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Dario Sciacqua

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Polymer enrobing of advanced carbon

THÈSE dirigée par :

M BERNDT Johannes
Mme KOVACEVIC Eva

Chercheur, Université d'Orléans
Professeure, Université d'Orléans

RAPPORTEURS :

M Uroš Cvelbar
M Nikša Krstulović

Professeure, Jozef Stefan Institute, Ljubljana
Chercheur, Institute of Physics, Zagreb

JURY :

M BRAULT Pascal
M Uroš Cvelbar
M Nikša Krstulović
M STRUNSKUS Thomas
M BERNDT Johannes
Mme KOVACEVIC Eva

DR CNRS, HDR, GREMI, Université d'Orléans, Président du jury
Professeure, Jozef Stefan Institute, Ljubljana
Chercheur, Institute of Physics, Zagreb
Chercheur, CAU, Kiel
Chercheur, Université d'Orléans
Professeure, Université d'Orléans

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Table of abbreviations

QCM	Quartz crystal microbalance
SCCM	Standard cubic centimeters per minute
PECVD	Plasma enhanced chemical vapor deposition
CNWs	Carbon nanowalls
CW	Continuous wave
DC	Direct current
D.C.	Duty cycle
FET	Field effect transistor
FTIR	Fourier transform infrared spectroscopy
NEXAFS	Near edge X-ray absorption fine structure
OES	Optical emission spectroscopy
PANI	Polyaniline
pPANI	Plasma synthesized polyaniline
PECVD	Plasma enhanced chemical vapor deposition
QMS	Quadrupole mass spectrometer
RF	Radio frequency
RGA	Residual gas analysis
SEM	Scanning electron microscopy
XPS	X-ray photoelectron spectroscopy

Chapter 1

1.1 Plasma Polymerization

1.1.1 Introduction

Plasma polymerization can be broadly defined as a technique that allows the production of “polymeric materials” through the application of plasmas [1]–[3]. The first development of this technique started with studies regarding the formation of organic compounds in vacuum systems under the effect of electric discharges. The resulting coatings were considered in the beginning as undesirable by-products and it took several decades, until the 1960s with Goodman, to acknowledge this process as a useful method to synthesize polymeric materials. It took more than 20 years for the scientific community to recognize plasma polymerization as not just “another” polymerization process but as a useful complementary technique that allows obtaining new, interesting, and unique features that conventional polymerization processes could not achieve such as higher stability, insolubility, and adhesion to any kind of substrate.

1.2 Low temperature plasmas

At the center of every plasma process is, of course, the plasma or, as it might be better to say in this context, the gas discharge. A plasma can be roughly defined as a partially or fully ionized quasi-neutral gas, i.e., a gas that contains positive (and sometimes negative) ions and electrons in addition to neutral atoms or molecules, and is neutral overall on scales smaller than the Debye length.

Plasmas are found in various forms in the universe. Prominent examples are the Sun or stars in general, lightning, the Earth's ionosphere, auroras, or flames [4]–[6]. The term *plasma* derives from the Greek *πλάσμα*, which means “that what is made”. Faraday performed pioneering studies regarding luminous discharges at low gas pressure (which he called **glow** discharges) already in 1831, but it was Irwin Langmuir the great pioneer of gas discharge physics who coined the term plasma [7], [8].

An important parameter for the characterization of a plasma is the ionization degree. The ionization degree f_i , can be described as the fraction of ionized species (atoms or molecules) with respect to the total amount of species. In the case of a singly ionized plasma f_i is defined as:

$$f_i = \frac{n_e}{(n_e + n_0)} \quad (\text{equation 1.1})$$

Plasmas used for material processing and in particular those used for the treatment of sensitive materials like polymers usually possess a low degree of ionization which ranges from 10^{-7} to 10^{-2} . For a pressure of 0.1 mbar, this results in electron densities in the range between 10^8 to 10^{13} cm^{-3} .

