF discharge of asymmetric electrodes as a ratio of electrode areas, practically all potential drop occurs between the small powered electrode and gaseous plasma due to the self-biasing effect. The available discharge power is partially absorbed in the sheath next to the electrode to ensure appropriate energy for ion bombardment of the electrode as well as for accelerating electrons, and partially for heating the electron fluid in bulk plasma. According to classical literature [15] the heating of electrons is dominant at the pressure of several Pa as adopted in this work. In spite of this, a substantial amount of energy is dissipated on the surface of the powered electrode causing its heating and enhanced deposition of the polymer film.

Fig. 2 The voltage and current versus the discharge power in a gas mixture plasma with HMDSO and oxygen flow of 10 and 200 sccm, respectively



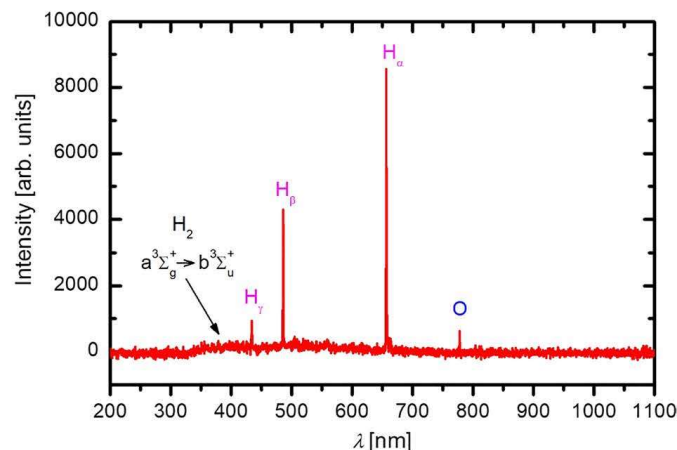
The electrode is therefore coated with a thin dielectric film. This effect complicates the traditional definition of the self-bias voltage as the mean of the RF waveform [16]. Still, the discharge voltage as shown in Fig. 2 represents a rough (overestimated) value of the potential drop next to the powered electrode and thus the kinetic energy of ions bombarding the electrode in the approximation of a collision-less sheath. The kinetic energy of ions is several keV. Knowing the current and kinetic energy of ions one can roughly estimate the density of ions in gaseous plasma:

$$n = \frac{I}{S \cdot v \cdot e_0} = \frac{I}{S \cdot \sqrt{\frac{2 \cdot W}{m}} \cdot e_0}. \quad (1)$$

Here, I is the measured current, S the area of the electrode, v and W the velocity and the kinetic energy of ions bombarding the electrode, respectively, e_0 the elementary charge and m the ion mass. The ion mass is not known since there are numerous ionized molecular fragments of different masses so the already simplified Eq. (1) gives only the order of magnitude of the ion density in the gaseous plasma facing the electrode. Still, it enables a rough estimation of the plasma density in systems where other (much more accurate) techniques for plasma diagnosis cannot be applied. The Laplace group [8] found the most abundant positively charged ions in their HMDSO reactor CH_4^+ and C_2H_2^+ at almost equal densities so the “average” mass of an ion in our reactor can be taken as 20 Da. Taking into account the values $I=1$ A, $S=0.5$ m², $W=5$ keV, $m=3 \times 10^{-26}$ kg, one obtains the plasma density just below 1×10^{14} m⁻³. This value is smaller than in most experimental plasma reactors. The ionization fraction is the ratio between charged and neutral particle densities. The latter is estimated from the measured pressure using the standard equation $p=n \cdot k \cdot T$. Taking into account the numerical values one obtains the ionization fraction around 10^{-7} . Here, we have to stress that the numerical values given in this paragraph are just rough estimates. Unfortunately, it is not feasible to place an electrical probe into this type of industrial reactor and measure the plasma density.

A suitable technique for remote plasma characterization is optical emission spectroscopy. An optical spectrum of gaseous plasma sustained at the base pressure i.e. the lowest possible pressure achievable with the roots pump operating at 4000 rpm (about 1 Pa) and discharge power 4 kW is shown in Fig. 3. The spectrum is dominated by H-atom transitions from higher excited to the first excited state (Balmer series). There are also weak

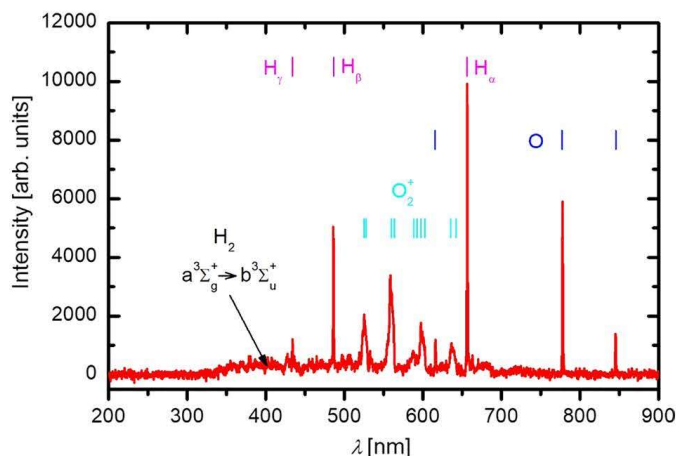
Fig. 3 An optical spectrum of plasma at the base pressure



transitions from excited oxygen atoms and a broad continuum arising from transition of neutral hydrogen molecules in the triplet state (transition $a^3\Sigma_g^+ \rightarrow b^3\Sigma_u^+$) at the excitation energy of about 11 eV. The spectra indicate rather high dissociation of water molecules. The dissociation occurs at inelastic collisions of plasma electrons with water vapor which is by far the most abundant gas at base pressure. The dissociation leads to formation of H and OH radicals, but the latter is not visible in the spectrum since the radiative transition of OH radicals occurs at the bandhead of about 309 nm where the optical window mounted onto the reactor is not transparent. The fact that the H Balmer series is so intensive is explained by a rather poor recombination of H atoms. At the pressure of 1 Pa the recombination does not occur in the gas phase since such recombination events are feasible only at a three body collision to satisfy conservation of energy and momentum. The frequency of three-body collisions increases as the square of the pressure and becomes important at pressure of roughly 1000 Pa [17]. The recombination of these radicals can occur only on surfaces of plasma reactor at the pressure of about 1 Pa. The recombination coefficient depends on the type of material. In our reactor, the surface is coated with a layer rich in Si and O. The H atoms tend to associate not only to water molecules but to H₂ as well. The coefficient for heterogeneous surface recombination of H atoms into H₂ molecules, however, is rather small. Several authors reported different values for association of H atoms on silica surface, but the values range from about 10^{-5} to 10^{-3} at room temperature [18]. The rather small recombination coefficient therefore ensures for a rather high density of H atoms as demonstrated qualitatively from Fig. 3. If the walls were not covered with a thin silica-like coating the loss of atoms on surfaces would have been much larger. For stainless steel, for example, the coefficient is as large as 10^{-1} [19], so several orders of magnitude larger than on silica.

Introduction of oxygen into the plasma reactor causes enrichment of the optical spectra. Figure 4 reveals an optical spectrum at 200 sccm oxygen flow, discharge power 4 kW and roots pump operating at 4000 rpm. The H lines still persist but are comparable to some other spectral features such as the atomic oxygen lines at 777 and 845 nm and radiation bands occurring at transitions of excited positively charged oxygen molecules. The dissociation of water molecules is therefore still high at such a rather high oxygen flow which corresponds to the gas pressure of 2.5 Pa as indicated by the Pirani gauge. Interesting enough, the continuum arising from hydrogen molecules is clearly distinguishable in Fig. 4 and comparable to that of Fig. 3. The addition of a large amount of oxygen obviously does not

Fig. 4 An optical spectrum of plasma at oxygen flow of 200 sccm



prevent association of H atoms to hydrogen molecules (and not to OH radicals or water molecules). The evolution of spectral features versus the flow of oxygen into the plasma reactor is shown in Fig. 5. The atomic hydrogen lines (H_α and H_β) are almost independent from the oxygen flow (in fact they even increase slightly with increasing oxygen flow) but the oxygen features increase with increasing flow monotonously. The introduction of oxygen into the gaseous plasma therefore does not inhibit the dissociation of H_2 molecules and excitation of H-atoms to radiative states so one can qualitatively conclude that the electron density and temperature does not depend much on the flow of oxygen into the plasma reactor.

The optical spectrum is different when HMDSO is introduced into the plasma reactor instead of oxygen. Figure 6 shows a spectrum acquired at the HMDSO flow of 200 sccm corresponding to the pressure of 6 Pa. All other discharge parameters (power, roots pump) were the same as in Figs. 3, 4 and 5. In this case, the O-atom lines at 777 and 845 nm became immeasurably small indicating consumption of oxygen atoms formed upon complete dissociation of water vapor for interaction with HMDSO fragments. The O atoms therefore interact chemically with the freshly deposited polymer-like layer. Furthermore, the hydrogenated carbon molecules which were detected in a smaller reactor by Ricci

Fig. 5 Behavior of selected spectral features in oxygen plasma

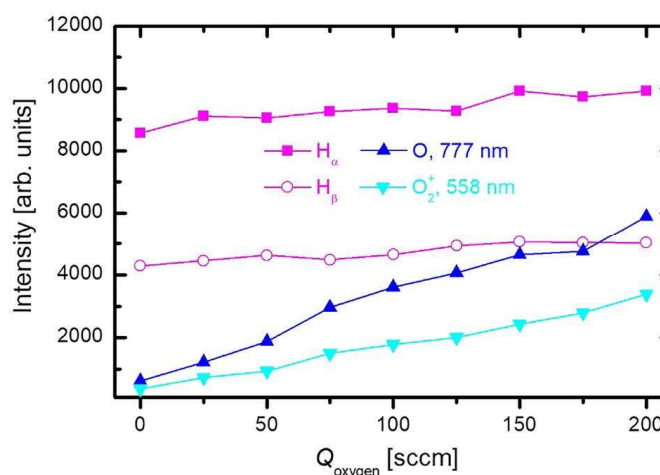
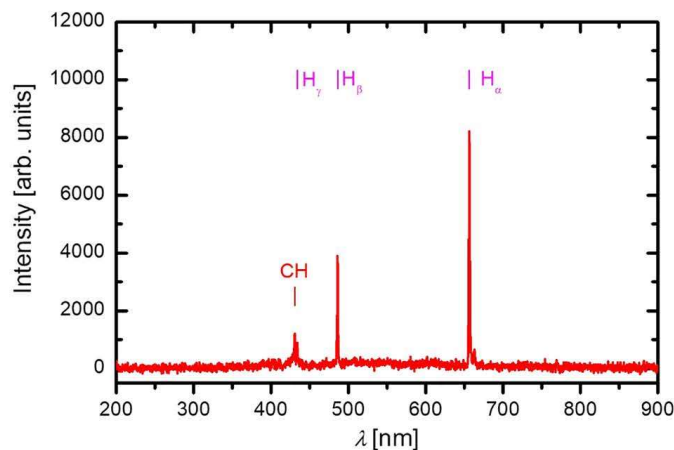


Fig. 6 An optical spectrum of plasma at HMDSO flow of 200 sccm



et al. [6] adsorb on the surfaces facing plasma where they can interact with oxygen atoms to form various compounds. The simplest is the CO molecule that should have emission bands in optical spectra (see further text). The bands are not observed in Fig. 6, what can be explained either by rather low concentration of CO molecules in the gas phase or poor excitation to radiative states. An important spectral feature in Fig. 6 arises from excited CH radicals with the bandhead at 431 nm. The presence of this radical confirms subtraction of the methyl radical from the HMDSO and also dissociation of CH₃ to CH (and probably also CH₂). Unfortunately, the CH₂ and CH₃ radicals cannot be detected with the used OES spectrometer, while their emission is either out of the measured range or is a part of the weak continuum that is probably lost in the noise. These radicals could be measured with optical absorption techniques, like in studies Ropcke et al. [20] or Nave et al. [21], but unfortunately these kind of measurements are usually applicable only in laboratory setups and not on industrial systems.

The evolution of spectral features in the range between 415 and 445 nm versus the HMDSO flow is presented in Fig. 7. One can observe gradual increase of the CH feature and simultaneous decrease of the H γ line with increasing flow of HMDSO. The behavior of selected spectral features for the case of HMDSO is shown in Fig. 8. The H-atom lines do not increase with increasing HMDSO flow as one would expect since the HMDSO

Fig. 7 The evolution of spectral features in the range between 415 and 445 nm versus the HMDSO flow

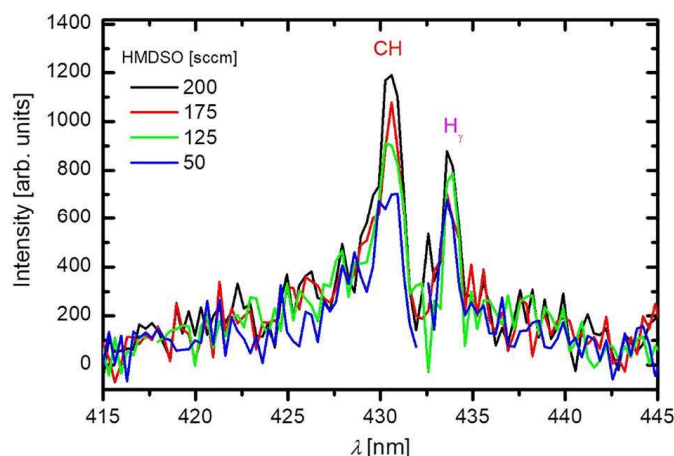
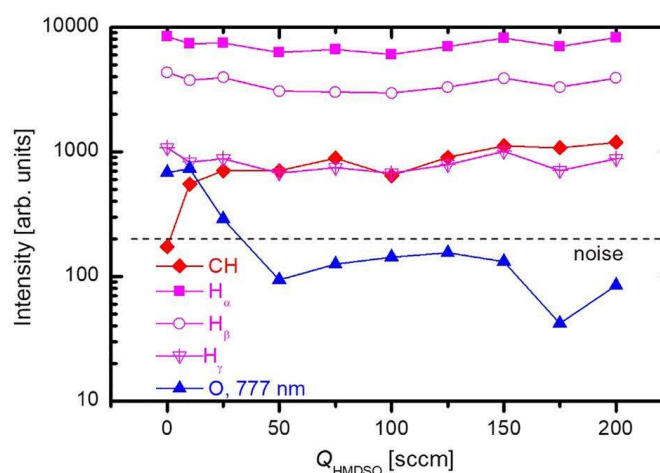


Fig. 8 Behavior of selected spectral features in HMDSO plasma



molecules contain hydrogen. This behavior of the H atom lines in Fig. 8 can be explained by poor excitation of atomic hydrogen at increasing flow of HMDSO. A feasible explanation of this effect has been already provided by [8]: the electron temperature in HMDSO plasma before formation of dust particles is much lower than in plasma of water vapor or oxygen. Namely, there are numerous channels for the loss of electron energy upon colliding with HMDSO molecules as well as their fragments. The electrons from the high-energy tail are lost by dissociation of the HMDSO molecules and excitation of numerous fragments so the excitation of atomic hydrogen to radiative states of Balmer series is rather suppressed.

Figure 9 represents an optical spectrum of plasma of gas mixture with HMDSO and oxygen flows of 10 and 200 sccm, respectively. The other parameters (discharge power, roots pump) were the same as in Figs. 3, 4, 5, 6, 7 and 8. Apart from previously observed features there are clearly distinguished bands corresponding not only to CO molecules but also CO^+ ions. The rather large flow of oxygen as compared to HMDSO obviously causes extensive oxidation of hydrocarbons that are released from HMDSO molecules upon dissociation by electron impact. The electron temperature in plasma sustained at large oxygen and low HMDSO concentrations is obviously large enough to assure for ionization of the CO molecules as well as significant excitation of CO^+ ions to radiative states. From

Fig. 9 An optical spectrum of gas mixture plasma with HMDSO and oxygen flows of 10 and 200 sccm, respectively

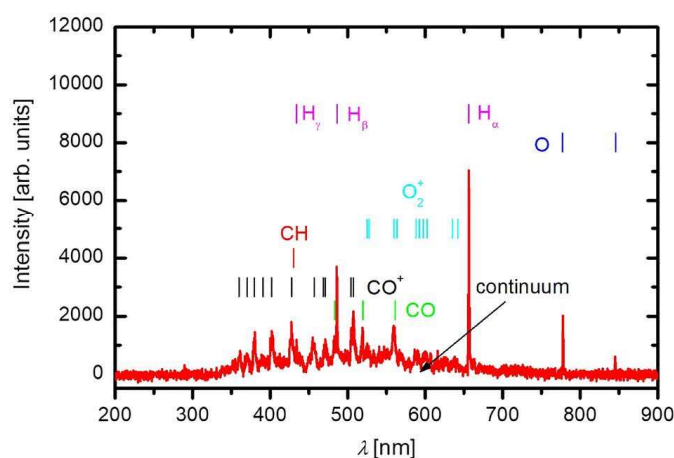


Fig. 10 Behavior of selected spectral features in plasma at 10 sccm HMDSO and variable flow of oxygen

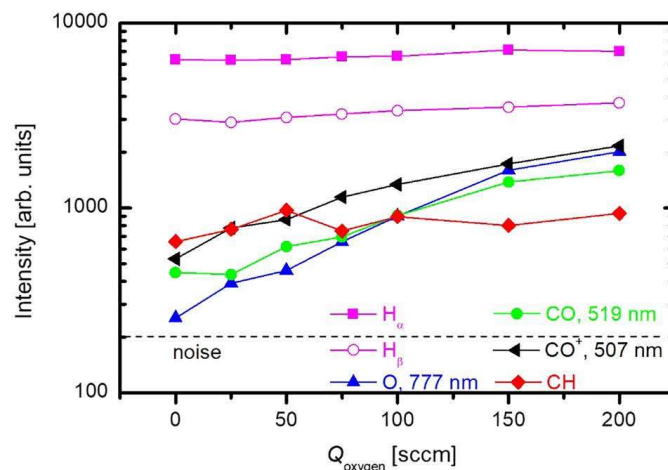
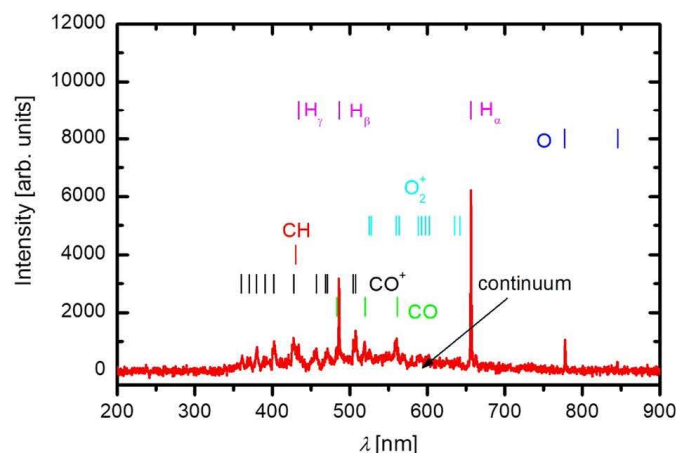


Fig. 11 An optical spectrum of gas mixture plasma with HMDSO and oxygen flows of 25 and 200 sccm, respectively



this point of view, plasma sustained in oxygen of 5% admixed HMDSO exhibit properties similar to “pure” oxygen rather than “pure” HMDSO. This observation is valid also for lower flows of oxygen as will become apparent from Fig. 10. Another interesting feature is appearance of a broad continuum between about 350 and 700 nm. Such continua have been already observed by numerous authors reporting on plasma treatment of polymers and have been explained by overlapping of several molecular bands arising from CO transitions [22].