Another crucially important parameter is the "plasma temperature". However, for many plasmas, a single parameter is often not sufficient to define their "temperature". In particular, many plasmas used for technological applications such as etching or polymer deposition are operated at low pressures and do not achieve complete thermalization of all species which often results in different temperatures of electrons T_e , ions T_i , and neutrals T_n . For this reason, those types of plasmas are defined as non-equilibrium plasmas. Put simply, this non-equilibrium character is due to the fact that electrons, ions, and neutral species gain and dissipate energy in different ways. An important example is the energy loss of electrons and ions in elastic collisions with neutral atoms/molecules - a process that is of particular importance in plasmas with a low degree of ionization. The average energy loss in such collisions is in the order of the mass ratio of the collision partners and thus much smaller for electrons. Another problem with the definition of a plasma temperature concerns the fact that in many non-equilibrium (low temperature) plasmas the electron energy distribution function can strongly deviate from a Maxwellian distribution rendering even the definition of an electron temperature problematic. Despite this fundamental problem the term electron temperature is frequently used (e.g. in connection with mean electron energy) for example to classify plasmas. According to the difference in temperature (and so energy) of electrons, ions, and neutral species plasma can be roughly classified into two main categories:

- thermal plasmas or hot plasmas when $T_e = T_i = T_n$
- non-thermal plasma or cold plasmas when $T_e \gg T_i \gg T_n$

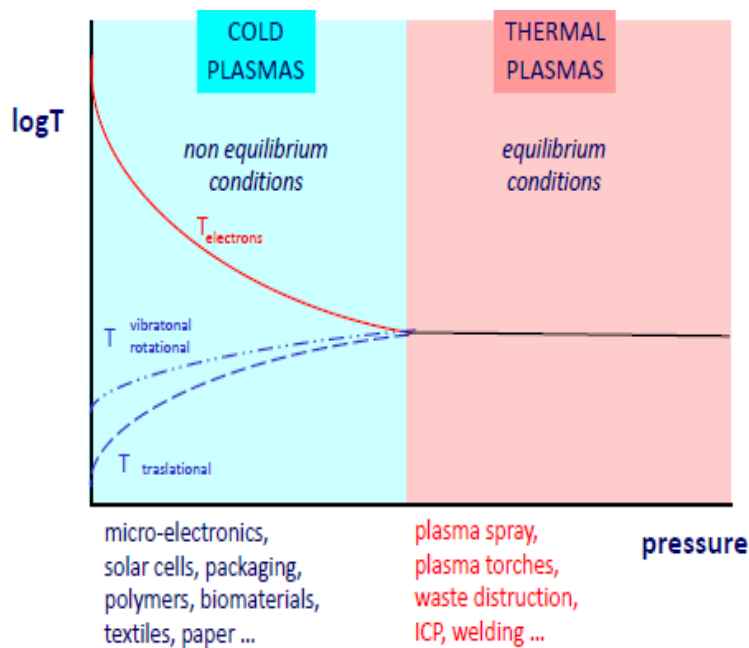


Figure 1.1 Difference between cold and thermal plasmas.

This work deals with Low Temperature Plasmas which are nowadays frequently used in industry, for example for etching processes. In particular, in the semiconductor industry plasmas are the most important etching tools for the production of integrated circuits. Other applications concern the treatment of surfaces [9]–[11] e.g. the activation of surfaces in order to change their surface energy and thus their wetting behaviors. Most of the plasmas employed for the treatment or production of sensitive materials (e.g. polymers) are also low temperature plasmas with average electron temperatures in the range $T_e = 10^4 - 10^5$ K, ion temperature in the range between 300-1000 K and neutral temperatures T_n at around room temperature.