The evolution of most interesting spectral features of plasma created in HMDSO at 10 sccm with increasing oxygen flow is presented in Fig. 10. The intensity of atomic hydrogen lines does not depend much on the oxygen flow. The dissociation events leading to formation of atomic hydrogen are therefore rather independent from the oxygen flow. The same applies for CH. The lines corresponding to oxygen, however, increase monotonously with increasing flow of oxygen. The ratio between CO and CO⁺ intensities remains practically unchanged over the entire range of oxygen flows. Unfortunately, such a behavior cannot be explained by behavior of plasma electrons due to complex mechanisms involved in both CO [23] and CO⁺ [24] excitations.

Figure 11 represents an optical spectrum of plasma at HMDSO and oxygen flows of 25 and 200 sccm, respectively. The other parameters were the same as in Figs. 3, 4, 5, 6, 7 and 8, 9 and 10. Surprisingly, the transitions from CO molecules and CO⁺ ions

are suppressed as compared to Fig. 9. One would expect even larger concentrations of CO molecules in plasma of 25 sccm HMDSO as compared to 10 sccm HMDSO at the same flow of oxygen since the supply of carbon is larger. The much lower intensity of CO and CO^+ “lines” (in fact these lines form bands) at larger concentration of HMDSO is explained by a lower electron temperature. As explained above, the abundance of HMDSO causes numerous channels for the loss of energetic electrons upon interaction with these molecules and their fragments, which in turn causes a decrease of electron temperature as compared to oxygen or water vapor plasma. The decrease of the electron temperature causes rather poor excitation of the CO molecules. Although extensive oxidation of hydrogenated carbon is supposed to occur in plasma of 25 sccm HMDSO and 200 sccm O_2 (as compared to lower HMDSO flow), the reaction products do not excite to radiative states extensively so the corresponding emission bands are rather indistinct. Here, it is worth stress that CO is not the only product of plasma oxidation of hydrocarbons. According to Ricci [6] the reactions cause also formation of CH_2O_2 and/or CH_2O radicals, but their emission cannot be observed and distinguished with the used optical spectrometer, while it is either out of the range or it would be a part of the continuum.

The evolution of most interesting spectral features with increasing oxygen flow at HMDSO flow of 25 sccm is presented in Fig. 12. Particularly interesting is comparison of this Figure with Fig. 10. While in Fig. 10 the intensities of both H lines and CH remained practically unaffected by the oxygen flow (in fact they even increased slightly) these spectral features decrease with increasing oxygen flow in Fig. 12. The excitation of these features is therefore somehow suppressed at this moderate HMDSO flow. The effect is not dramatic, though.

The discharge power also influences the rich plasma chemistry. Figure 13 represents the behavior of selected spectral features versus discharge power at 10 sccm HMDSO and 200 sccm O_2 . As a general rule, the intensity of radiation increases with increasing discharge power. This effect is explained by increasing discharge current with increasing power (see Fig. 2). According to the simple model taking into account in Eq. (1) the plasma density is proportional to the discharge current. As the current increases for a factor of about 2 from the lowest discharge power of 2 kW to the highest of 8 kW the plasma density as estimated according to Eq. (1) is doubled. The higher electron density causes more intensive excitation and thus more intensive radiation.

Fig. 12 Behavior of selected spectral features in plasma at 25 sccm HMDSO and variable flow of oxygen

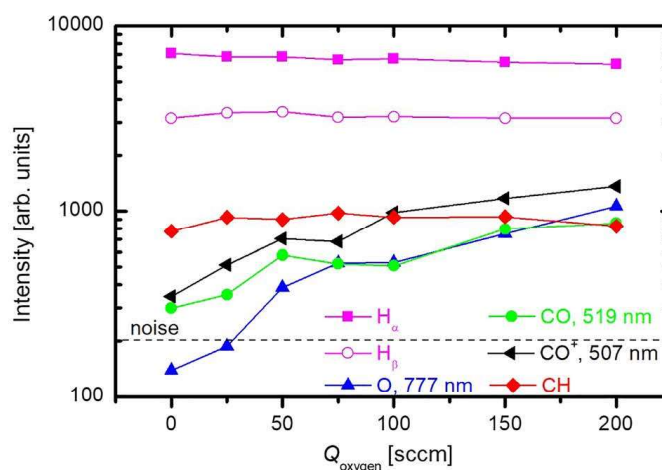
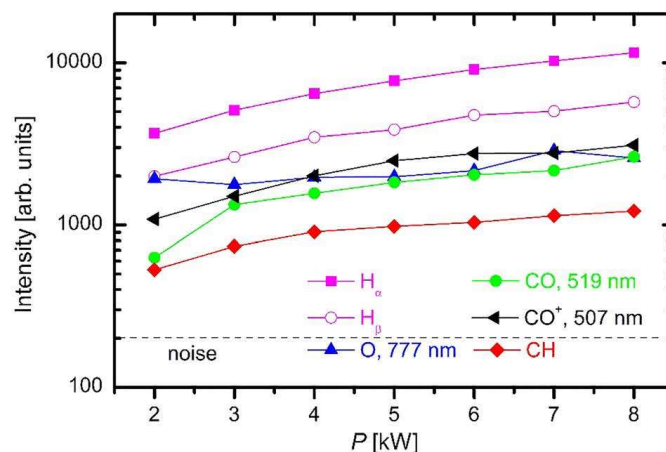


Fig. 13 Intensity of selected spectral features in plasma at 10 sccm HMDSO and 200 sccm O₂ versus discharge power



The intensity of spectral features versus the discharge power depends on the flows of the gases introduced into the plasma reactor. Figure 14 reveals the intensities at 10 sccm HMDSO and 50 sccm O₂, i.e. the same HMDSO flow as in Fig. 13 but much smaller O₂ flow. The intensities of H and CH lines are practically the same in both figures, but the intensities of O, CO and CO⁺ are smaller than in Fig. 13 which can be explained with a simple fact that the density of molecules (and pressure) is lower.

Experiments with different discharge powers have been also performed in “pure” HMDSO. Figure 15 reveals the intensities of spectral features at 10 sccm HMDSO without intentional leakage of oxygen, so the gas in plasma reactor contains almost only HMDSO and water vapor. Irrespective from the power, the intensity of oxygen lines is near the detection limit. Although water vapor is dissociated at such conditions (see Fig. 3 and discussion thereabout) the O atom most intensive emission line is still near the noise limit even at the largest discharge power of 8 kW. The only spectral feature arising from an oxygen-containing molecule is the band around 507 nm that corresponds to a radiative transition of the CO⁺ ion. This line increases significantly with increasing discharge power. At the lowest power of 2 kW it is hardly recognizable from the noise, but at the largest it is clearly detectable. The behavior of this line indicates intensity of chemical reactions of O atoms. As stressed above, the atoms originate from water vapor at these experimental

Fig. 14 Intensity of selected spectral features in plasma at 10 sccm HMDSO and 50 sccm O₂ versus discharge power

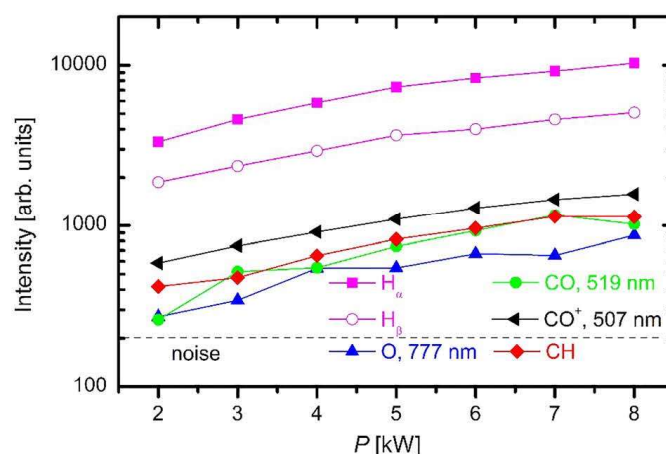
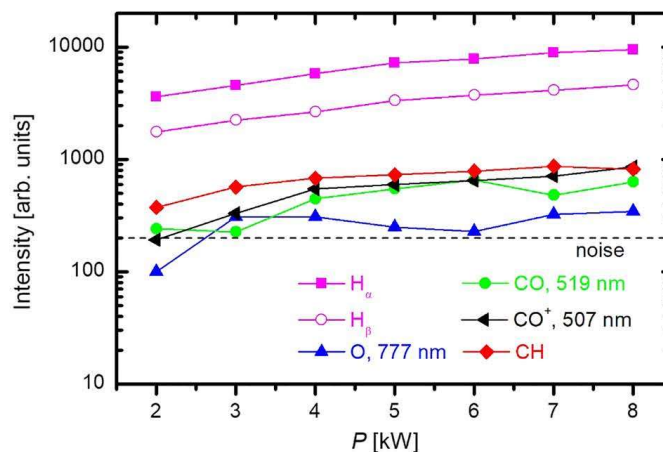


Fig. 15 Intensity of selected spectral features in plasma at 10 sccm HMDSO versus discharge power



conditions. The atomic oxygen is highly reactive and interacts with hydrocarbons adsorbed on the surfaces causing formation of radicals including CO. The production of O atoms increases with increasing discharge power. At the lowest discharge power, the production is not sufficient to make the radiation from CO ion detectable.

An important parameter that influences the quality of deposited films is the residence time of gaseous molecules in the plasma reactor. A method for variation of the residence time is changing of the effective pumping speed. A simple way is suppressing the rotational speed of the roots pump. Figure 16 shows plasma spectra at 10 sccm HMDSO and 200 sccm O₂ at the rotational speeds of 250 and 4000 rpm. The discharge power was 8 kW. The roots pump is almost inefficient at 250 rpm so the effective pumping speed is almost identical to the nominal pumping speed of the two-stage rotational pump, i.e. 1260 m³/h. At 4000 rpm the roots pump assumes the nominal pumping speed, i.e. 8800 m³/h. The intensity of spectral features is larger at low rotational speed which has been already explained: the lower pumping speed assures for a larger pressure and thus more molecules in the chamber at the same flow of inlet gas.

The behavior of spectral features versus the rotational speed of roots pumps at discharge power of 8 kW, 200 sccm O₂ and 10 sccm HMDSO is shown in Fig. 17. No significant deviation from the general behavior of all spectral features is observed. The results of

Fig. 16 Optical spectra at 10 sccm HMDSO and 200 sccm O₂ at the roots pump rotational speeds of 250 and 4000 rpm

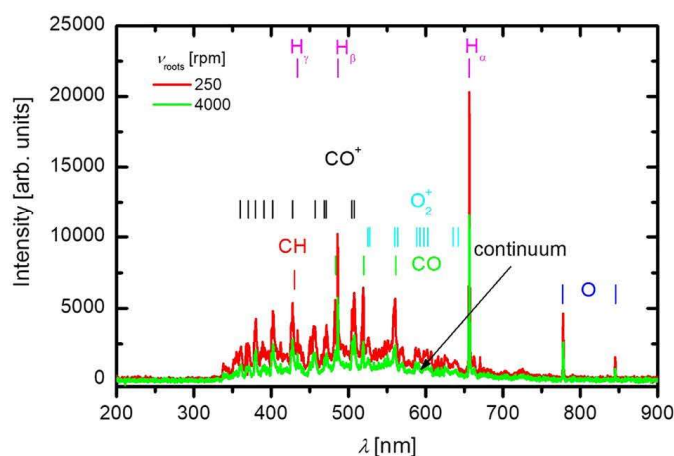
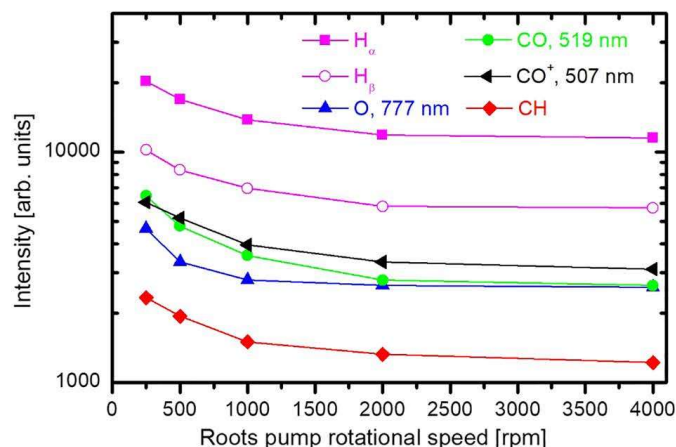


Fig. 17 Behavior of spectral features versus the rotational speed of roots pumps at discharge power of 8 kW, 200 sccm O₂ and 10 sccm HMDSO

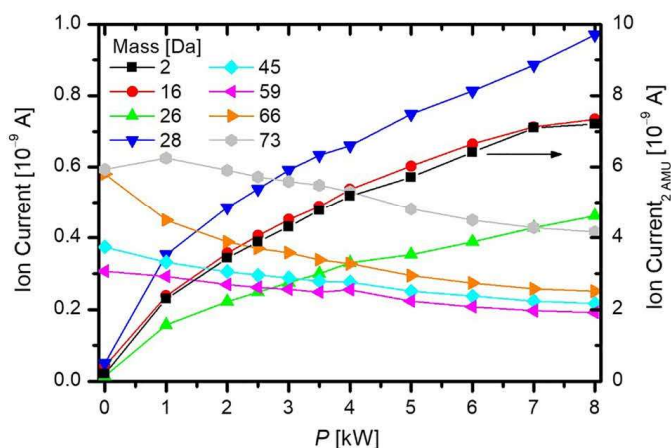


plasma characterization by optical emission spectroscopy therefore indicates rather stable conditions in a broad range of discharge powers and pumping speeds.

A complementary technique to optical emission spectroscopy feasible to apply for characterization of gaseous plasma in the industrial reactor is mass spectrometry. We used a differentially pumped residual gas analyzer—the pressure at the position of the analyzer was about three orders of magnitude lower than in the plasma chamber. The gaseous radicals that are formed upon plasma conditions therefore suffer numerous collisions with the walls before reaching the analyzer. The radicals tend to stick to the surfaces or just recombine to more stable molecules so the measured mass spectra do not reveal the concentration of radicals in the plasma reactor but rather the concentration of molecules of reasonable sticking coefficient. For example, hydrogen atoms were not detected by mass spectrometry although the radiation intensity in optical spectra usually prevail. The ion current corresponding to CH radicals was also below the detection limit.

Figure 18 shows the variation of ion currents versus the discharge power for selected molecules as detected by the residual gas analyzer in the case only HMDSO at 200 sccm was leaked into the plasma reactor. The following masses were chosen: 2 (hydrogen molecules), 16 (methane), 26 (acetylene), 28 (ethylene), 45 (could be SiOH), 59 (could be either SiOCH₃ or SiC₂H₇), 66 (could be either SiC₃H₂ or Si₂OC₄H₁₂²⁺) and 73 (Si(CH₃)₃). The

Fig. 18 Ion currents versus discharge power for HMDSO at 200 sccm. The right-hand axis is for hydrogen, the left-hand for all other molecules



ion current corresponding to hydrogen was about an order of magnitude larger than for other masses so the mass 2 is presented in another y-axis as indicated with an arrow in Fig. 18. As a general rule, the intensity of low-mass molecules increases with increasing discharge power but the intensity of higher masses decreases.

Molecular hydrogen is clearly observed even at zero discharge power where plasma was not ignited at all. The appearance is a result of partial dissociation of HMDSO molecules in the ionization chamber of the gas analyzer. As the discharge in plasma reactor is on, the intensity increases significantly. As already explained on the base of optical spectra (Figs. 6, 7, 8) HMDSO dissociates upon plasma conditions and the simplest radical formed is atomic hydrogen. The atoms recombine to molecules by heterogeneous surface recombination and contribute significantly to the ion current even at the lowest power of 1 kW. Since the increase of the hydrogen signal is an order of magnitude from 0 to 1 kW one can conclude that the major consequence of plasma conditions is subtraction of H atoms from the original precursor. The H_2 signal increases monotonously with increasing discharge power as do some other light molecules.

The formation of methane, acetylene and ethylene upon plasma conditions is evident from the evolution of masses 16, 26 and 28, respectively. They follow the evolution of hydrogen almost perfectly as revealed from Fig. 18. The production of these molecules is marginal in the ionization chamber of the gas analyzer since the corresponding ion currents at zero discharge power are close to the detection limit. These molecules therefore originate from the gas in the plasma reactor. The formation of these gases is not straight-forward. A simple dissociation of HMDSO by electron impact would form preferentially H and CH_3 radicals. The radicals do not interact significantly in the gas phase but rather adsorb to the surfaces where rich chemical reactions take place to form molecules that are stable enough to enter the gas analyzer. It is interesting that molecules like ethane or propane are not detectable by the gas analyzer although ample hydrogen is available in the plasma reactor as revealed from Figs. 6, 7 and 8. Hydrogen atoms therefore rather recombine to H_2 molecules in the plasma reactor than interact with adsorbed CH_x radicals to form fully hydrogenated molecules. The light hydrocarbons partially dissociate upon plasma conditions as revealed from Fig. 7 but the CH radicals either recombine to hydrocarbons or stick to the surfaces before entering the gas analyzer.

Opposite behavior is observed in Fig. 18 for heavier molecules. The masses attributed to SiOH, $SiOCH_3$ or SiC_2H_7 , SiC_3H_2 or $Si_2OC_4H_{12}^{2+}$ and $Si(CH_3)_4$ exhibit large ion currents when the discharge is off (power 0 in Fig. 18). These molecules are therefore formed in the ionization chamber of the residual gas analyzer. They might be formed also in the reactor upon plasma conditions but they obviously do not survive the way to the analyzer—they rather stick to surfaces. The monotonously decreasing signals of heavy molecules therefore reflect the loss of original HMDSO molecules due to dissociation upon plasma conditions in the reactor. The loss, however, is not complete since the signals drop only by a factor of 2 even at the largest discharge power of 8 kW. The biggest signal drop (by almost a factor of 3) is observed for the mass 66, which could be a sign that this mass is also attributed to heavy ion $Si_2OC_4H_{12}^{2+}$. The results of these measurements therefore indicate incomplete dissociation of HMDSO molecules upon plasma conditions.

The correlation between the results obtained by optical emission spectroscopy and mass spectrometry is shown in Fig. 19. The left-hand y-axis indicates the ion currents and the right-hand the radiation intensity. The correlation of the H_α and H_β lines with the mass 2 ion current is almost perfect and so is the correlation between the CH radiation and mass 16 ion current. The optical emission spectroscopy is a qualitative technique for plasma characterization but mass spectrometry is semi-quantitative. The correlations shown in

Fig. 19 Comparison between intensities of selected emission lines and ion currents versus discharge power

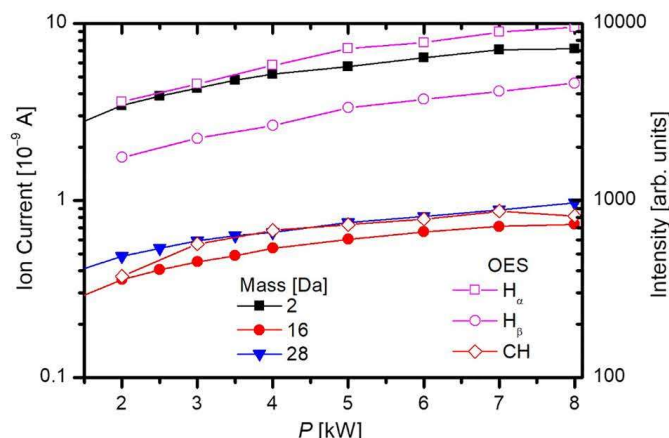


Fig. 19 therefore enable controlling plasma stability using the qualitative technique only. The optical emission spectroscopy therefore represents a simple and economic method for monitoring the properties of gaseous plasma in the industrial-scale reactor despite the complexity of gas-phase and surface chemical reactions.

Conclusions

Optical emission spectroscopy is a suitable tool for monitoring properties of gaseous plasma in the industrial-scale reactor suitable for deposition of thin films containing Si, C, O and H in spite of the fact that it enables determination of few radicals only. Experiments were performed in the reactor of a very low power density—typically less than a kW/m³. Correspondingly, the plasma density was below $1 \times 10^{14} \text{ m}^{-3}$ as estimated from measured discharge voltage and current. Such a low power density is not feasible in experimental reactors of volume of a few liters since plasma could not ignite at all. The large volume and low pressure conditions adopted in this study assured for inhibited loss of plasma electrons even at the power density well below 1000 W/m³. The mass spectrometry revealed the dissociation fraction of the order of 10%. The radicals formed at these conditions in a mixture of HMDSO and water vapor were predominantly hydrogen atoms. The H-atoms recombined on surfaces facing plasma to preferentially form hydrogen molecules. These molecules were detectable by both mass spectrometry (the signal of mass 2 increased for an order of magnitude upon plasma conditions even at lowest discharge power of 1 kW) and optical spectroscopy (the continuum arising from radiative transitions of excited H₂ was clearly distinguishable). The HMDSO molecules were dissociated upon plasma conditions also to CH_x radicals which associated to light hydrocarbons, preferentially ethylene followed by methane. A suitable method for detection of such molecules was monitoring the evolution of the CH bandhead at 431 nm and comparison with the intensity of H γ line at 434 nm. The introduction of oxygen into the plasma reactor did not cause significant suppression of atomic hydrogen formation, but caused oxidation of the deposited films. The formation of CO molecules was clearly observable by monitoring the CO and CO⁺ bands in optical spectra. Such chemical reactions occurred even at very low discharge powers but increased with increasing power.

Acknowledgements This research was funded by Slovenian Research Agency (research core funding No. P2-0082—Thin film structures and plasma surface engineering, as well as project No. L2-8179—Evaluation of the range of plasma parameters suitable for nanostructuring of polymers on industrial scale).

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Chapter 4

Deposition Kinetics of Thin Silica-Like Coatings in a Large Plasma Reactor

The kinetics of the reactive plasma species and deposition rates are explained on the basis of measurements of various parameters in this scientific article. In a previous couple of papers, we neglected the temporal behavior of plasma parameters, so we decided to elaborate on such effects in this paper. The effective pumping speed was calculated using the measured values of the flow rates and pressures. We demonstrated the pressure dependence of the effective pumping speed. We plotted the effective pumping speed versus the measured flow of HMDSO precursor to stress the influence of the residual atmosphere on the deposition kinetics. We also presented the residence time, which is among the key parameters governing the deposition kinetics. We clearly showed that the predictions which may be valid in experimental systems are not justified in the industrial reactor shown in Figure 1. Namely, the industrial reactor's residence time was about a minute, which is at least an order of magnitude longer than in experimental reactors. An interesting behavior of the discharge current versus the HMDSO flow was observed. The discharge current exhibited a minimum at the flow between 50 and 100 sccm, indicating optimal conditions regarding the density of charged particles in gaseous plasma. The density of charged particles in such reactors is practically impossible to measure, so we deduced it from other measurable parameters. Due to uncertainties and assumptions that might not be all justified, we plotted the range of possible densities of charged particles with clearly indicated upper and lower limits, taking into account different models. The difference between the limits is almost two orders of magnitude, but we managed to discuss the justification of extreme assumptions, so we were able to recommend the most probable value of the density of charged particles in our plasma. We also demonstrated excellent agreement between the measured thickness of the deposited film and the linear fit. The deposition rates in the middle of the industrial reactor were measured versus the HMDSO flow and the discharge power. The relation is linear up to about 120 sccm where deviations from linearity were observed and discussed, taking into account the density of charged particles and the ionization kinetics. On the other hand, the deposition rate versus the discharge power at a fixed HMDSO flow expressed a broad maximum which was explained by competitive events. The depth profiles of the deposited films were measured by SIMS. A rather uniform composition of the deposited film was confirmed. The structure of the films was further elaborated by high-resolution XPS spectra of C1s, O1s, and Si2p peaks. Excellent agreement between the peaks was observed, and the results confirmed that the

deposited films were actually close to the polydimethylsiloxane with an almost negligible concentration of silica in the deposited film.

Article

Deposition Kinetics of Thin Silica-Like Coatings in a Large Plasma Reactor

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Received: 20 August 2019; Accepted: 28 September 2019; Published: 3 October 2019



Abstract: An industrial size plasma reactor of 5 m³ volume was used to study the deposition of silica-like coatings by the plasma-enhanced chemical vapor deposition (PECVD) method. The plasma was sustained by an asymmetrical capacitively coupled radio-frequency discharge at a frequency of 40 kHz and power up to 7 kW. Hexamethyldisiloxane (HMDSO) was introduced continuously at different flows of up to 200 sccm upon pumping with a combination of roots and rotary pumps at an effective pumping speed between 25 and 70 L/s to enable suitable gas residence time in the plasma reactor. The deposition rate and ion density were measured continuously during the plasma process. Both parameters were almost perfectly constant with time, and the deposition rate increased linearly in the range of HMDSO flows from 25 to 160 sccm. The plasma density was of the order of 10¹⁴ m⁻³, indicating an extremely low ionization fraction which decreased with increasing flow from approximately 2 × 10⁻⁷ to 6 × 10⁻⁸. The correlations between the processing parameters and the properties of deposited films are drawn and discussed.

Keywords: plasma-enhanced chemical vapor deposition (PECVD); hexamethyldisiloxane (HMDSO); industrial-size plasma reactor; capacitively coupled radiofrequency (RF) discharge; ion density; real time deposition rate measurement; time-of-flight secondary ion mass spectrometry (ToF-SIMS)

1. Introduction

A widely used method for deposition of thin coatings onto solid materials at low temperatures is plasma-enhanced chemical vapor deposition (PECVD). A precursor is leaked into a plasma reactor where it is partially ionized and dissociated, and the resulting species stick to a surface to form a thin and often compact coating. Various precursors can be used to deposit films of appropriate properties. Organosilicon precursors are suitable for deposition of coatings containing silica. Depending on plasma parameters, films of various properties are deposited from almost pure silicon dioxide to a polymer-like coating resembling polydimethylsiloxane. The following literature survey presents important results obtained by various authors using various discharge configurations.

The deposition of silicon dioxide coatings was elaborated by Bourreau as early as 1991 using both hexamethyldisiloxane (HMDSO) and tetraethoxysilane (TEOS) [1]. They found significant changes in deposition kinetics at elevated gas and/or substrate temperatures. Kashiwagi et al. applied HMDSO and oxygen at the pressure inside an experimental plasma reactor of approximately 10 Pa to

obtain various coatings from almost pure silicon dioxide to a coating resembling polydimethylsiloxane (PDMSO) [2]. They also used other precursors such as tetramethyl-1,3-bis(chloromethyl)-disiloxane (CMDISO), tetramethyl-1,3-bis(hydroxybutyl)-disiloxane (HBDSO), and tetramethyl-1,3-bis(amino propyl)disiloxane (APDSO). They sustained plasma by an inductively coupled radio-frequency (RF) discharge and studied the composition and structure of deposited films using various surface-sensitive techniques. Ropcke et al. [3] used three different discharges for plasma sustenance in experimental reactors, i.e., a planar microwave (MW) plasma source operating at the standard MW frequency of 2.45 GHz, an RF planar reactor at 13.56 MHz, and an electrodeless capacitive coupled RF discharge at 460 KHz. Argon was used as the main gas with an admixture of HMDSO and helium. All sources were characterized by various techniques to determine the rotational and optical excitation temperatures as well as the behavior of various plasma radicals at different discharge conditions. Spatially resolved optical emission characterization enabled observation of large gradients in those plasma reactors, in particular the glass reactor powered with an electrodeless capacitively coupled plasma (CCP). However, the standard CCP revealed a huge H-atom temperature of approximately 2000 K next to the powered electrode, indicating importance of the gas excitation within and next to the sheath. The H-atom temperature was below 500 K at a distance of a couple of centimeters from the powered electrode. In contrast, Theil et al. reported experiments at room gas kinetic temperature, neglecting any temperature gradients [4], using mixtures of oxygen and HMDSO. They found a gradual decrease of the carbon content in deposited Si_xO_y films with an increasing concentration of oxygen in the gas mixture. The mechanisms of plasma polymerization of various silico-organic monomers were reported by Rau et al. [5]. Apart from HMDSO, they also used divinyltetramethyl disiloxane (DVTMDSO), and octamethyl cyclotetrasiloxane (OMCATS) to deposit films of different structure. Argon was added to gaseous plasma in order to enhance the dissociation of precursors, similar to Ropcke [3]. They reported that the decisive parameters determining the polymer growth rates were plasma power and the monomer evaporation temperature. Unlike other precursors, the DVTMDSO also enabled polymerization under remote conditions. The influence of substrate temperature on the growth kinetic was studied by Sahli et al. [6]. They found the deposition rate decrease with increasing oxygen concentrations in a broad range of temperatures up to approximately 400 °C and reported decreasing carbon concentrations in the films with increasing oxygen concentration in the gas mixture. Korzec et al. [7] compared direct and remote plasma deposition of coatings using HMDSO admixed with argon and oxygen. Microwave discharge was used as a plasma source. The remote technique was found favorable because it prevented otherwise unwanted deposition of coatings on reactor walls, as reported by Korzec. A similar device was also used by Tierich et al. [8] except that they used a remote RF source. A remote microwave plasma was also used by Bieder et al. [9]. Kurunczi et al. [10] also used tetramethylsilane (TMS) and measured optical spectra arising from excited gaseous species upon excitation with electrons of various kinetic energy. The extensive experimental work brought the conclusion that the single-step dissociative excitation processes were unlikely to play a dominant role in the low-temperature processing plasma of these precursors because the excitation thresholds were large compared to typical electron temperatures in plasma reactors. Alexander et al. [11] characterized plasma sustained in HMDSO also by mass spectrometry. Extensive molecular oligomerization of positively charged gaseous species was observed in the plasma gas phase at a rather low discharge power, whereas at large powers, fragmentation prevailed, similar to what was reported by Ropcke [3]. Interestingly enough, the oligomerization was not observed for neutral gaseous species irrespective of the discharge power. They concluded that ion-molecule reactions were responsible for deposit-formation at a low discharge power, but at a high power, the ionic component became important. Fujii et al. [12] investigated the composition of thin films prepared by plasma polymerization from HMDSO with an admixture of fluorine-containing gases to obtain deposits of low dielectric constant. They applied remote inductively coupled plasma as a radical source. Similar results were reported by Borvon et al. [13] except that they admixed methane to a HMDSO- O_2 gas mixture. Shioya et al. [14] also reported low-k dielectric films, but they

used HMDSO admixed with water vapor. Gengenbach et al. [15] also used hexamethyldisilazane (HMDSA) apart from HMDSO and studied the ageing mechanisms stressing the post-deposition kinetics. Hagemann [16], on the other hand, used a mixture of HMDSO and oxygen to obtain coatings of various silicon-to-carbon ratios. In another paper [17], they reported results of experiments obtained using both symmetric and asymmetric discharges and found the crucial correlation between the gas flow and the discharge power on the deposition rate. An interesting electrode configuration was reported by Nema et al. [18], who reported the excellent quality of films deposited using HMDSO and oxygen precursors. Zywitzki et al. [19] used other types of discharges, i.e., reactive pulsed magnetron sputtering and hollow cathode activated electron beam evaporation, for plasma deposition of coatings from HMDSO. They reported extremely high deposition rates up to 600 nm/s using these powerful discharges. Qi et al. [20] reported much smaller deposition rates using microwave discharge where the electron cyclotron resonance (ECR) conditions were obtained. The deposition rates were several tens of nanometers per second. One of the highest deposition rates was observed by using a plasma micro-jet as reported by Silmy et al. [21]. They reported deposition rates as large as 0.1 mm/s. Fang et al. [22] applied HMDSO admixed with various gases and studied the deposition rate in inductively coupled RF plasma at the same discharge conditions and found the lowest rate for the case of the hydrogen admixture and highest for oxygen. Xiao et al. [23] admixed ammonia to HMDSO and observed a solid growth of a coating resembling silicon nitride of excellent hardness. Ammonia was also admixed to HMDSO and hydrocarbons by Hagemann et al. [24]. Vautrin et al. [25] studied the influence of substrate biasing and observed that RF bias induced a densification of the coatings associated with modifications in their morphology and chemical composition. Lee et al. performed deposition of PDMS using PDMS/O₂/He mixture [26]. The deposition rate increased with increasing PDMS flow rate as well as surface roughness. The deposition rate also increased with increasing O₂ flow rate; however, surface roughness decreased. At some certain conditions, SiO₂-like coatings were obtained with a deposition rate of 12 nm/min.

All authors cited above used low-pressure experimental plasma reactors. A somehow elevated HMDSO pressure of 133 Pa was used by Goujon et al. [27], who also applied moderate discharge power to sustain plasma in HMDSO-oxygen mixture using a capacitively coupled RF discharge to obtain strong fragmentation of the precursor.

The brief review of relevant literature reveals a variety of discharges used for deposition of silica-like coatings. The useful pressure upon plasma polymerization was in the range of few Pascals. The advantage of low pressure discharges is the ability to sustain rather uniform plasma in a large volume and at a reasonably low discharge power density. In fact, most current commercial devices for deposition of such thin films on solid substrates employ low pressure reactors to insure reasonable uniformity and stoichiometry of the coatings and to prevent formation of dust particles in the gas phase. Such particles are detrimental for protective coatings because they cause the formation of porous films of poor quality, as explained by Gosar et al. [28].

Gaseous plasma created at low pressure conditions was characterized by various techniques, but only few papers report quantitative results such as the density of charged particles, let alone the densities of molecular fragments. Plasma density is usually measured with an electrical probe. The probe is immersed into an experimental reactor and its characteristics (current versus voltage) is measured. The charged particle density is then deduced using an appropriate model. The calculation requires known ion mass (if ion saturated current is used for calculation of the plasma density), which is generally not available because the precursor dissociates to various fragments upon plasma conditions, and the fragments ionize at various rates. Furthermore, any electrode is quickly covered with a dielectric film, which complicates the interpretation of results. Particularly difficult is determination of charged particle density in industrial reactors where it is often difficult if not impossible to mount a suitable probe inside the reactor.

The properties of thin films are typically characterized with a remote instrument that enables determination of the film composition and/or structure, such as X-ray photoelectron spectroscopy

(XPS) or secondary ion mass spectrometry (SIMS) depth profilers. Very few authors ever attempted to measure the deposition rate in situ due to the lack of appropriate methods. It is particularly difficult to adopt a standard technique for measuring the deposition rate into an industrial reactor, so the users of PECVD technology for deposition of silica-like coatings from organometallic precursors do not have a reliable method for controlling the deposition rate upon treatment of their products in large reactors. In the present paper we report such a method and discuss the deposition rates in the view of plasma parameters.

2. Materials and Methods

An industrial-size plasma reactor was used to study the deposition of silica-like films onto polymeric substrates. The system has been presented in detail elsewhere [28]. The discharge chamber of a volume of approximately 5 m³ was powered with an RF generator at a frequency of 40 kHz using an asymmetrical capacitively coupled RF discharge. The powered electrode had an area of 0.8 m², whereas the total surface of the grounded housing was approximately 15 m². HMDSO was introduced into the reactor through numerous small holes, thus assuring for a rather uniform distribution of the precursor leaked into the reactor. The HMDSO flow was measured with a flow-meter calibrated for this gas. The pressure was measured inside the reaction chamber with a Pirani gauge. The reactor was pumped through connecting tubes of various diameters separated by valves with a roots blower with a nominal pumping speed of 8800 m³/h backed with a rotational pump of pumping speed 1260 m³/h. The measured gas flow and pressure enabled for estimation of an effective pumping speed and thus the gas residence time inside the plasma reactor. Several samples made from stainless steel were carefully polished and mounted into the plasma reactor. The deposition of thin films resembling polydimethylsiloxane was accomplished at a discharge power of 3.4 kW and a HMDSO flow of 130 sccm.

The deposition rate of the coating was measured with a homemade optical sensor. The optical sensor consists of an all-fiber Fabry-Perot resonator that is formed at the tip of an optical fiber. More detailed information about the sensor and its construction has been presented elsewhere [29,30]. The sensor measures the thickness of the deposited layer every second in a resolution below 1 nm. At certain plasma conditions, the thickness of the coating was measured for approximately 100 s. From the slope of the thickness-to-time evolution curve, a deposition rate was determined.

The coating thickness of one selected sample was analyzed by scanning electron microscope (SEM). The JSM-5800 microscope from Jeol (Scan d.o.o., Ljubljana, Slovenia) was used. To determine the coating thickness, a cross-section of the sample was prepared. The procedure for the preparation of the cross-section included inserting the sample into a special powder that was sintered at a high temperature and then polished to remove a part of the material. It should be noted that this procedure can cause some irregularities in the uniformity of the coating.

Moreover, the coating thickness and composition was also examined by time-of-flight secondary ion mass spectrometry (ToF-SIMS). The ToF-SIMS 5 instrument (ION-TOF, Münster, Germany) equipped with a bismuth liquid metal ion gun with a kinetic energy of 30 keV was used. The SIMS spectra were measured by scanning a Bi₃⁺ cluster ion beam over an area of 100 × 100 μm². The beam current was 0.6 pA, and the total measuring time to acquire the SIMS spectra was 30 s. The SIMS spectra were processed with the software SurfaceLab 6.3 supplied by ION TOF (Münster, Germany).

Surface chemical composition was also investigated using X-ray photoelectron spectroscopy (XPS). The PHI-TFA XPS spectrometer (Physical Electronics, München, Germany) was used. Samples were exposed to X-ray radiation from monochromatic Al source with a photon energy of 1486.6 eV. High resolution spectra were measured at a pass energy of 29.35 eV and 0.125 eV energy step for the deposited coatings and also for the reference samples of pure PDMS and SiO₂. An additional electron gun was used during spectra acquisition for surface charge compensation. All spectra were referenced to the main C1s peak of the carbon atoms C-Si, which was assigned a value of 284.4 eV [31]. Quantification of the surface composition was performed using Multipak v8.1c software (Ulvac-Phi

Inc., Kanagawa, Japan, 2006), which was supplied with the spectrometer. The spectra were fitted with Gauss-Lorentz functions. A Shirley type background subtraction was used. The FWHM was fixed during the curve fitting process (1.2 eV for C1s and 1.4 eV for O1s and Si2p). First, the reference samples of PDMS and SiO₂ were fitted to obtain the best fitting parameters, which were used for further fitting of spectra recorded for the deposited coatings.