In low temperature low pressure plasmas, the most frequent collisions which happen are the ones between electrons and neutrals. These collisions can lead to the dissociation of molecules, the excitation and ionization of atoms and molecules, and other types of reactions. The following summary has been given by Milton Ohring [12] and includes also some reactions between heavy species (table 1):

Electron collision		
1	Ionization	$e^- + A \rightarrow A^+ + 2e^-$ $e^- + A_2 \rightarrow A_2^+ + 2e^-$
2	Excitation	$e^- + A \rightarrow A^* + e^-$ $e^- + AB \rightarrow (AB)^* + e^-$
3	Dissociation	$e^- + AB \rightarrow A^* + B^* + e^-$
4	Dissociative Ionization	$e^- + AB \rightarrow A + B^+ + 2e^-$

5	Dissociative attachment	$e^- + A_2 \rightarrow A^+ + A^- + 2e^-$
6	Recombination	$e^- + A^+ \rightarrow A$ (3-body or radiative)
Atom – molecule – ion collision		
7	Symmetrical charge transfer	$A + A^+ \rightarrow A^+ + A$
8	Asymmetric charge transfer	$A + B^+ \rightarrow A^+ + B$
9	Metastable-Neutral (penning ionization)	$A^* + B \rightarrow A + B^+ + e^-$
10	Metastable-metastable ionization	$A^* + B^* \rightarrow A^+ + B + e^-$

This table already gives a hint about the complexity of plasma processes in general. Complicating matters further, plasmas that use organic precursors, for example, also involve a variety of chemical reactions - usually triggered by radicals or ions produced by electron collisions with the original precursor molecules.

1.3 Mechanism of plasma polymerization

The term plasma polymer was introduced in 1960 by Goodman [13] but works intended to clarify the process were performed only in 1980 by Yasuda [14], [15] and then completed during the last 20 years [16], [17]. These new studies gave an insight into the mechanism of plasma polymerization opening a new door for the realization of unique materials.[18]

To understand this process, a comparison between classic chemical polymerization and plasma polymerization may be helpful.

The classic conventional polymerization techniques are based on a two-step mechanism: step-growth polymerization [19] and chain-growth polymerization [20].

In the first mechanism, the polymerization process is continued by carrying out the same chemical reaction step by step over and over again. The process can proceed for an infinite time and the only condition to respect is the availability of the monomer and the removal of the by-products (water) – both constraints can slow down the process. This process does not have a termination step; the only condition to terminate the reaction is the total consumption of the monomer. The long chain of produced polymer reacts with others to produce larger chains.

In the second mechanism, the chain-growth polymerization is performed by adding single monomeric units to the extremity of long-chain molecules produced. At the end of the

polymeric chain, reactive groups serve as anchor sites for the new monomer units. This process provides a termination step in which the reactive group is neutralized and thus does not allow anymore any addition of new units. This termination step is performed e.g. by adding hydrogen to the process or can happen automatically when a long chain combines with another one instead of a monomeric unit. The total process then can be resumed in three separate steps: initiation, propagation, and then termination. Examples of this type of polymerization are the “Radical” and the “Ionic” polymerization.

In radical polymerization, the propagation reaction is performed by radical species (reactive groups) placed at the end of the polymeric chain while in the ionic one it is performed by a chain containing ion groups at the extremity. There is a sub-process of ionic polymerization called radiation-induced polymerization, which involves the use of a light beam (UV photon, γ rays) to promote the initiation process [21].

The mechanism is resumed in the following table (table 2):

	Step growth	Chain growth Radical	Chain growth ionic
Initiation	$M + M \rightarrow M_2 + H_2O$	$A^* + M \rightarrow M^*$	$A^- + M \rightarrow MA^-$
Propagation	$M_2 + M \rightarrow M_3 + H_2O$	$M^* + M \rightarrow M_2^*$ $M_2^* + M \rightarrow M_3^*$ $M_n^* + M \rightarrow M_{n+1}^*$	$MA^- + M \rightarrow M_2A^-$ $M_2A^- + M \rightarrow M_3A^-$ $M_nA^- + M \rightarrow M_{n+1}A^-$
Termination	$M_n + M_m \rightarrow M_{n+m} + H_2O$	$M_m^* \rightarrow M_m$	$M_mA^- + B \rightarrow M_mB + A^-$

Plasma polymerization can be explained by a combination of all those mechanisms plus additional ones. At the start, it was proposed that plasma polymerization consisted of a chain-growth ionic process assisted by plasma which had the role of producing the necessary ions.[16], [22], [23]. Later some others proposed the mechanism of the radical polymerization [17], [24], [25]. In 1980, finally Yasuda stated that neither radical nor ionic polymerization was possible due to the impossibility of step-growth reaction to proceed in the gas phase and proposed a new mechanism of polymerization called *atomic polymerization* [15], [26], [27]. The monomers present in the gas are dissociated by pre-existing species (electrons, ions, and radicals) into molecular fragments that can recombine together into larger molecules. These

reactions can happen both in the gas phase or on the surface of a substrate [28].