3. Results and Discussion

The pressure in the plasma reactor was measured versus the flow of HMDSO when the discharge was off. The pressure dependence is plotted in Figure 1. The pressure at zero flow of HMDSO represents the residual atmosphere. Because the system was hermetically tight, the finite pressure at zero flow is attributed to desorption of gases, in particular water vapor, from the surface of the materials mounted into the plasma reactor. Although a Pirani gauge is not the most accurate device for measuring the pressure in the range of few Pascals, Figure 1 indicates a rather large density of water molecules in the plasma reactor. As expected, the pressure increases with the increasing flow of HMDSO, but the curve in Figure 1 is not linear.

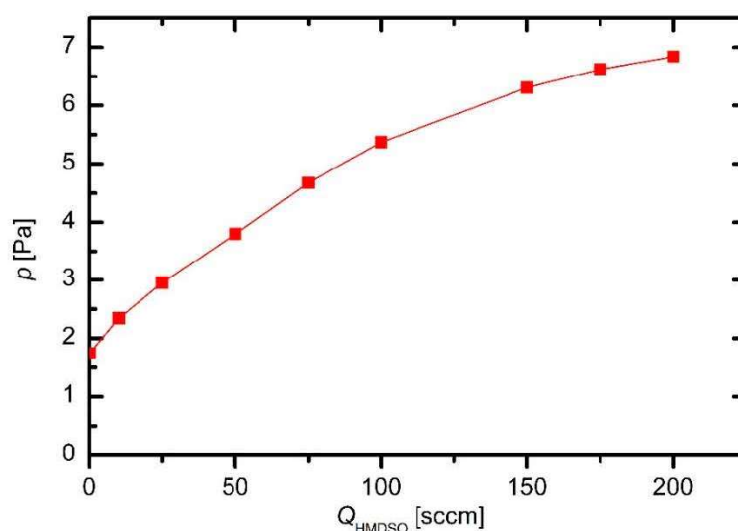


Figure 1. The pressure in the plasma reactor versus the hexamethyldisiloxane (HMDSO) flow.

The deviation from linearity in Figure 1 is explained by the pressure-dependent effective pumping speed. Because the discharge was off, there was no loss of the precursors, which otherwise occurs upon plasma conditions because a fraction of precursor is spent for growing the films. The device was hermetically tight, therefore the mass flow through the system was constant at a given leakage of HMDSO and the continuity equation is applicable:

$$p_1 S_1 = p_2 S_2 \quad (1)$$

Here, S_x ($x = 1, 2$) is the effective pumping speed (the volume flow) at the position where pressure p_x is measured. The pressure at the flow controller where the flow is measured is by definition 1 bar, i.e., $p_2 = 1$ bar, whereas S_2 is the flow measured with the flowmeter. The pressure p_1 is measured in the plasma reactor, hence the effective volume flow through the reactor is

$$S_1 = p_2 S_2 / p_1 \quad (2)$$

It is not feasible to calculate the effective pumping speed from the values represented by points in Figure 1, therefore Equation (2) should be modified to consider continuous desorption of water vapor:

$$S_1 = p_2 S_2 / (p_1 - p_{\text{res}}) \quad (3)$$

where p_{res} is the pressure of the residual atmosphere. The effective pumping speed versus the HMDSO as determined from Equation (3) is shown in Figure 2. It increases with increasing flow, which is explained by two effects: increasing compression rate of the roots pump in the pressure range of several Pascals with increasing pressure, and the finite conductivity of the vacuum components between the plasma reactor and the roots pump. The effective pumping speed is much smaller than the nominal pumping speed of the roots pump. As stated in the previous section, the nominal pumping speed of the roots pump was 8800 m³/h at optimal pressure and fore-pumping.

The residence time of the gas leaked into the plasma reactor is estimated from the effective pumping speed and the cross-section of the reactor:

$$t = (l A) / S_1 \quad (4)$$

where l is the length of the plasma reactor (i.e., distance between the gas inlet and the pumping duct), A is the cross-section of the plasma reactor, and S_1 is the effective pumping speed calculated from Equation (3). Taking into account numerical values, i.e., $l \approx 2$ m, with $A \approx 2$ m² the residence time is of the order of 100 s. The exact values are plotted in Figure 2 (right y-axis). The residence time is therefore large enough to assure the decent fragmentation of the HMDSO upon plasma conditions.

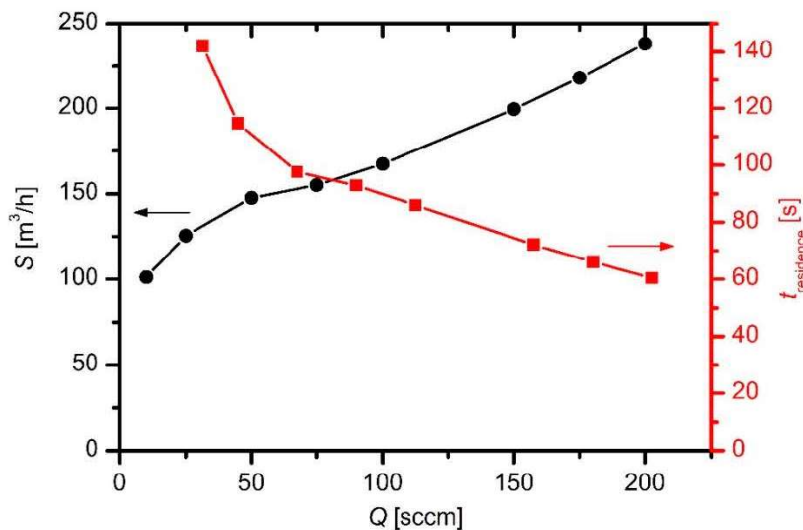


Figure 2. The effective pumping speed and the gas residence time in the plasma reactor versus the HMDSO flow.

The plasma reactor does not allow for insertion of a probe for measuring plasma density, thus this parameter is estimated taking into account some simplifications. The plasma inside the reactor is assumed to be rather homogeneous, with comparable densities of free electrons and positively charged ions. The electrons are rather hot in low-pressure non-equilibrium gaseous plasma sustained by a discharge of a low power density with a typical temperature of a few electronvolts. The positive ions are thermal at the temperature similar to the neutral gas kinetic temperature, which in turn is close to the wall temperature. While the powered electrode is heated to several tens of kelvins above room temperature upon continuous discharge, the temperature of the chamber walls remains almost at room temperature even for prolonged plasma duration; therefore, it can be assumed that the ions in bulk

plasma are close to the room temperature, i.e., 300 K. The ions are accelerated in the pre-sheath next to electrodes, gaining directed velocity, but their concentration in the pre-sheath remains almost the same as in bulk plasma. According to classical literature [32], the ions gain Bohm velocity across the pre-sheath:

$$v_{Bohm} = \sqrt{(kT_e)/M} \quad (5)$$

where k is Boltzmann constant, T_e is the electron temperature in bulk plasma, and M is the ion mass. The ions therefore enter the sheath next to electrodes with the velocity as in Equation (5). The ions are accelerated in the potential drop next to the electrodes. In the case of capacitively coupled RF discharges, the self-biasing of the electrodes occurs. In our case, the discharge is heavily asymmetrical with the ratio of the powered and grounded electrode areas at almost two orders of magnitude. Because the RF self-biasing is roughly proportional to the square of the area ratio, it can be assumed that practically all DC voltage due to electrode self-biasing occurs on the powered electrode. The ions are accelerated in the time-averaged voltage across the sheath and bombard the electrode with the kinetic energy of

$$W_{kin} = e U, \quad (6)$$

where e is the ion charge, and U is the time-averaged voltage across the sheath next to the powered electrode (i.e., the DC voltage due to self-biasing). Practically all ions in weakly ionized plasma sustained by a discharge of a low power density are singly-ionized, so e from Equation (6) is substituted with the elementary charge, i.e., $e = e_0 = 1.6 \times 10^{-19}$ As. In a rough approximation, the voltage drop U can be replaced with the effective voltage of the power supply. There are voltage and current meters on the power supply. The voltage and current versus the HMDSO flow are plotted in Figure 3.

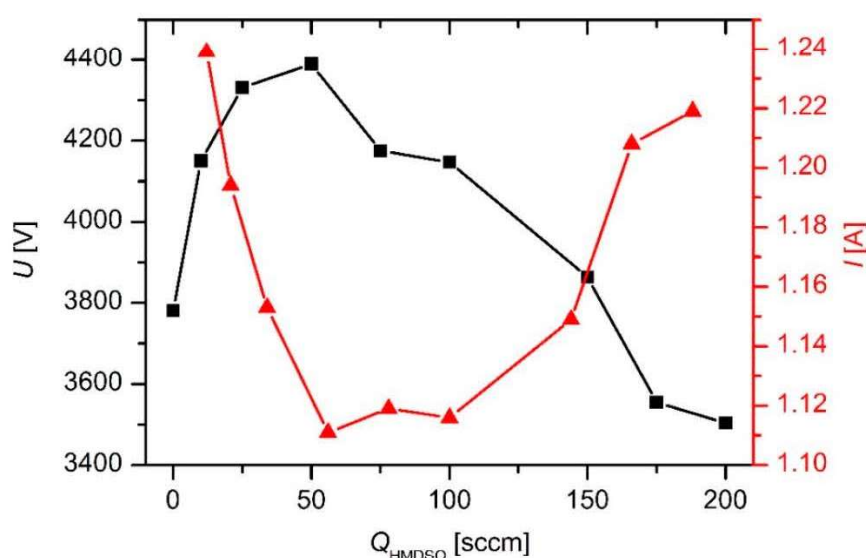


Figure 3. The voltage (left-hand y-axis) and current (right-hand y-axis) versus the HMDSO flow.

The average velocity of the ions bombarding the powered electrode is obtained from its kinetic energy and Equation (6):

$$v = \sqrt{2W_{kin}/M} = \sqrt{2e_0 U/M} \quad (7)$$

As in Equation (5), M is the ion mass. There are ions of various masses from H_2^+ to $C_6H_{18}OSi_2^+$, so the choice of velocities in Equation (7) is somehow arbitrary. Furthermore, Alexander et al. [11] reported oligomerization of positively charged ions. Still, in a very rough approximation, the velocity v can be attributed to the mass of the most common molecular fragments. According to Gosar et al. [28],

who performed measurements of the fragments in this particular plasma reactor by mass spectroscopy, the densest fragments are the positively charged ions of a mass of approximately 30.

The flux (j) of ions onto the powered electrode is a product of the ion density (n_+) next to the electrode and the “most probable” velocity (v), i.e., $j = n_+ v$, thus the ion current (I) is

$$I = e_0 j A_{el} = e_0 n_+ v A_{el} \quad (8)$$

where n_+ is the density of positive ions next to the powered electrode, and A_{el} is the geometrical area of the powered electrode. The Equation (8) makes a reasonable approximation if the electrical current next to the electrode is conducted by ions only. In practice, it never happens for at least two reasons: (1) additional current due to electrons emitted from the powered electrode by ion bombardment; and (2) the effects within the short time interval when the voltage on the powered electrode is at its maximum. Still, Equation (8) gives a useful approximation of the ion density deep in the sheath next to the electrode. The ion density in plasma far away (tens or even hundreds of Debye lengths away) from the powered electrode is larger, and therefore the value of the plasma density as determined from Equation (8) can be taken only as the lower limit. This lower limit is plotted in Figures 4 and 5 versus the discharge power and precursor flow, respectively.

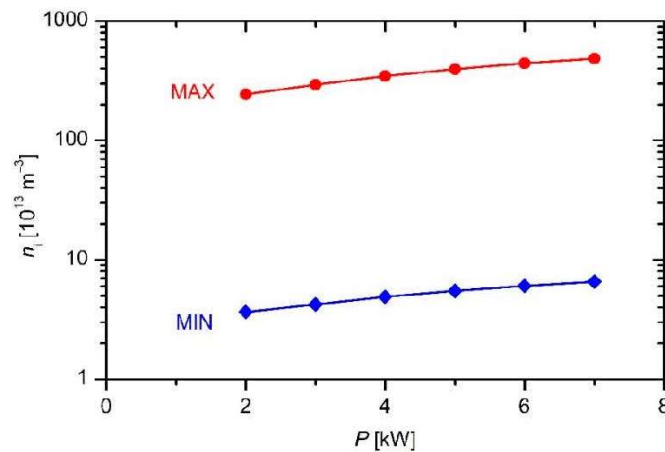


Figure 4. The limits of the plasma density versus the discharge power at an HMDSO flow of 130 sccm.

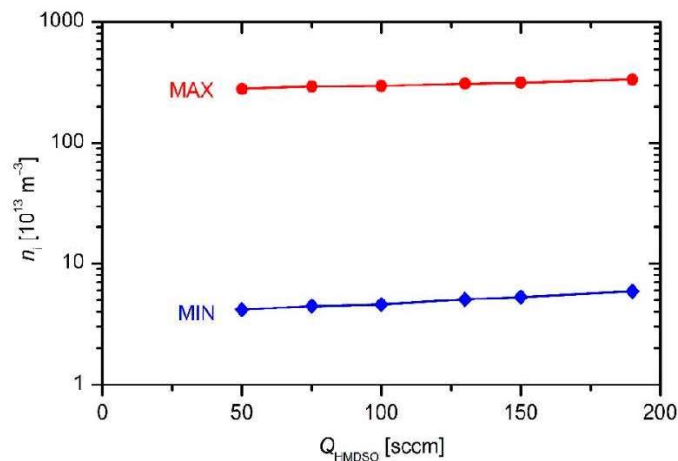


Figure 5. The limits of the plasma density in the industrial reactor versus the HMDSO flow at a discharge power of 3.4 kW.

The upper limit of the plasma density can be stated by considering the conditions at the interface of the sheath and pre-sheath. The ion velocity at this interface is determined from Equation (5). If the ions were the major current carriers at the interface, Equation (8) would have been applicable for the estimation of the ion density in gaseous plasma just by replacing the ion velocity v in Equation (8) with the Bohm velocity as in Equation (5):

$$n = I / (e_0 v_{\text{Bohm}} A_{\text{el}}) \quad (9)$$

Such an assumption, however, is not justified due to the much larger mobility of electrons as compared to massive ions. Despite the potential drop between the unperturbed plasma and the interface between the pre-sheath and the sheath, the electrical current is predominantly conducted by electrons because of their much larger mobility, thus any calculation of the plasma density using Equation (9) will give an overestimated value. Still, Equation (9) is useful for estimation of the upper limit of the ion density in a plasma reactor where adoption of a probe is not feasible. The upper limits of the plasma density as calculated from Equation (9) are plotted in Figures 4 and 5. The numerical values of plasma density also requires the electron temperature that is generally unknown. Happily, the electron temperature in any plasma sustained by an asymmetric RF discharge at the pressure of few Pascals in a molecular gas is roughly a few electronvolts. The Bohm velocity depends on the square of the electron temperature, and therefore any mistake because of the wrong T_e is marginal as compared to other simplifications taken into account to estimate the upper value of the plasma density.

Again, it should be stressed that the values obtained from Equation (9) are highly overestimated because the electron contribution to the electrical current as measured for the electrical circuit used for sustaining plasma in our industrial reactor is higher than the ion current. On the other hand, the values obtained using Equation (8) are highly underestimated because they do not take into account the gradient of the ion density across the sheath. Fortunately, the upper and lower limits of the ion density are not too far away from each other as revealed from Figures 4 and 5, and therefore they represent useful data in the reactor where an electrical probe could not be mounted.

The results of such simplifications only give the order of magnitude. Obviously, the plasma density in the reactor is of the order of 10^{14} m^{-3} . Examining both the upper and lower limit one can deduce a rather weak increase of the plasma density with increasing discharge power or flow rate.

Plasma density influences the gas-phase reactions and, correspondingly, the deposition of coatings containing carbon, hydrogen, silicon, and oxygen on the surfaces of substrates facing plasma. To investigate the deposition kinetics, we immersed several optical probes for real-time measuring of the deposition rate. Details of the probes are given in Section 2. Typical deposition kinetics are revealed in Figure 6. The thickness of the deposited film increases almost perfectly linearly with increasing deposition time, indicating very stable conditions. The coating thickness was also confirmed by SEM analysis of a cross-section of one selected sample. This image is shown as an inset in Figure 6. Although its resolution is not the best because of using low-resolution SEM microscopy and because of the procedure for the preparation of the cross-section (see Section 2), it is nevertheless clear that the coating thickness is in agreement with the measured curve.

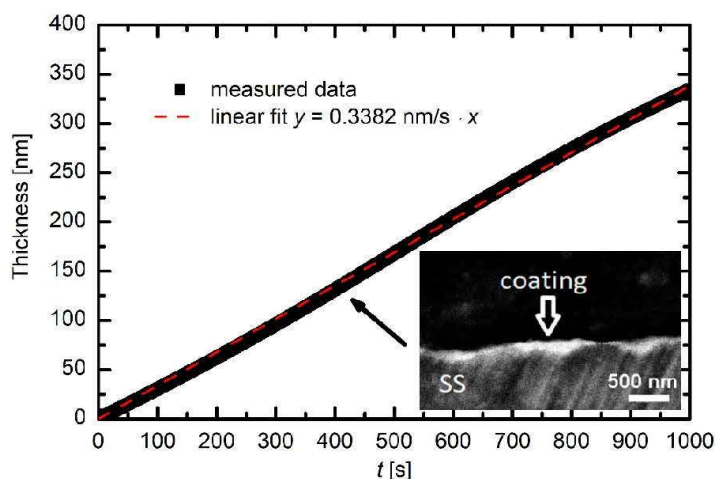


Figure 6. The film thickness versus deposition time. Inset shows a scanning electron microscope (SEM) image of a cross-section of a selected sample after deposition for approximately 400 s.

The slope of the curve in Figure 6 allows for determination of the deposition rate. The rates measured at different HMDSO flows are shown in Figure 7. One can observe an almost linear increase of the deposition rate with increasing precursor flow. Compared to the behavior of plasma density (Figure 5), the slope of the deposition curve is much larger than the slope of the plasma density. The discrepancy is attributed to the fact that the major building units of the deposited films are not positively charged, but they are rather neutral reactive particles. In fact, the deposition rate is of the order of 10 nm/min, which is much larger than the maximal deposition rate calculated from the estimated ion flux onto the sample surface using results presented in Figures 4 and 5. This observation is different from results reported for the case of rather small experimental reactors. For example, Ropcke [3] reported strong gradients in radical emissions that in turn caused spatial dependence of the deposition rate. The deposition rate correlated well with the intensity of optical emission. They used a capacitive coupled electrodeless RF discharge for sustaining plasma in a tube of a volume of approximately 50 cm³ and a discharge power of a few tens of watts, and therefore the power density was of the order of 10⁵ W/m³. Furthermore, they used argon as a major gas with a small admixture of HMDSO. At such conditions, the precursor was highly dissociated already upon entering the gas into the plasma zone, and therefore the thickness of the deposited film decreased with increasing distance from the injection point. In the electrodeless CCP configuration, no significant change of the electron temperature (as derived from the H_{α}/H_{β} ratio) was detected, although the gas composition changed significantly along the glass tube. This observation indicated the importance of the argon/hydrogen kinetics at a relatively low level of HMDSO.

The deposition rate at the highest flow deviates significantly from the general trend (Figure 7), although the ion density (Figure 5) keeps increasing with increasing HMDSO flow in the entire range of flows. The discrepancy can be explained by the fact that the ion density was deduced from the measured electrical current on the powered electrode, whereas the thickness sensor was mounted far from the electrodes. In one configuration, Ropcke [3] employed a standard capacitive RF discharge and observed a huge gradient in the hydrogen atom kinetic temperature (as deduced from H_{α} line broadening) next to the powered electrode. This observation indicates important differences between the sheath and plasma kinetics in capacitive RF discharges. The tendency toward a saturation of the deposition rate at higher HMDSO ratios in plasma far away from the powered electrode may be a consequence of the more extensive collisions next to the powered electrode and thus unwanted film deposition on the electrode on the expense of a film deposited on the surface of any other material mounted into the plasma reactor.

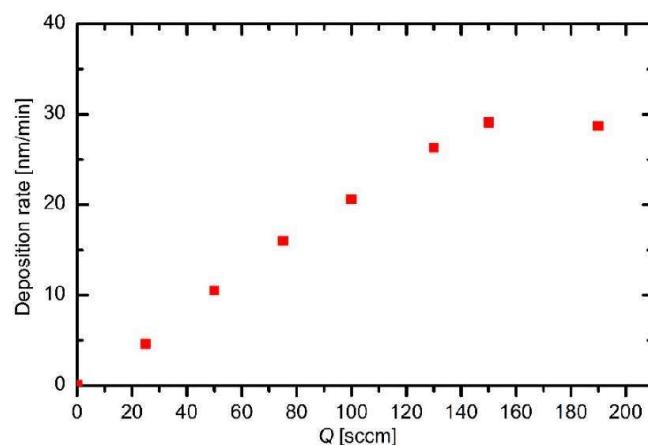


Figure 7. Deposition rates versus HMDSO flow at a discharge power of 3.4 kW.

The deposition rate versus the discharge power exhibits a more interesting behavior. A maximum at a power of approximately 5 kW is observed in Figure 8. Though these measurements were performed only at the flow rate of 130 sccm, and thus they cannot be regarded a general trend, they indicate rather interesting deposition kinetics. Here, it is worth recalling the densities of particles in the plasma reactor. The plasma density is of the order of 10^{14} m^{-3} as revealed from Figures 4 and 5, whereas the density of neutral gaseous molecules is of the order of 10^{21} m^{-3} . The ionization rate is therefore only of the order of 10^{-7} . The original HMDSO molecules will not contribute to the growth rate, but some of their fragments would. A larger discharge power results in the larger plasma density and thus more intensive fragmentation of the precursor molecules. Not all fragments, however, are suitable as the building units for the deposit. Furthermore, a larger power represents a higher thermal load for the powered electrode, which in turn causes higher temperatures and thus preferential deposition of the coating on the powered electrodes. In fact, Ropcke et al. [3] reported strong gradients in plasma parameters at elevated power densities causing an interesting behavior of deposition kinetics.

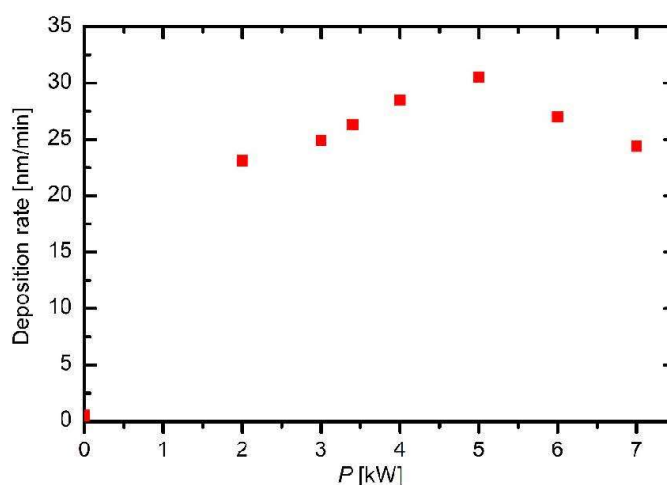


Figure 8. Deposition rates versus discharge power at an HMDSO flow of 130 sccm.

In any case, the deposition rate is of the order of 10 nm/min (see Figures 7 and 8). At this point, it should be stressed that these deposition rates were measured rather near the electrodes, and therefore, these values are the upper limit of the deposition rates inside the reactor. Further away from the electrodes, the deposition rates are smaller. The flow in Figure 8 was set at 130 sccm. The mass flow

(Φ_{mas}) through the system is calculated as the product of the volume flow (S_2) and mass density (ρ) at the pressure where the volume flow is measured ($\Phi_{mass} = S_2 \rho$). The mass density (ρ) of gas is calculated from the number density and the mass of the molecule taking into account an ideal gas law, and therefore the mass flow is

$$\Phi_{mass} = S_2 \rho = S_2 M_{HMDSO} p_2 / (kT) \quad (10)$$

where M_{HMDSO} is the mass of a HMDSO molecule (i.e., 2.8×10^{-25} kg), S_2 is the volume flow as determined by the flowmeter, and p_2 is the pressure at the flow meter, i.e., 1 bar. The mass flow through the system at the flow rate of 130 sccm ($= 2.17 \times 10^{-6}$ m³/s) is therefore approximately 1.5×10^{-5} kg/s. At these conditions, the measured deposition rate is approximately 25 nm/min (see Figure 8). The mass deposited in unit time on the surfaces of any components placed in the plasma reactor is calculated from the measured deposition rate and the estimated density of the deposit and total surface area of any materials facing plasma:

$$dm/dt = dx/dt \rho_{dep} A_{tot} \quad (11)$$

The parameters in Equation (11) can only be roughly estimated. Taking into account the density of the PDMSO-like coating $\rho_{dep} = 10^3$ kg/m³, the total surface area $A_{tot} = 15$ m², and the measured deposition rate $dx/dt = 25$ nm/min, one gets the quantity of mass deposited on the surface of the reactor in unit time $dm/dt = 0.6 \times 10^{-5}$ kg/s. This value is surprisingly close to the mass flow as calculated from Equation (10). However, this value again is the upper limit due to the fact that the upper limit deposition rate, measured near the electrodes, is used for this calculation. The average deposition rate throughout the reactor is probably almost an order of magnitude lower, and consequently, the dm/dt is lower.

Several small stainless steel samples were mounted onto planetaria in the plasma reactor. The samples were kept in the plasma reactor for 20 min at a flow of 130 sccm and 3.4 kW power and then characterized by ToF-SIMS depth profiling. A typical profile is shown in Figure 9. One can recognize a polymer-like coating resembling polydimethylsiloxane.

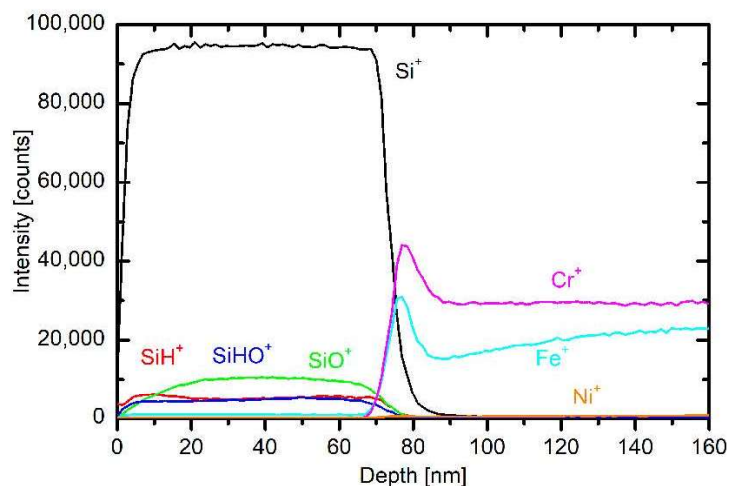


Figure 9. A typical secondary ion mass spectrometry (SIMS) depth profile of the polydimethylsiloxane (PDMSO)-like coating where only the most intense mass peaks are presented.

The concentrations of elements are somehow different from the theoretical value, but SIMS is not the best technique for determination of absolute concentrations of the elements. Still, the depth profile shows a reasonably uniform coating that is useful as a protection coating. The depth profile of the sample, which was positioned on the other side of the reactor furthest from the electrode, also proves that the deposition rate is not uniform across the reactor, and the average deposition rate is smaller than the ones measured near the electrode.

Additional surface analyses were performed using XPS to reveal a detailed chemical composition of the coating. The surface composition as calculated from the survey spectra showed similar concentrations of oxygen and silicon, i.e., approximately 26 and 25 at%, respectively, whereas the concentration of carbon was approximately 49 at%. Such surface composition of the deposit is very similar to the theoretical composition of PDMS, indicating that PDMS is a dominant component of the coating. Similar results were also found by other authors [33,34]. However, to get more insight into the chemical composition, high-resolution spectra of C1s, Si2p, and O1s were also measured and compared to the spectra measured for the reference samples of pure PDMS and SiO₂. Deconvolution of high-resolution XPS spectra for C1s, Si2p, and O1s is shown in Figure 10, whereas the comparison of the spectra with the reference samples is shown in supplemental information in Figure S1 (Supplementary Materials). The results showed that the coating consists mostly of PDMS with some presence of a SiO₂ component. Some additional analysis of the chemical composition of the samples can be also found in our recent paper [28].

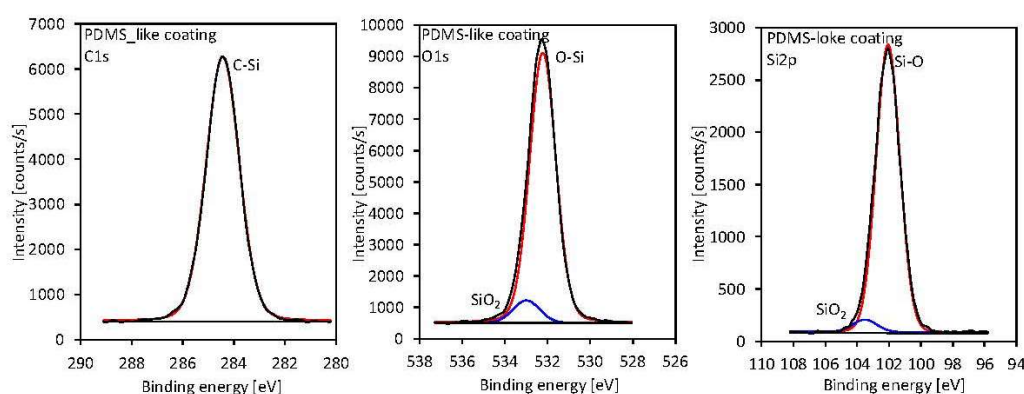


Figure 10. High-resolution X-ray photoelectron spectroscopy (XPS) spectra of carbon C1s, oxygen O1s, and silicon Si2p for the deposited coating.

4. Conclusions

The deposition kinetics for thin films by plasma-enhanced chemical vapor technique using hexamethyldisiloxane in a large industrial plasma reactor was studied. The available discharge parameters were the gas pressure and flow; the pumping speeds of the pumps; the voltage, current, and power of the RF generator used for sustaining an asymmetrical discharge in the capacitive mode; and the geometry of the system. The deposition kinetic was measured by optical interferometry using a custom-designed miniature fiber-optics sensor, whereas the structure of the deposited films was determined after the treatment by SIMS depth profiling. The combination of available data allowed for an insight in the deposition kinetics. The plasma density was roughly estimated from measured discharge parameters because the industrial system did not allow for the immersion of a suitable electrical probe. The ionization fraction was of the order of 10^{-7} , but the residence time of gas in the reactor was approximately 100 s, so the gaseous precursor was well-dissociated to various radicals. This enabled the growth of a film of a composition close to polymethyldisiloxane. The available material for the growth of the thin film was rather well utilized because the amount of material as

calculated from the measured deposition rate was comparable to the available mass calculated from the flow of gas through the system.

Supplementary Materials: The following are available online at <http://www.mdpi.com/1996-1944/12/19/3238/s1>, Figure S1: Comparison of XPS spectra of the coating with the reference samples of PDMS and SiO₂ for (a) C1s, (b) O1s, and (c) Si2p, and detailed surface spectra of the coating with subcomponents for (d) C1s, (e) O1s, and (f) Si2p.

Author Contributions: Conceptualization, Ž.G., M.M., and R.Z.; methodology, A.V., D.Đ., and J.K.; validation, G.P., S.P., and A.V.; formal analysis, R.Z., S.P., and J.K.; investigation, R.Z., J.K., S.P., D.Đ., and Ž.G.; resources, Ž.G., R.Z., D.Đ., and J.K.; data curation, J.K., R.Z., S.P., and G.P.; writing—original draft preparation, Ž.G. and M.M.; writing—review and editing, Ž.G., M.M., A.V., and R.Z.; visualization, R.Z.; supervision, Ž.G. and M.M.; project administration, A.V. and G.P.; funding acquisition, M.M. and D.Đ.

Funding: Some authors acknowledge the project (Innovative sensors for real-time monitoring of deposition rates in plasma-enhanced chemical vapor deposition (PECVD) systems, ID L2-1835), which was financially supported by the Slovenian Research Agency. Other authors acknowledge the financial support from the Slovenian Research Agency (research core funding No. P2-0082).

Conflicts of Interest: The authors declare no conflict of interest.

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Chapter 5

PECVD of HMDSO in Extremely Asymmetric Capacitive RF Discharge

The deposition rates of polymer-like films in the large industrial-size plasma reactor shown in Figure 1 are rather low. Industry wants larger deposition rates, which are not achievable in the reactor because of the limitations of the discharge configuration. We plan to change the configuration in the industrial reactor, but before doing this, we wanted to check our hypothesis. To evaluate possibilities for depositing quality films at much larger deposition rates, we constructed a smaller reactor of a volume of about 25 liters. The deposition kinetics was studied in this smaller reactor using an innovative configuration: instead of moderately asymmetric configuration of the industrial-size reactor, we used an extremely asymmetric electrode configuration. The size of the powered electrode was orders of magnitude smaller than in the industrial reactor. The configuration allows much larger power densities, and we studied the evolution of the polymer-like film on the surface of substrates versus the discharge power. We used different flow rates of oxygen and HMDSO, resulting in different gas-phase chemistry. The plasmas sustained in mixtures of these gases were characterized by optical spectroscopy. The optical spectrum of plasma sustained in pure oxygen was similar to the spectrum acquired in the large reactor. The spectral features when using HMDSO as the precursor, however, were different. In particular, the strong emission from the excited hydrogen molecules (Fulcher band) was observed and related to extensive recombination of H-atoms to H_2 molecules. The continuum, which was hardly visible in the industrial reactor, was now the major source of radiation from gaseous plasma. Since the water vapor concentration was low, the spectra acquired in pure HMDSO were free from emission arising from CO bands. Therefore, the continuum was not a consequence of the peak overlapping but the presence of radicals that emit continua. We were not able to identify the radicals because numerous three- or multi-atom molecules are capable of emitting continua. On the other hand, the spectra in mixtures of oxygen and HMDSO were rich in CO radiation, indicating extensive oxidation of organic components in the experimental reactor. No atomic oxygen lines were observed in the spectra, which was another confirmation of rich chemistry. Aluminum substrates were used to study the kinetics of polymer-like film deposition. The deposited films were characterized by X-ray photoelectron spectroscopy. Systematic research was performed at different deposition times and discharge powers, and only selected depth profiles are shown in this scientific paper. As long as the treatment times in pure HMDSO were reasonably short and the discharge power reasonably low, the deposited films were similar to those obtained in the industrial reactor. Prolonged deposition, however, caused modification of the film composition. The silicon and oxygen concentrations in the deposited film increased at the expense of the carbon concentration. The film was not any more stoichiometric polymer

but rather a polymer matrix with embedded silica-rich grains. As explained in the introduction to this thesis, the grains indicate the formation of clusters in the gas phase. A similar effect was observed at relatively short deposition times but with high discharge powers. The main conclusion of this research is a serious limitation of the discharge parameters that enable the deposition of thin films of desired properties. Therefore, the experiments published in this paper are useful for future modification of the discharge configuration in the industrial-size reactor shown in Figure 1.

Article

PECVD of Hexamethyldisiloxane Coatings Using Extremely Asymmetric Capacitive RF Discharge

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Received: 19 February 2020; Accepted: 4 May 2020; Published: 6 May 2020



Abstract: An extremely asymmetric low-pressure discharge was used to study the composition of thin films prepared by PECVD using HMDSO as a precursor. The metallic chamber was grounded, while the powered electrode was connected to an RF generator. The ratio between the surface area of the powered and grounded electrode was about 0.03. Plasma and thin films were characterised by optical spectroscopy and XPS depth profiling, respectively. Dense luminous plasma expanded about 1 cm from the powered electrode while a visually uniform diffusing plasma of low luminosity occupied the entire volume of the discharge chamber. Experiments were performed at HMDSO partial pressure of 10 Pa and various oxygen partial pressures. At low discharge power and small oxygen concentration, a rather uniform film was deposited at different treatment times up to a minute. In these conditions, the film composition depended on both parameters. At high powers and oxygen partial pressures, the films exhibited rather unusual behaviour since the depletion of carbon was observed at prolonged deposition times. The results were explained by spontaneous changing of plasma parameters, which was in turn explained by the formation of dust in the gas phase and corresponding interaction of plasma radicals with dust particles.

Keywords: PECVD; HMDSO; PDMS; extremely asymmetric CCP; OES; XPS depth profiling; dust particles

1. Introduction

Plasma-enhanced chemical vapour deposition (PECVD) can be used for deposition of polymer-like silicon-containing coatings such as polydimethylsiloxane (PDMS) coatings. For deposition of such coatings, various precursors [1] can be used. Often the precursor is hexamethyldisiloxane (HMDSO) [2–4]. Gaseous plasma is sustained by various discharges, and a commonly applied one is a radio-frequency (RF) discharge where the RF power is applied in capacitive mode, i.e., the RF voltage is applied to a couple of electrodes. One electrode is usually just the grounded housing of a vacuum chamber, while the powered electrode is immersed into the metallic vacuum chamber using electrically-insulated feedthrough. Both electrodes are usually of large surface area. The powered electrode is often mounted into the vacuum chamber in such a way that the distance to the grounded housing is low enough to enable rather uniform plasma in the entire volume of the plasma chamber except in the gap between the powered electrode and the housing. The breakdown follows the Paschen

curve, which has the minimum at roughly 1 cm torr [5]. The pressure inside the plasma chamber is often around 10 Pa, so the breakdown is likely to occur in the chamber volume rather than in the gap, providing the gap thickness is less than a few cm. An alternative is a discharge chamber with two electrodes of same dimensions mounted symmetrically in the chamber. The chamber can be metallic or made from a dielectric material with a couple of circular electrodes of equal dimensions inserted into the chamber. The configurations are schematically presented in Figure 1a,b. These configurations have been used by several authors.