Yasuda proposed the introduction of a particular parameter named Yasuda Parameter [29], that takes into account the power and the flow rate chosen for the experiment and also the mass of the monomer:

$$Y = \frac{W}{F \cdot M} \text{ (J/kg) (equation 1.2)}$$

where W is the power of the discharge, F is the flowrate, and M is the molecular weight of the precursor monomer.

This parameter is important in order to tune the plasma polymerization process because it gives a first estimation of the initial deposition parameters in particular providing information regarding the amount of energy necessary to polymerize the precursor [30]–[33]. In particular, low values of Y will result in less fragmentation of the monomer and therefore in a higher chance to preserve the original structure of the monomer in the final polymeric product while high values will lead to a higher fragmentation degree and therefore to the production of a more crosslinked polymer [31]. Despite the usefulness of the Yasuda parameter, it should be emphasized that the full complexity of a plasma process cannot, of course, be described by a single parameter. The effect of pulsed discharges on the confinement of negative ions, for example, is not captured by this parameter, nor is the exact influence of the discharge geometry. The question to what extent the film deposition is caused by (neutral) radicals or by positive (or in the case of pulsed discharges by negative) ions can also not be answered by the numerical specification of a single parameter.

1.4 Conductive polymers – Polyaniline

The main protagonist of this work is the plasma process but it loses its importance without the presence of a good partner. In this experimental work, this role has been attributed to the aniline and its polymerized form polyaniline which belongs to the family of the conductive polymers. Conductive polymers [34]–[38] are a class of conjugated polymers that have attracted the attention of the scientific community in the last 50 years due to their appealing properties (on the edge between conductor and semiconductor state) which make them suitable for a wide range of application ranging from the realization of electrodes, organics LEDs [39]–[41], energy storage (supercapacitors and batteries) [42]–[46], transistors [47]–[49], photovoltaic applications [50], [51], anticorrosion coatings [52] and also sensors [53]–[56].

Among the big family of conductive polymers, polyaniline stands out due to its high electrical conductivity, oxidative properties, thermal and environmental stability, and ease of

processability [57], [58]. Polyaniline has been the first conductive polymer to be discovered (in 1840 by Fritzsche) [59] but only recently, in the last 20 years, it has attracted the interest of the scientific community following the award of the Nobel prize in chemistry to Heeger, MacDiarmid, and Shirakawa [60]–[62] who have -with their studies on intrinsically conductive polymers- opened a new domain of technological applications.

Polyaniline or PANI can exist in a variety of forms that can be different in chemical and physical properties. Depending on the method of synthesis, polyaniline base can be produced into three main forms: fully reduced form (leucoemeraldine), partially reduced form (emeraldine), and fully oxidized form (pernigraniline) [63].

The main chemical structure of polyaniline is shown in figure 1.2:

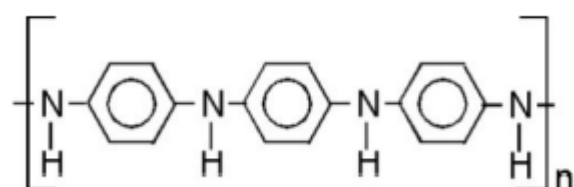
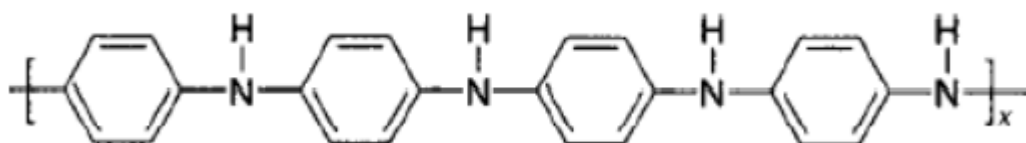