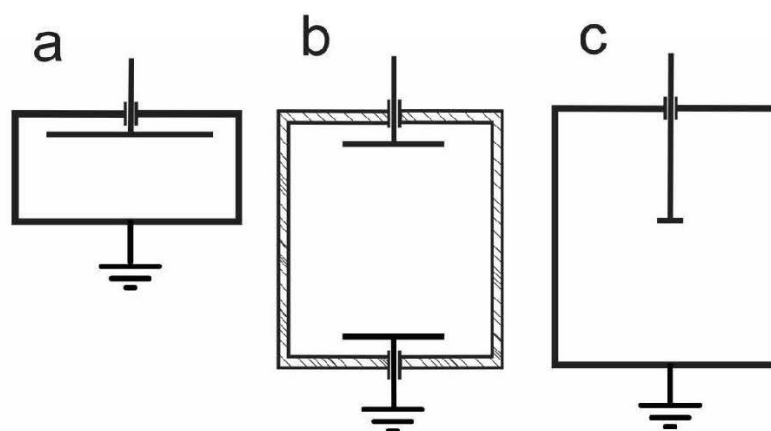


Figure 1. Three configurations of RF discharges sustained in capacitive mode: (a) moderately asymmetric; (b) symmetric; and (c) extremely asymmetric.

Ropcke et al. [6] used symmetric RF discharge (Figure 1b) operating at the standard industrial frequency of 13.56 MHz. The diameter of both electrodes was 13 cm, and the distance between the electrodes was 4 cm. They studied plasma properties using optical emission spectroscopy. Although the configuration was symmetric, they found some variation of the plasma parameters in the gap between the electrodes. The ratio between hydrogen emission lines H_{α}/H_{β} was somewhat independent of the distance between the electrodes, indicating a rather uniform electron temperature in the entire volume between the electrodes. In contrast, the gas temperature as deduced from Doppler line broadening was almost 2000 K close to the powered electrode and below 500 K next to the grounded electrode.

Li et al. [7] used an asymmetrical capacitive discharge (Figure 1a) at 13.56 MHz and RF power up to 200 W. Plasma was sustained in the pulsed mode in a metallic reactor of volume 20 L at pressures between 10 and 100 Pa. Plasma was characterised by IR absorption spectroscopy and mass spectrometry, whereas the film thickness by ellipsometry. The reactor was filled with HMDSO, and its fragmentation was evaluated versus discharge time. The differences in the fragmentation degree clearly influenced the quality of the deposited film. As long as the molecular fragmentation was low, the structure of the films deposited on the powered electrode and the floating substrates was rich in an organic component. The concentration of this component in the films decreased with increasing fragmentation of the precursor in the gas phase. The difference, however, was not dramatic. The deposition rate, on the other hand, increased monotonously with increasing fragmentation in the gas phase, indicating a rather poor sticking of large molecules on the substrates. The deposition rate at the powered electrode was over an order of magnitude larger than on the floating substrates, which was explained by gradients of plasma density next to the powered electrode: more intensive fragmentation occurred next to the powered electrode while fragmentation in the positive column of plasma far from the sheath was not complete.

An asymmetric RF discharge was also used by Naddaf et al. [8]. They employed a hollow electrode and powered it with an RF generator operated at 13.56 MHz and power up to 300 W. The plasma density of the order of 10^{17} m^{-3} was estimated with a Langmuir probe. Both the deposition rate and Si–O–Si bond in the deposited film increased with increasing RF power at the constant pressure of 3 Pa.

Hydrogen de-trapping was observed at higher power where the deposited film contained less Si-CH₃ bonds as well. Increasing the precursor flow rate at constant pressure and power caused a significant increase of the film thickness indicating substantial consumption of the precursor for growth of the solid film at low flow rates (higher gas residence time).

A moderately asymmetric RF discharge in capacitive mode was applied by Garofano et al. [9]. The powered electrode was of diameter 10 cm, the grounded of diameter 12 cm and the metallic chamber was grounded, too. The background gas was argon with a small admixture of Ne, Kr and Xe, and the HMDSO was injected in pulses. The pressure was between 5 and 6 Pa. At the RF power of 30 W, the self-bias voltage on the powered electrode was about −550 V. Plasma was characterised by optical emission spectroscopy. In such experimental conditions, dust appeared in the plasma reactor and peaked within a minute after injecting the precursor.

Santos et al. [10] employed a similar reactor as Garofano to study the deposition kinetics of thin PDMS films using an admixture of 70% HMDSO, 10% Ar and 20% O₂. The electrodes were made from stainless steel, and the films were deposited primarily onto the powered electrode. The total gas pressure was 8 Pa and the deposition time half an hour. The RF power was varied between 15 and 75 W. The reported self-bias was several 10 V, and it increased almost linearly with increasing RF power. The film thickness was almost perfectly linear with the reported self-bias. The increasing thickness was explained with increasing electron density in the gap between the electrodes, which was 3.5 cm. Increasing the power beyond 75 W resulted in the detachment of the films from the substrates, which was explained by an increase in the intrinsic stress with increasing film thickness. Pre-cleaning of the substrates with plasma treatment was found beneficial for adhesion of the coating. The relative concentration of C, Si and O in the solid film as deduced from XPS measurements did not depend on the RF power significantly.

A similar moderately asymmetric configuration in the reactor of volume 0.1 m³ was also applied by Corbella et al. [11]. A round electrode of diameter 30 cm was powered with an RF generator at 13.56 MHz and powers 160 and 200 W. Argon was added to HMDSO to enhance the monomer fragmentation and stabilise the discharge. Unlike other authors, they also reported the gas residence time, which was about 1 s. The key parameter governing the quality of the films produced at that condition was found to be input power per gas flow.

Fanelli et al. [12] also employed the moderately asymmetric configuration. The 13.56 MHz generator was used for powering a stainless-steel plate. Various mixtures of argon, HMDSO and O₂ were used, but the total pressure was kept almost constant at 27 Pa. A liquid-nitrogen-cooled trap was used to collect the products of plasma-induced fragmentation of the precursor. As many as 20 compounds were detected upon heating of the trap after sampling the fragments for 20 min. The predominant fragments observed at the selected conditions were tetramethylsilane and octamethyltrisiloxane. They found Si–O bond cleavage in HMDSO an important reaction at various conditions. Furthermore, they provided solid proof that oligomerisation occurred at those conditions. About 20% of HMDSO was lost upon plasma-induced fragmentation, and this value was independent of the concentration of oxygen in the original gas mixture. Oligomerisation was also observed by mass spectrometry by Alexander et al. [13]. They observed molecular oligomerisation of positively charged gaseous species at a rather low discharge power, whereas at large powers fragmentation prevailed.

Plasma sustained by capacitive discharges is famous for the spontaneous formation of dust particles [14]. The plasma reactor was powered with a standard 13.56 MHz RF generator coupled in moderately asymmetric mode. Pulsed plasma was created in mixtures of argon and HMDSO. The formation of dust particles in gaseous plasma was observed in about one minute. With prolonged plasma duration, the dust particles disappeared from the gas phase, which was explained by ion drag forces. The dust was deposited on all surfaces facing plasma after turning off the discharge. The authors also discussed the sputtering of the organosilicon coating due to large self-biasing of the substrate, which was placed onto the powered electrode.

The above-cited authors used either an almost symmetric coupling or moderately asymmetric coupling of the RF discharge in the capacitive mode (Figure 1a,b). Various discharge parameters were used by different authors, thus it is difficult to compare their results. However, it is possible to deduce qualitatively that the organic component in the deposited films decreased with increasing molecular fragmentation (discharge power) and with increasing oxygen admixture to the HMDSO or a mixture of HMDSO and a noble gas. Very little work, however, was reported on the behaviour of plasma and properties of deposited films for the case of extremely asymmetric coupling. Such a coupling may be interesting from both scientific and technological points of view. Although it is rarely mentioned in scientific literature, the symmetric (or moderately asymmetric) configuration of capacitive RF discharge has a technological drawback: the deposition of thin films from gaseous precursors occurs predominantly on the electrodes. This is because the electron heating occurs predominantly within the volume next to the electrodes. The samples that are kept away from the electrodes at the floating potential receive much less deposit than any sample placed onto an electrode. This effect might be suppressed using small electrodes. The properties of thin films deposited onto samples kept at floating potential are shown in this paper. Possible explanations of rather unexpected results are also provided. The objective of this paper is therefore a feasibility study on using extremely asymmetric capacitive coupled RF discharge for depositing thin films by PECVD method.

2. Materials and Methods

Three configurations of RF discharges sustained in capacitive mode are schematically presented in Figure 1. First two configurations (Figure 1a,b), show a moderately asymmetric and symmetric configuration, respectively. These configurations are commonly used, as already mentioned in the Introduction. In the symmetric configuration (Figure 1b), both electrodes are of the same size, and the discharge tube is made from a dielectric—often glass. The electrons are heated in the volume next to the electrodes where the oscillating electric field is large. The electric field is marginal in the volume far from the electrodes and therefore only diffusing plasma is sustained in the majority of the discharge chamber volume. The heating of electrons is the same next to both electrodes. Both electrodes assume the same DC self-biasing, and the deposition rates are the same on both electrodes.

In the case of moderately asymmetric RF discharge (Figure 1a), the area of the powered electrode is smaller than the grounded electrode. As a result, the DC self-biasing occurs practically only on the powered electrode. Any sample placed onto the powered electrode is thus subjected to bombardment by energetic positively charged ions. On the other hand, the DC self-biasing of the large grounded electrode is much smaller than on the biased electrode, so kinetic effects caused by ion bombardment are much less pronounced than in the case of the symmetric coupling. Many experimental and most industrial devices for deposition of thin films using the PECVD technique employ the moderately asymmetric configuration. The objects to be coated with a thin film are often placed into the entire volume of the discharge chamber where diffusing plasma is sustained. The objects are often placed onto a planetarium and rotated upon plasma treatment to suppress negative effects of any gradients of gaseous radicals. The moderately asymmetric configuration still suffers from the loss of radicals on the powered electrode where the deposition rate is often ten times larger than on the objects kept within the diffusing plasma at a floating potential.

Figure 1c represents a case of extremely asymmetric configurations. By our definition, such a configuration is characterised by a large ratio between the area of the grounded and powered electrodes, often several 10-times. In this paper, we define extremely asymmetric RF discharge in a capacitive mode as a configuration where the ratio between the grounded and powered electrode areas is over 20. In such a configuration, the DC self-biasing of the grounded electrode is negligible, so any object placed onto the grounded electrode or on a planetarium in the volume filled with diffusing plasma receives almost the same flux of radicals (providing there are no large gradients in radical density within diffusing plasma). A small powered electrode should represent a small sink for plasma radicals since the loss rate is a product of the radical flux, sticking probability and surface area.

Experiments in this study were performed in a plasma reactor using the extremely asymmetric coupling of an RF generator, as shown schematically in Figure 1c. The experimental setup is shown in Figure 2.

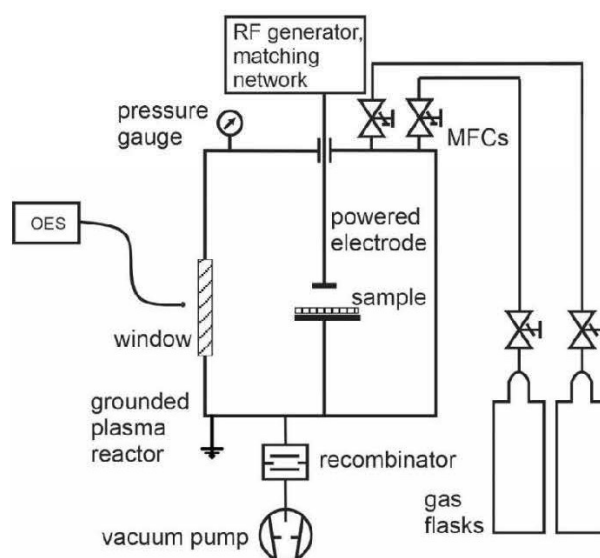


Figure 2. Schematic of the experimental system.

The reactor was made from stainless steel. It was pumped with a two-stage rotary pump of nominal pumping speed $80 \text{ m}^3/\text{h}$. A trap made from nickel network was placed between the discharge chamber and the vacuum pump in order to assure for at least partial recombination of gaseous radicals and adsorption of molecular fragments and thus prevent such species enter the pump. The pressure was measured with an absolute vacuum gauge of pressure range 1–1000 Pa. Gases were introduced into the chamber via flow controllers calibrated for corresponding gases. Both HMDSO and oxygen were introduced at different rates in order to assure for desired gas mixtures. The total surface of the grounded walls was estimated to about 0.41 m^2 . The powered electrode was a small disk on a stainless-steel rod with a surface of approximately 1.5 dm^2 . The ratio between the area of the powered and grounded electrode was therefore about 0.03, thus assuring for extremely asymmetric conditions shown schematically in Figure 1c.

The RF generator operated at the standard industrial frequency of 13.56 MHz and variable output powers up to about 1000 W. In such conditions, the sheath between gaseous plasma and the grounded housing was practically identical to a sheath that forms spontaneously on any floating object. The difference between space and floating potentials is, therefore, easily estimated from the electron temperature, as explained in classical literature [15]. The powered electrode assumed DC self-biasing, as explained in classical literature [15]. The DC self-biasing is roughly the same as the effective voltage of the power supply, which in our case is about 600 V. The sheath next to the powered electrode is not only characterised by a large oscillating bias but also expands much further from the surface as compared to the sheath next to grounded housing. The oscillating sheath of luminous plasma next to the powered electrode was visible with a naked eye, and its thickness was about 1 cm. Optical spectra were acquired from the plasma away from the sheath. We used a 0.5 nm resolution optical spectrometer Avantes AvaSpec 3648 (Avantes, Apeldoorn, The Netherlands) spectrometer that works over the range of 200–1100 nm, connected to an optical fibre. The lenses on the other side of the fibre were mounted in such a way that we sampled optical spectra from plasma close to substrates. These were placed onto the grounded housing, as shown in Figure 2. The optical window mounted on one flange was made from Pyrex glass which absorbs radiation in the UV range below about 320 nm.

The substrates were made from aluminium. A commercial Al sheet of thickness 0.3 mm was cut to rectangular pieces of about $1\text{ cm} \times 1\text{ cm}$. The samples were roughly cleaned with ethanol before insertion into the plasma reactor. No polishing was applied. A part of each sample was covered with an adhesive tape which was carefully removed after performing plasma experiments. The step formed between the uncovered and covered parts of a substrate was then probed by atomic force microscopy (AFM, NT-MDT Spectrum Instruments, Moscow, Russia) to estimate the thickness of the deposited film. This thickness was then used for calibration of depth profiles which were acquired by XPS.

The samples were placed into the reactor, which was then pumped for a few minutes until the pressure, as measured with the gauge, stabilised at $1.7 \pm 0.2\text{ Pa}$. Then, gases were introduced upon continuous pumping, and the discharge was turned on for an appropriate period. Treatment times were up to 1 min. The uniformity of the coatings was checked with a scanning electron microscope (SEM, JEOL, Tokyo, Japan). A typical SEM image of an HMDSO coated sample is presented in Supplementary Materials (Figure S1).

Samples were characterised by X-ray photoelectron spectroscopy (XPS). A TFA XPS instrument from Physical Electronics (Chanhassen, MN, USA) was used with the base pressure in the analysis chamber of about $6 \cdot 10^{-10}\text{ mbar}$. The samples were excited with X-rays over a specific $400\text{ }\mu\text{m}$ area using monochromatic $\text{Al K}_{\alpha 1,2}$ radiation at 1486.6 eV. For the photoelectron detection, a hemispherical analyser, positioned at an angle of 45° with respect to the surface normal, was used. The energy resolution was about 0.6 eV. The measured spectra were analysed using MultiPak v7.3.1 software from Physical Electronics, which was supplied with the spectrometer. Ar-ion sputtering during XPS depth profiling was performed with the Ar-ions of energy of 4 keV. Ar sputtering with monoatomic gas may induce preferential sputtering and changes in surface chemistry, in particular for organic films. Usually, the preferential sputtering of O-atoms is present during profiling of organic films containing oxygen species. For inorganic SiO_2 -like films, the change in composition during XPS depth profiling due to preferential sputtering is much smaller. From both mentioned effects we expect that for our films, which are hybrid inorganic–organic C–Si–O films, probably a smaller extent of preferential sputtering of oxygen may be expected. This might be relevant for the depth of films, where an organic component was still present, i.e., at the film/substrate interface. Regardless, we expect that preferential sputtering of oxygen in this region will cause a relative reduction of O for about 10% of the reported atomic concentration of oxygen, which is not so relevant for our results. In depth profiles, the Ar sputtering time is replaced with depth even though the sputtering rates are not the same for Al-oxide and SiOCH films. However, the rough approximation about similar sputtering rates [16] is still good enough for the subject of this study, which is mainly a comparison of thicknesses and composition of the SiOCH films and less related to the thickness of the Al-oxide layer covering the Al substrate.

3. Results and Discussion

3.1. Optical Spectra

Plasma was characterised by optical emission spectroscopy. Typical spectra are shown in Figures 3–5. Figure 3 represents an optical spectrum of plasma sustained in oxygen.

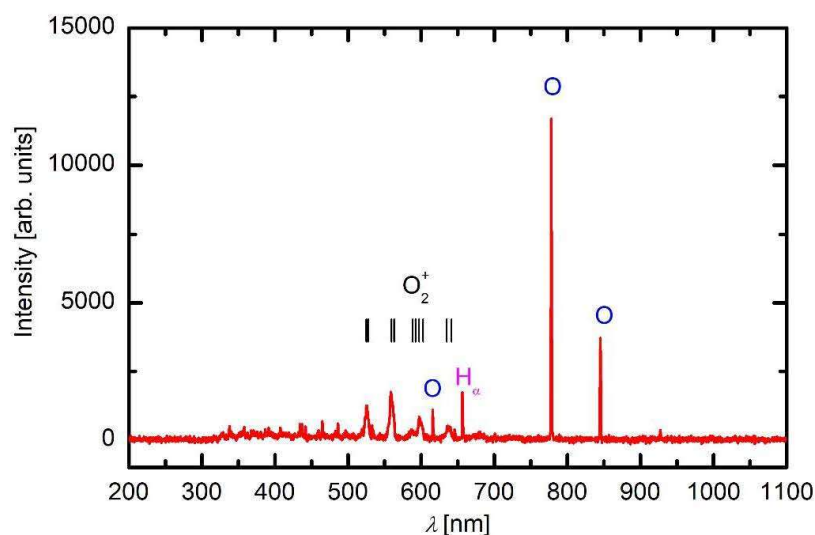


Figure 3. A spectrum of plasma in oxygen at 10 Pa and 200 W.

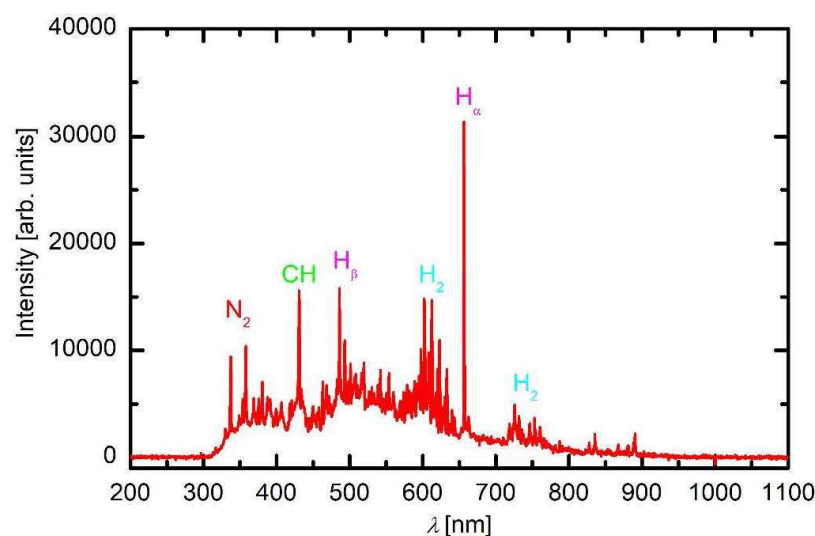


Figure 4. A spectrum of plasma in HMDSO at 10 Pa and 200 W.

The predominant peaks at about 777 and 845 nm correspond to radiative transitions of neutral oxygen atoms. Apart from these ones can observe other features such as H_{α} line at 656 nm, and O_2^+ bands in the range from about 500 to 650 nm which arise from radiative transitions of ionised oxygen molecule [17]. The appearance of hydrogen atomic line is typical for gaseous plasma sustained in chambers which have never been baked and are pumped by fore pumps only. Namely, the residual atmosphere in such vacuum systems usually contains water vapour which dissociates to OH and H radicals upon plasma conditions. The OH band which should appear at the bandhead of 309 nm is not visible in the spectrum due to poor transmission of the glass window in the UV range. There are some weak spectral features also in the range from about 320 and 550 that could be attributed to CO bands. The CO is a product of an interaction between O-atoms and O_2^+ ions or both with any carbon in the system. The origin of carbon is in the deposited films. Namely, the spectra were acquired after performing numerous experiments with HMDSO. Upon these experiments, a layer containing Si, O, C,

and H were deposited on the walls, and the carbon is slowly etched when such layers are exposed to oxygen plasma.

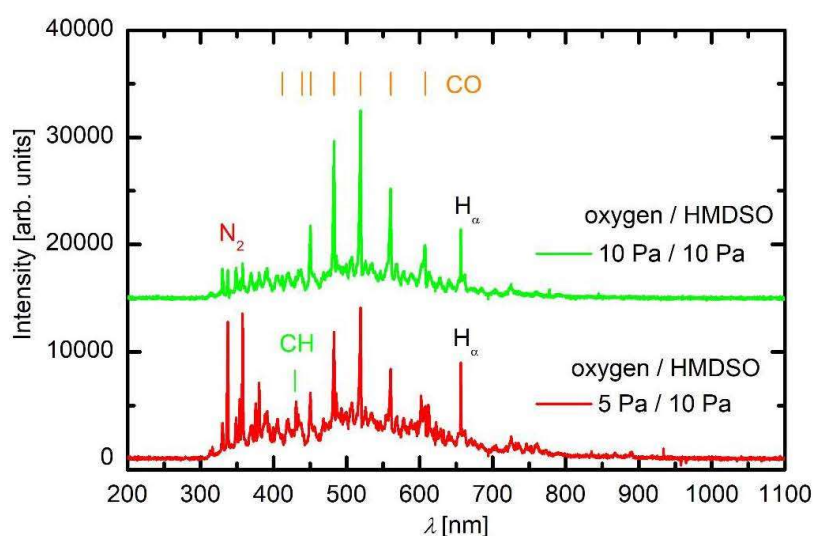


Figure 5. A spectrum of plasma in oxygen/HMDSO mixture 1/2 (bottom curve) and 1/1 (top curve) at 200 W.

An optical spectrum acquired in HMDSO plasma is shown in Figure 4. The spectrum is completely different from that acquired in oxygen. The O lines are not distinguishable, and the highest peak is H_{α} . Apart from the dissociation of water vapour, the atomic hydrogen appears as a result of dissociation of both precursor molecules and their fragments. There are numerous other bands and lines in the visible range which form a virtual continuum, probably because of overlapping of numerous molecular bands. The significant lines were identified and are marked in Figure 4. Among them, the molecular hydrogen bands (Fulcher bands) are most extensive. Such intensive bands indicate a qualitatively large concentration of hydrogen molecules in gaseous plasma created in HMDSO.

The origin of hydrogen molecules in gaseous plasma of hydrocarbons sustained at low pressure is usually attributed to the surface association of H atoms to H_2 molecules. A clearly distinguished CH band with the bandhead at 431 nm indicates another channel for the radicalisation of the precursor molecule. At electron impact, methyl radicals are likely to be formed [18], and these radicals are further dissociated upon plasma conditions to form CH radicals. Although the sticking coefficient for CH on any surface kept at room or slightly elevated temperature is very large [19], their production in the gas phase is obviously large enough to identify the bandhead doubtlessly. The nitrogen band is probably due to slight leakage of the system, but the broad virtual continuum expanding over the entire visible range could be attributed to various effects. Both CO molecules, C_2 dimers and H_2 molecules radiate in the visible part of the optical spectrum, so any distinguishing is regarded as impossible. However, the spectrum presented in Figure 4 indicates a number of atoms, molecules and radicals in plasma sustained in HMDSO and thus a variety of gas-phase dissociation reactions.

Figure 5 represents optical spectra of plasma sustained in the mixture of 2/3 HMDSO and 1/3 O_2 (bottom curve) and 1/2 HMDSO and 1/2 O_2 (top curve). Apart from the virtual continuum, which is still dominant in integral radiation in the visible range, the spectrum is much different from that in HMDSO plasma. The CH bandhead at 431 nm is suppressed, and so is the radiation arising from hydrogen molecules and atoms. The major radiation in this gas mixture arises from CO bands. The major “lines” arising from CO Angström system are marked in Figure 5. There are a couple of other systems (Asundi bands and the triplet bands) that partially overlap with the Angström system, but they are not marked in this figure for the sake of clarity. The production of CO molecules in the experimental

plasma reactor is therefore extensive. The formation of the CO molecule upon a collision of oxygen radical with a carbon-containing molecule is highly improbable since the reaction is highly exothermic and would require a super-elastic collision to assure for the conservation of energy and momentum. The production of CO is therefore likely to occur on surfaces. As mentioned in the previous paragraph, the sticking coefficient of CH radicals on surfaces kept at room temperature is large. For CH₂ radicals, it is lower but still significant. According to Tichmann [19], the sticking coefficient of low-energy CH₃ radicals on a surface at room temperature is still about 0.5. The CH_x radicals ($x < 4$) therefore stick well to surfaces. Many radicals undergo surface association to light stable hydrocarbons that desorb from the surface, but many interact with atomic oxygen. The atomic oxygen interacts readily with such deposits and causes rapid removal of the deposited hydrocarbons so the deposited film does not contain a measurable amount of hydrogenated carbon, as becomes obvious from results of film characterisation presented below. The extensive CO bands, as observed in Figure 5, are therefore attributed to surface reactions.

Further addition of oxygen causes even more pronounced CO radiation, as shown in Figure 5 (top curve). The CH bandhead is hardly recognisable, and the entire spectrum is rich in CO radiation. The virtual continuum is further suppressed (as compared to Figures 4 and 5, bottom curve), thus one can speculate that an important contribution of radiation to the virtual continuum is arising from radiative transitions of molecules other than CO radicals. Moreover, as mentioned above, quantification of radiation in the virtual continuum between about 300 and 700 nm is regarded as speculation. However, the predominant CO radiation indicates extensive oxidation of carbon-containing molecules.

Figure 6 represents the intensities of most prominent spectral features in HMDSO plasma versus discharge power.

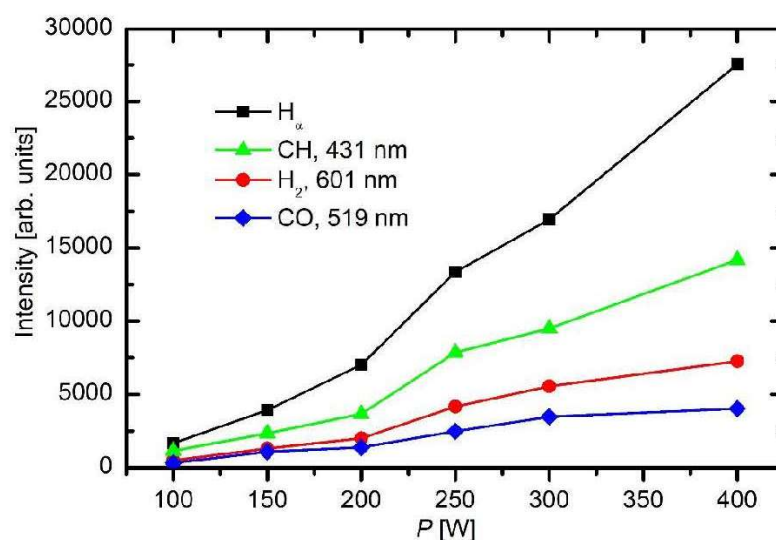


Figure 6. Intensities of some spectral features versus RF power in HMDSO plasma at 5 Pa.

As expected, all spectral features increase with increasing power. This is explained by higher electron density and temperature at elevated powers. The differences between the lowest power (100 W) and highest (400 W) are huge. For example, the height of the H_α peak at 400 W is over an order of magnitude larger than at 100 W.

3.2. XPS Characterisation

Samples were exposed to a gaseous plasma created in HMDSO with or without admixture of oxygen. After the treatment at different gas concentrations, discharge powers and treatment times,

they were characterised by XPS. The depth profiles were acquired upon etching of the deposited films with Ar ions until the signal from the substrate prevailed. Figure 7 represents a typical depth profile of an untreated sample.

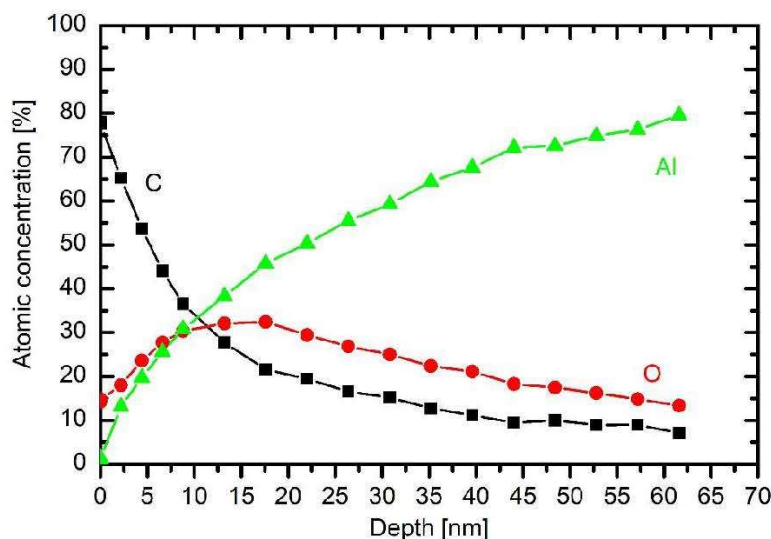


Figure 7. XPS depth profile of an untreated sample.

The sample was taken as received, so the aluminium surface is oxidised. The oxygen concentration on the very surface is larger than Al concentration, but after about 10 min of Ar ions etching, the concentrations become equal. The concentration of oxygen slowly decreases with prolonged etching. Such a depth profile is typical for rough metals covered with an oxide film. The slow decrease of the oxygen concentration is explained by rich surface morphology rather than diffusing layer containing partially oxidised aluminium. On top of the oxide layer, there is a layer of organic impurities. The concentration of carbon in the interface between the oxide and bulk aluminium follows the concentration of oxygen, which is again typical for rough substrates. Carbon is therefore not present in the substrate but rather forms a surface film of organic impurities.

3.2.1. Influence of Oxygen Concentration in the Gas Mixture

Figure 8 represents a depth profile of a sample treated in HMDSO plasma for half a minute. The broad interface between bulk aluminium and the coating is explained as for the untreated sample whose depth profile is in Figure 7.

The broad maximum in the oxygen concentration peaking at a depth of about 60 nm is therefore explained by the persistence of the initial oxygen film on the as-received substrate. The coating contains about 50 at.% carbon, 30 at.% silicon and 20 at.% oxygen. Taking into account the accuracy of determination of atomic concentrations from XPS spectra acquired upon Ar ion sputtering, the coating's composition is close to polydimethylsiloxane ($(C_2H_6OSi)_n$). The different ratio between Si and O right on the surface observed practically on all samples could be attributed to the differences in the sputtering yields for Si and O with Ar ions (sputtering yield for oxygen is larger than for Si). The composition of the coating is rather uniform throughout the coating, which indicates little change of plasma parameters during the deposition process.

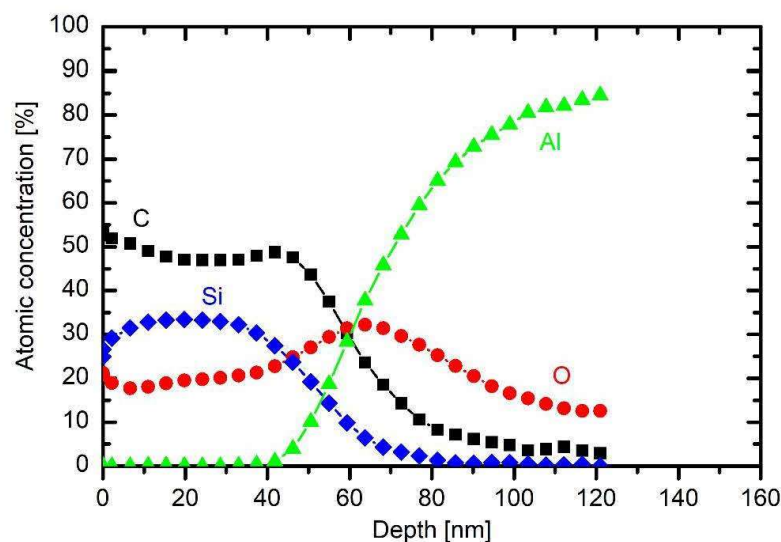


Figure 8. XPS depth profile of a sample exposed to plasma of 10 Pa HMDSO for 30 s at 200 W.

Addition of a small concentration of oxygen into HMDSO plasma causes depletion of the organic component in the coating, as deduced from the results in Figure 9. This effect is consistent with the results of optical emission. The concentration of about 20% oxygen in the gas mixture enables deposition of the coating with about 40 at.% of carbon, as revealed in Figure 9. The concentration of oxygen is still lower than silicon, but the difference is smaller than in the case of HMDSO plasma. The broad interface between the coating and the bulk aluminium is practically the same as in Figure 8. The same applies for interfaces in the depth profiles at larger oxygen concentrations in the original gas mixture. Figure 9 also shows a typical wide energy range XPS spectrum obtained on the surface of the sample. It contains peaks O 1s, C 1s, Si 2s, Si 2p and O 2s. No other elements were detected on the surface of this coating.

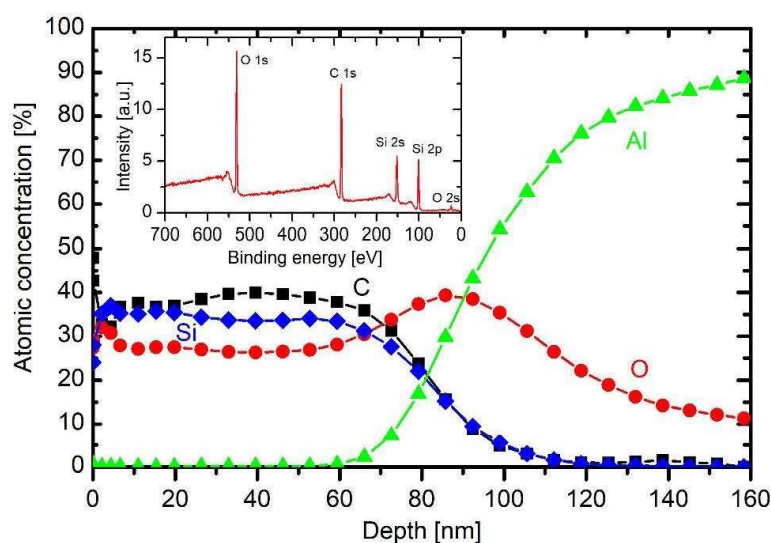


Figure 9. XPS depth profile of a sample exposed to plasma of 10 Pa HMDSO and 2.5 Pa O₂ for 30 s at 200 W, with inserted wide energy range XPS spectrum obtained on the surface of this sample.

The behaviour of carbon concentration at the interface indicates that the layer of organic impurities persists at the interface, although a substantial concentration of oxygen was added to the gas mixture. From this observation, one can conclude that even 43% oxygen in the gas mixture used for deposition of coatings does not cause significant oxidation of the organic impurities, which are presented on the surface of as-received substrates. Instead, they are buried at the interface by depositing the coating rich in silicon and oxygen.

The concentration of 1/3 oxygen and 2/3 HMDSO causes a significant difference in the composition of the deposited coating. Next to the interface (i.e., between 40 and 70 nm), the composition is as expected, i.e., similar concentrations of Si and O and larger concentration of carbon. On top of this film, however, there is a coating depleted from carbon. Namely, the concentration of Si and O in the film between a few nm and about 25 nm is almost twice as the concentration of carbon. The discharge parameters (gas flows, power) remained the same throughout the deposition process, thus the broad minimum in the C concentration should be explained by changeable plasma parameters without changing the discharge conditions.

This effect is even more pronounced for the case of 43% oxygen and 57% HMDSO. There is a thin film containing Si, O and C on the interface between the coating and the substrate, but the majority of the coating contains little carbon. The depth evolution of Si, O and C is similar to that of 1/3 oxygen and 2/3 HMDSO mixture, except that the depletion of the organic component is more pronounced in the case of 43% oxygen addition. The rather unexpected depletion can be explained with a progressive change of gas-phase or surface kinetics during the deposition.

As revealed from the literature survey in the Introduction, the HMDSO plasma tends to develop clusters, often called oligomerisation [12]. These clusters grow with time and eventually form dust particles [9]. Once a critical size of particles is achieved, they become negatively charged due to attachment of slow plasma electrons. The negative charge of small particles prevents their contact to any walls of the plasma reactor (including substrates) due to repulsive electric field in the sheath between the bulk plasma and the wall. The particles remain levitating in the plasma and keep growing as radicals stick to them. A variety of radicals form upon plasma conditions in mixtures of oxygen and HMDSO as confirmed by optical spectra. When the radicals collide with the particles, they may undergo exothermic reactions. Condensation itself is an exothermic event, but the released energy is marginal. On the other hand, there are surface reactions that dissipate significant energy upon interaction. Among them, heterogeneous surface recombination usually prevails in weakly ionised gaseous plasma. There are both oxygen and hydrogen atoms in plasma sustained in a mixture of oxygen and HMDSO, but O atoms are consumed extensively by surface chemical reactions that lead to the formation of CO radicals, as revealed in Figure 5. Namely, the O-atom peaks at 777 and 845 nm are hardly observable in Figure 5. Hydrogen atoms are observable in all plasma spectra presented in Figures 3–5, while oxygen atoms definitely form in such plasma but are only clearly recognised in Figure 3 due to the consumption by chemical reactions. The energy released on a particle surface due to surface recombination is about half of the dissociation energy of parent molecules, i.e., about 2 eV per atom recombining on the surface. As a result, any particle levitating in plasma rich in H atoms warms up significantly. Upon steady conditions, the temperature of a particle levitating in plasma depends on the recombination coefficient. The coefficients have never been determined for dust formed in such complex plasma, so it is impossible to speculate about the temperature of the particles, but it is clear that the temperature increases with time. The recombination coefficients usually increase with increasing temperature [20]. Increasing temperature causes a dramatic increase in the oxidation rate of organic material upon treatment with oxygen atoms [21]. The final consequence of the interaction between oxygen atoms and particles is, therefore, extensive oxidation of the organic matter of the particle. In fact, the H_{α} peak in the optical spectrum of plasma rich in oxygen (Figure 5) is much smaller than peaks of the CO band, indicating qualitatively strong oxidation of organic component. The H_{α} peak in HMDSO plasma is much larger than any other spectral features (Figure 4).