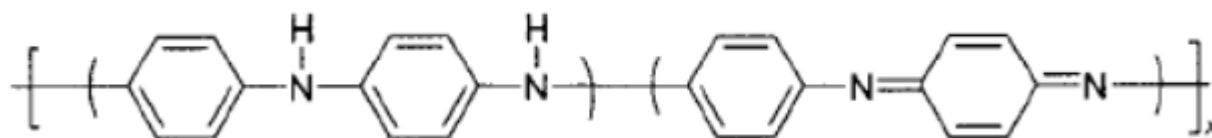
Figure 1.2 Generalized structure of Polyaniline base.

The main chemical structure consists of alternating reduced and oxidized repeat units. According to the number of these reduced/oxidized units, the structure can vary and so do the properties of the material. The average oxidation state (1-y) can be varied from zero to one and gives the three main forms of PANI:

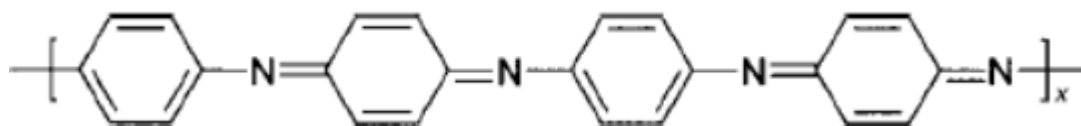
- when $x=0$ give the “completely reduced” polymer form named Leucoemeraldine PANI



- when $x=0.5$ give the “half-oxidized” polymer form named Emeraldine PANI



- when $x=1$ give the “completely oxidized” polymer form named Pernigraniline PANI



Among the three possible forms of polyaniline, only the half-oxidized form (emeraldine) possesses the conductivity on a semiconductor level in the order of 10^0 S cm^{-1} [58], [64]–[66]. To increase the conductivity a process of doping is necessary, turning the emeraldine base into the conductive emeraldine salt [67]. In order to dope PANI, several ways have been explored; mainly the doping process is performed with an acid media (HCl or HI) [68]–[70] in an aqueous environment where the acid carries out a process of protonation of the nitrogen atoms which lead to a formation of a particular structure which can be polaronic or bipolaronic [71]–[73]. The conductivity of the polymers arises from this structure.

Several methods are described in the literature for the production of Polyaniline [74], [75]. The most used and common method is the chemical synthesis through chemical oxidative polymerization of aniline [76]–[79]. This method provides as final product directly the emeraldine structure. Another method that attracted attention in the latest years is the synthesis of PANI through plasma deposition techniques [80]–[84] using discharges such as capacitively and inductively RF discharges, DC glow discharges, etc. Due to the complexity of the deposition process a better understanding of the underlying physical and chemical mechanism is crucial in order to improve the process and thus control and tune the structure and the properties of the synthesized material.

1.5 The motivation of the thesis work

The Nobel laureate Prof. A.G. MacDiarmid stated that: "there are as many different types of Polyaniline as the people who synthesize it" [77], [85]. This sentence expresses simply and clearly that the properties (optical and electrical properties, stability) and the composition of Polyaniline strongly depends on the method and the condition of synthesis.

In particular, the use of a complex synthesis method such as plasma polymerization makes this process even more difficult to understand.

In this Ph.D., this complex challenge has been accepted and has been rendered the aim of this work. Clarification of the various mechanisms involved in plasma polymerization should provide new ways to control the process and enable the production of films that can be tailored to the desired application in terms of structure and properties.