The rather unexpected depth profiles of 33% and 43% oxygen addition in gas mixtures can therefore be explained by the time evolution of the oxygen consumption in gaseous plasma. At the beginning of the deposition, there is practically no cluster in plasma so the oxygen, although present in the gas phase in rather large concentration, does not cause chemical reactions in the gas phase, so the coating contains a significant amount of the organic component. As particles appear and grow, more oxygen is used for oxidation of the organic component and the CO bands prevail in optical spectra. Carbon monoxide practically does not stick to surfaces, but the silica-rich particles do upon turning off the discharge. This could be a feasible explanation for the gradual decrease of the carbon concentration at prolonged deposition time. The effect is more pronounced at larger oxygen concentration.

The high concentration of carbon on the very surface (Figures 8 and 9) is due to secondary contamination of samples on the way between the plasma lab and XPS characterisation. In fact, the concentration on the very surface is almost the same for all depth profiles.

The coating obtained upon treatment of a sample in HMDSO with a large concentration of oxygen is completely different. Figure 10 shows a profile at oxygen/HMDSO mixture 2/1.

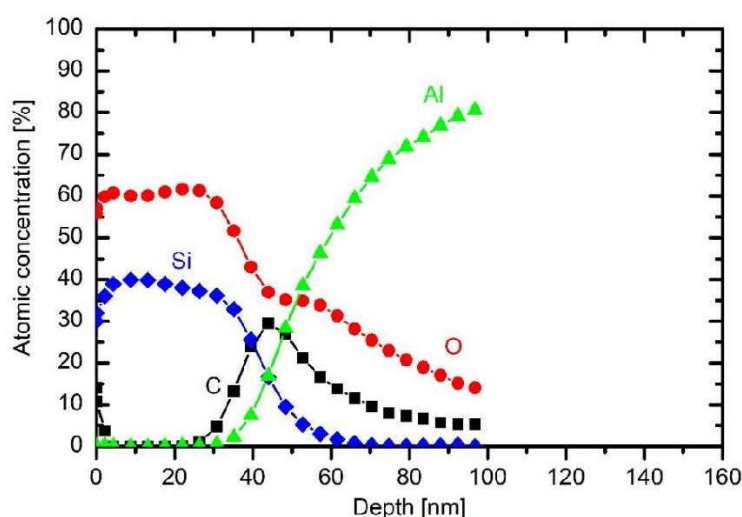


Figure 10. XPS depth profile of a sample exposed to plasma of 10 Pa HMDSO and 20 Pa O₂ for 30 s at 200 W.

The coating is free from carbon, and the ratio between oxygen and silicon is close to stoichiometric SiO₂. The result is consistent with the observation reported by other authors [10]. The carbon at the interface between the substrate and the coating still persists; such oxygen atoms, although rather dense at these conditions, were not able to oxidise the impurity layer before it was buried by the deposit. Although the HMDSO is rich in carbon, the oxygen flux on the surface was obviously large enough to cause immediate oxidation of any organic compound that might have stuck on the surface upon film growth. The film thickness is much smaller than at lower oxygen concentration in the gas mixture due to the absence of an organic component.

The extremely asymmetric capacitive discharge sustained by RF generator, therefore, enables deposition of different coatings, depending on the oxygen addition to the HMDSO precursors, but one should beware of temporal effects of oxygen consumption, as described above.

3.2.2. Influence of Discharge Power

The discharge power governs the plasma parameters, in particular the electron density, which in turn governs the gas-phase reactions and thus the fragmentation of the precursor. A set of experiments

was performed at different discharge powers between 50 and 750 W with constant other parameters. The results of these coatings are presented in Figures 11–13 and in Figure 8.

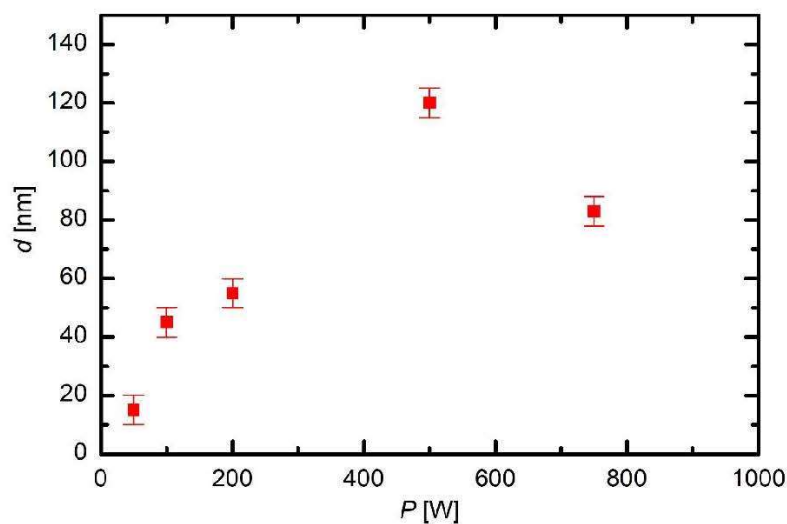


Figure 11. The thickness of coatings on samples versus the discharge power (30 s in HMDSO plasma at 10 Pa).

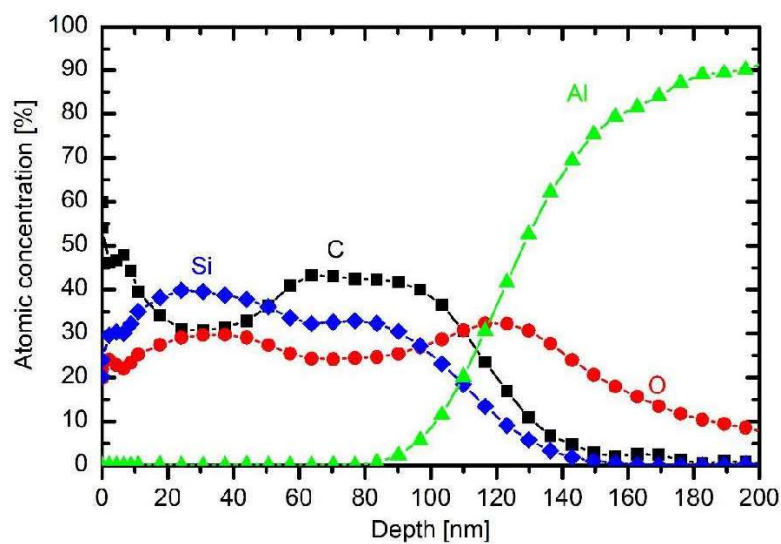


Figure 12. XPS depth profile of a sample exposed to plasma of HMDSO at 10 Pa for 30 s and 500 W.

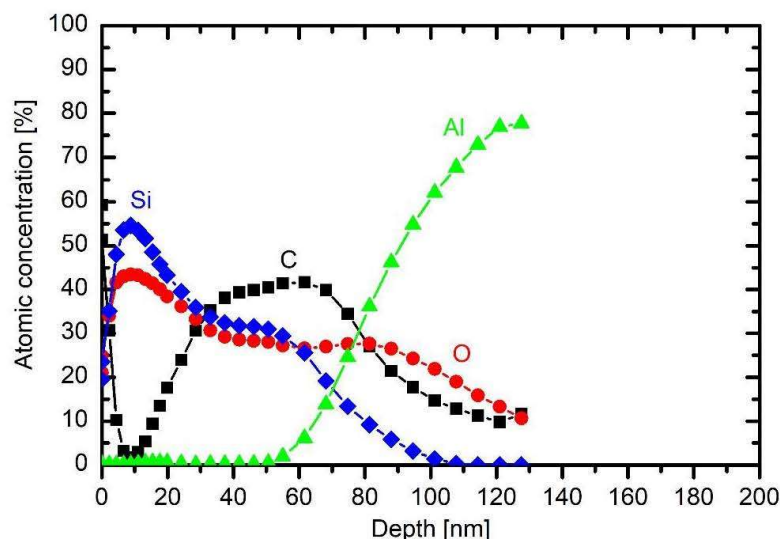


Figure 13. XPS depth profile of a sample exposed to plasma of HMDSO at 10 Pa for 30 s and 750 W.

Figure 11 represents the thickness of coatings versus discharge power. The coatings were deposited in 30 s of HMDSO plasma at 10 Pa. It can be observed that, at low powers, the thickness of coatings increases almost linearly with power. However, at higher power, the thickness starts to decrease. This can be explained by a closer inspection of the depth profiles.

The thickness of the coating of a sample treated at the lowest discharge power of 50 W is much smaller than at 200 W (Figure 8). The observation is explained by poor fragmentation of the precursor upon plasma conditions. As mentioned above, the extremely asymmetric discharge causes practically all available power absorbed in the oscillating sheath next to the powered electrode, so the concentration of electrons in bulk plasma is small. The distribution of carbon is similar to that of an untreated sample (Figure 7). There is some silicon on the surface, so even this very low discharge power enables deposition of a film rich in organic component, but the deposition rate as estimated from the XPS depth profile is below nm/s.

A double discharge power enables the deposition of a thicker coating as revealed from the depth profile of a sample treated with HMDSO plasma at 100 W. Carbon prevails in the depth profile indicating a large fraction of organic component in the film. The result is similar to that reported by Naddaf [8] for the case of moderately asymmetric coupling. Aluminium persists right to the very surface so one could speculate that the coating at this power is not uniform enough to shade the substrate completely. Namely, the average thickness of the deposited film is several 10 nm. On the other hand, Si also persists deep from the surface so the speculation may not be correct. The original roughness of this sample at the spot sampled by XPS might be particularly large.

The depth profile of a sample treated at 200 W is shown in Figure 8 and is discussed above. The depth profile at 500 W is shown in Figure 12. The coating is thicker than at lower powers, indicating that such a rather large power causes significant fragmentation, which is useful for more rapid deposition of the thin film. The composition of the coating on the substrate is somewhere in between those obtained at 200 W without oxygen and 200 W with 2.5 Pa oxygen: roughly 45 at.% C, 28 at.% O and 37 at.% Si. The increased power has therefore similar effect to the coating composition as the addition of a small amount of oxygen to the gas mixture.

More pronounced is the effect at the largest power adopted in this work. Figure 13 presents the depth profile at 750 W and the same other conditions as in Figures 8 and 12. The deposit on the substrate contains a significant fraction of organic compound, but, closer to the surface, the carbon is heavily depleted. The depth profile in Figure 13, therefore, resembles those of 33% and 43% oxygen

addition in HMDSO. Thus, one can conclude that large discharge power results in a coating of similar properties as the addition of moderate amounts of oxygen to the gas mixture. The depletion of the organic compound at such a large discharge power in the extremely asymmetric coupling but in HMDSO plasma could be explained by different effects. The trivial one is the persistence of water vapour in the experimental reactor. As mentioned above, the reactor is only pumped with a rotary pump and never baked, thus the “base pressure” (i.e., the pressure achieved in the reactor before introducing precursor) is rather poor. The base pressure was approximately 1.7 Pa. The pressure increased to 10 Pa upon continuous introduction of the precursor (and also continuous pumping of the system). As mentioned above, the residual atmosphere contains mainly water vapour. The oxygen concentration in the reactor upon deposition of the coating is therefore much less than the concentration of carbon. Even if all oxygen from water vapour interacts with carbon from HMDSO, there should be excessive carbon in the system, thus the negligible concentration of carbon in the surface film down to about 20 nm in Figure 13 cannot be attributed to complete oxidation of carbon-containing materials.

The poor concentration of carbon in the deposited film is instead explained by partial transformation of HMDSO to light hydrocarbons that are pumped away from the plasma reactor. The formation of methane, acetylene and ethylene has been already confirmed by residual gas analyses for the case of plasma sustained in a moderately asymmetric RF discharge [14,22,23]. The high power as adopted for the experiment whose result is shown in Figure 13 enables extensive fragmentation of precursor, so dust particles form quickly. The dust particles assume a high temperature so thermal decomposition cannot be neglected. As shown by Pressinger and Bruggemann [24], the thermal decomposition of HMDSO causes the formation of methane and ethane with some other light hydrocarbons. The remaining composition of hot clusters or dust particles contains silicon and oxygen. Due to the shortage of any other source of oxygen (water vapour), the particles retain a larger concentration of silicon than oxygen. As the discharge is turned off, the potential drop across the sheath between plasma and any surface vanishes so the particles rich in Si and O stick to the surface of the sample. The required condition for such an evolution of gas chemistry is oligomerisation, clustering and final evolution of dust particles. The reactions propagate with time and are faster at higher powers. This is a feasible explanation of why the Si-rich film appears only at high powers at given plasma treatment time and pressure (30 s and 10 Pa in Figures 11–13).

4. Conclusions

The extremely asymmetric electrode configuration in a low-pressure plasma reactor powered by an RF generator in capacitive mode was found to be useful for the deposition of various coatings using HMDSO with different admixtures of oxygen as source gases. Dense plasma in such a configuration is confined to an oscillating sheath next to the powered electrode and rather uniform diffusing plasma occupies the entire volume of the discharge chamber at the pressure of 10 Pa. The deposition rate and the composition of the coating depend on the discharge power and the gas composition. The organic fraction of the coating decreases dramatically with increasing power and increasing oxygen concentration at such discharge conditions. At low power and oxygen concentration, the coating is rather uniform, and its composition does not depend much on the treatment time. At large discharge power, the initial coating growing of a substrate resembles polydimethylsiloxane, but, for prolonged treatment, the composition changes and the organic component almost vanishes, although the discharge parameters remain constant. A similar effect was observed at increasing oxygen concentration. It was found that, in both cases, a feasible explanation for the observed carbon depletion of the film is the formation of clusters and dust particles, which heat upon plasma conditions due to exothermic surface reactions. The high temperature of the particles adds other channels for the loss of radicals and thus influences the growth of the coating. The surface reactions play an important role in the composition of both the particles in the gas phase and the coating. The heterogeneous surface recombination of hydrogen and oxygen atoms cause a thermal load, which was found particularly extensive for dust particles levitating in the gas phase. As the temperature of dust particles increase, the thermal

decomposition becomes a significant source of light hydrocarbons that are pumped away from the system, so the coating at high power becomes almost free from carbon.

Supplementary Materials: The following are available online at <http://www.mdpi.com/1996-1944/13/9/2147/s1>, Figure S1: SEM image of the HMDSO coating.

Author Contributions: Conceptualisation, Ž.G. and R.Z.; Methodology, I.J., A.V., D.Đ. and J.K.; Validation, G.P., S.P. and A.V.; Formal Analysis, R.Z., S.P. and J.K.; Investigation, R.Z., J.K., S.P., D.Đ. and Ž.G.; Resources, Ž.G., R.Z., D.Đ. and J.K.; Data Curation, I.J., J.K., R.Z., S.P. and G.P.; Writing—Original Draft Preparation, Ž.G. and R.Z.; Writing—Review and Editing, I.J., Ž.G., G.P., A.V. and R.Z.; Visualisation, I.J., R.Z.; Supervision, Ž.G. and R.Z.; Project Administration, A.V. and G.P.; and Funding Acquisition, R.Z. and D.Đ. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Slovenian Research Agency: project ID L2-1835 (Innovative sensors for real-time monitoring of deposition rates in plasma-enhanced chemical vapor deposition (PECVD) systems) and research core funding No. P2-0082.

Acknowledgments: Authors would like to thank Janez Trtnik for technical support.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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Chapter 6

Conclusions

The results of extensive and systematic work on plasma and surface characterisation enabled an insight into the complex phenomena occurring both in the gas phase of plasma conditions and on material surfaces facing the plasma. The most important conclusions are as follows:

- Optical emission spectroscopy and mass spectrometry are useful techniques for measuring the fragmentation of precursor molecules in an industrial plasma reactor and enable the estimation of the most important plasma parameters.
- Gaseous plasma sustained by an asymmetric RF discharge in the capacitive mode in the reactor with a volume approximately 5 m³ is temporarily stable, providing constant discharge parameters.
- The density of charged particles in gaseous plasma in an industrial size reactor is in the order of 10¹⁴ m⁻³. The density depends on discharge parameters. This value is at least an order of magnitude smaller than in any experimental reactor used by other authors.
- The fragmentation of precursor molecules in an industrial plasma reactor occurs largely in the volume next to the powered electrode. Fragmentation away from the electrode is far from complete since the major plasma constituent as determined by residual gas mass spectrometry remains the precursor itself.
- Stripping of H atoms from the precursor molecules is the most abundant reaction in the gas phase in plasma conditions. The H atoms partially associate and form H₂ molecules by heterogeneous surface recombination.
- Plasma sustained in HMDSO gas is a rich source of UV and VUV radiation. The radiation mainly arises from the relaxation of highly excited hydrogen molecules and atoms. Extensive radiation occurs despite very low power density and very low density of electrons in plasma at distance from the powered electrode.
- Hydrogenated carbon radicals are formed in the gas phase. These associate to form light hydrocarbons at surface reactions. Heavy hydrogenated carbon molecules are not formed at measurable rates.
- The composition of protective coatings obtained by plasma polymerisation is different from the composition of the precursors. This result is explained by various mechanisms, which are stated below.
- The precursors themselves do not contribute to the growth of the protective film despite plasma conditions. The adsorption kinetics for precursors upon bombardment with ions and irradiation with VUV radiation from plasma are insufficient to cause significant chemical modification of the precursor upon adsorption on activated surfaces facing the plasma.

- The protective film resembles carbon-depleted polydimethylsiloxane. The deposited material is smooth and represents good protection of the metalised film against corrosion and other unwanted effects.
- The interface between the polymer substrate and the aluminum film is rich in oxygen, indicating optimal surface functionalisation of the polymer substrate prior to film deposition.
- The deposited aluminum film is almost free from chemically bonded oxygen or any other impurity providing that high-vacuum conditions are achieved before and during the evaporation.

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Biography

The author of this thesis Žiga Gosar was born 06.11.1983 in Ljubljana. He attended the Vič Elementary School, and continued his education at the Jože Plečnik Gymnasium in Ljubljana, which he successfully completed with Matura exam. In 2003, he applied to the Faculty of Mechanical Engineering in Ljubljana – filed of interest – engineering - mechanics - non-linear mechanics of structures and graduated in August 2010 with diploma. During his undergraduate studies, he gained his work experience in laboratories at the Faculty of Mechanical Engineering in the field of design, laser technology, project work and experiment design. For his innovation, he received a reward on a public tender for the sustainable development of the community.

He is also a sportsman and has a degree in fitness training for athletes at Fitness Association of Slovenia and at Olympic Committee of Slovenia.

After completing undergraduate studies, in 2010 he applied to postgraduate studies; where in September 2014 he received a doctorate from the field of nonlinear mechanics of structures, stability – snap through system - temperature switches/sensors. During his PhD study he was employed in company ELVEZ as a Young researcher for industry and was responsible for applying new technology into the company. This technology was high vacuum metalization process.

In 2012 he developed a machine vision for surface defect detection on high gloss surfaces. After finishing his first PhD, in 2014 he applied to Jožef Stefan International Postgraduate school for his second PhD. He studied plasma technology and surface treatment in the field of ecotechnologies.

He is still employed in company ELVEZ and working as Director of Research, Development and Technology department.