The key steps/points that will be addressed in this work are:

- the synthesis of plasma Polyaniline through PECVD
- the control of the deposition process by using new techniques (home-made structured electrodes)
- the characterization of the produced thin films
- the doping of the films
-

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Chapter 2

2.1 The experimental chamber

The experimental chamber in which the plasma process is performed consists of a custom-build reactor that operates with a capacitively coupled RF plasma system ($f=13.56$ MHz). The reactor has a cylindrical shape and is made of stainless steel with a diameter of 70 cm and 72 cm high. The inner walls of the reactor are anodized to protect the chamber when operating with reactive gas mixtures or oxygen. The electrode system consists of a two parallel plate electrode with a diameter of 12 cm and a variable electrode distance (up to 15 cm). A vacuum pump system consisting of a coupled primary (Duo 20 M/MC by Pfeiffer Vacuum) plus turbo molecular pump (ATH 500 M by Pfeiffer Vacuum) is used to pump down the chamber to UHV (Ultra High Vacuum) 10^{-8} mbar before each process in order to have reproducible chamber conditions before each process.

The chamber is connected with different gas system injection lines (made of stainless steel), making this system suitable and adaptable to several different processes employing different gas mixtures based on inert gases like Ar or He or reactive gases like O_2 , C_2H_2 , N_2 . Additionally, the chamber is equipped with a particular injection device developed in partnership with Omicron Technologies, which allows the injection of different polymer precursors (in this work mainly focused on aniline monomer).

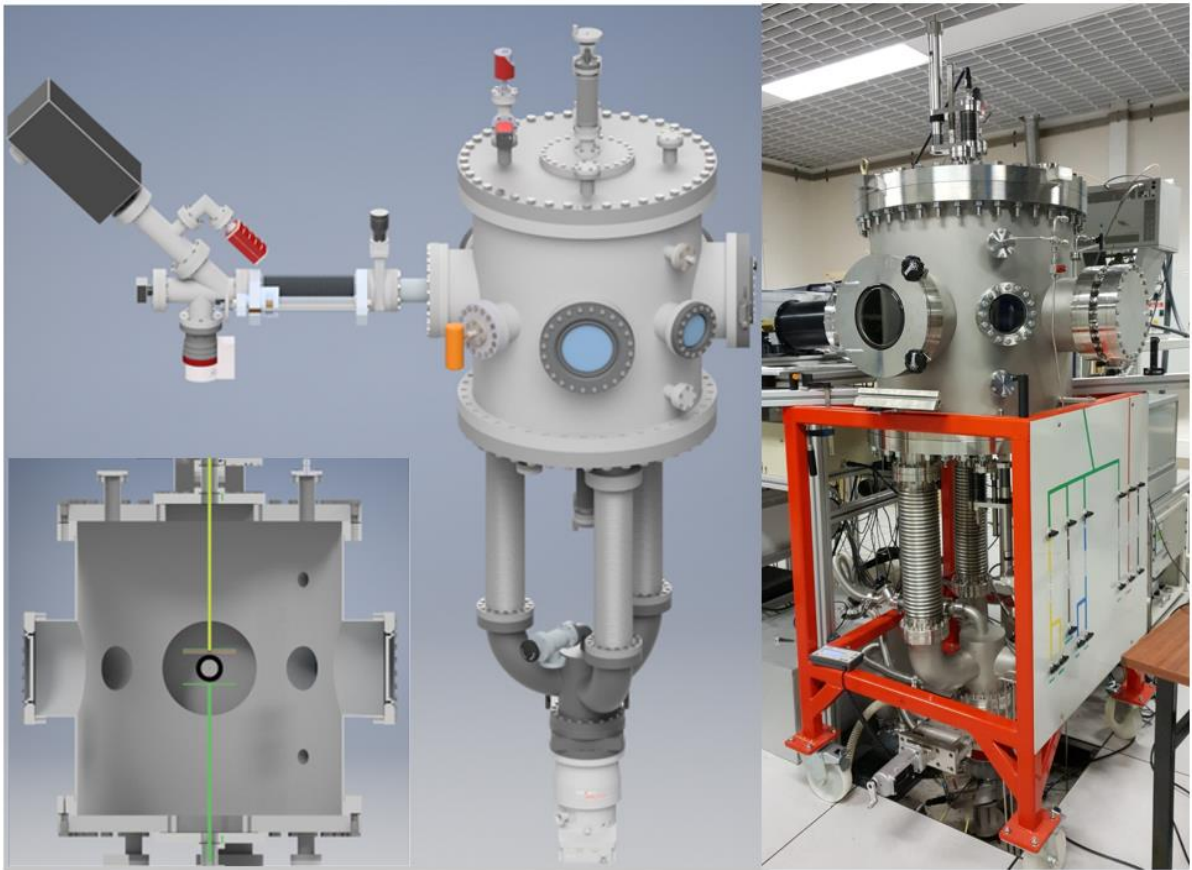


Figure 2.1 Scheme of the experimental set-up used in this Ph.D. for the deposition of thin film by plasma polymerization.

The inlet gas system and the pump system are placed respectively on the side and the bottom of the chamber far away from the electrodes, to minimize and avoid undesirable gas flow turbulence and works with a stable and homogeneous gas flow during plasma processes.

The RF system consists of a signal generator (SMC100A by Rhode&Schwarz) with a variable applicable frequency up to 1.1 GHz coupled with a broadband amplifier (BBA100 by Rhode&Schwarz) and a matchbox. The power used for plasma experiments ranges from 1 to 50W with the possibility to apply different duty cycles and pulsing frequencies.

The pressure monitor system is equipped with 2 different detectors: a compact full-range gauge (PKR 251 by Pfeiffer Vacuum), working from 10^{-9} mbar to 1 bar and with $\pm 30\%$ accuracy in the range 10^{-8} to 100 mbar that is mainly used for the global monitoring of the pressure and a capacitance gauge (CMR 36 by Pfeiffer Vacuum with $\pm 0.20\%$ accuracy in the range from 10^{-3} mbar to 10 mbar, mainly used during plasma processes.

Several diagnostics are connected to the chamber allowing to perform analysis and monitoring of plasma and material characterization techniques of the resulting samples:

- Mass spectrometer (used for gas analysis)
- In situ FTIR (used for study infra-red absorption of gas mixtures in plasma)
- Microwave interferometry (used for electron density measurement)
- Laser (used for detection of scattering of nanoparticles)
- Quartz microbalance (used to monitor the real-time growth during processes)

Particular attention needs to be put on the in situ FTIR system coupled to the main chamber. The specific design of the in-situ FTIR system involves using a white cell system with golden mirrors (total passes through the plasma = 22) as shown in Figure 2.2, leading to the exposure of golden mirrors inside the vacuum chamber to a reactive environment where the ignition of plasmas is very likely to lead to the deposition of carbonaceous thin-films on the mirrors. In order to minimize this effect, a specific gas introduction system was designed: two gas showers are located at the vicinity of mirrors on each side, leading to an increased neutral drag force going from the mirrors to the plasma, reducing the number of reactive species reaching it.

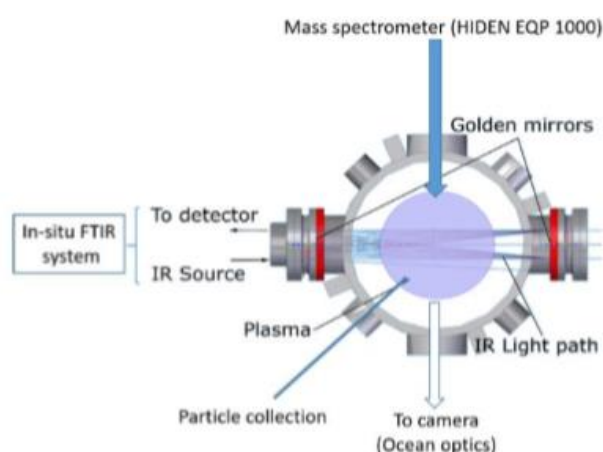


Figure 2.2 Scheme of the In-situ FTIR system installed within the experimental chamber.

The monomer for the polymerization process is a volatile liquid and in order to be used for polymerization processes needs to be transformed in the gas phase by means of an evaporation process. The precursor injection system developed with Omicron Technologies consists of an evaporator system that includes a heated chamber. The pressure and temperature of the liquid precursor contained in the chamber, are monitored by a pressure sensor and a thermocouple system which allow the user to control the vaporization process before and during the experiment since the vapor pressure of this monomer is sensitive to the temperature. The bottle containing the liquid precursor is connected to the main deposition chamber by a small pipe

called “manifold” controlled as well by a thermocouple system. The manifold is equipped with a needle valve, which allows regulating the flow of monomer entering the chamber. Particular attention before the experiment needs to be put since the gas entering the chamber is at a higher temperature (around 82°C) while the wall of the reactor is at room temperature and this can lead to starting phenomena of condensation which lower the pressure in the chamber during first minutes of the process. For this reason, a certain amount of time is required to stabilize the gas flow before starting a deposition process.

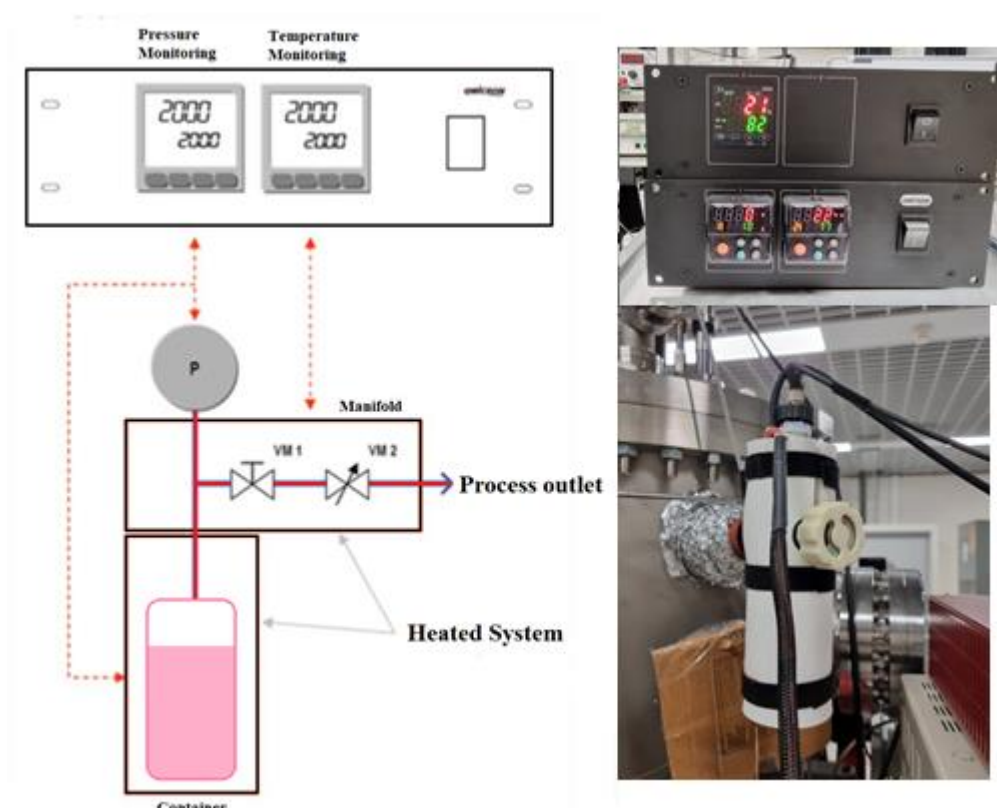
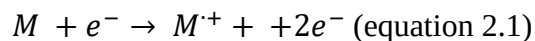


Figure 2.3 Scheme and photos of precursor injection device plus temperature controller.

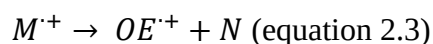
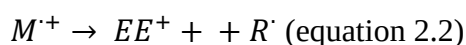
2.2 Mass spectroscopy

The mass spectrometry was developed from experiments of J. J. Thomson and others on the behavior of charged particles in electric and magnetic fields in 1913. Mass spectrometry (MS) is used to analyze the plasma phase composition. It is a highly sensitive tool that can detect both ionic and neutral species. The general working principle of MS involves ionization of vapor from a solid, liquid, or gaseous sample, and separating the charged particles (molecules, molecular fragments, atoms) according to their mass to charge (m/z) ratio, where mass is expressed in atomic mass units (a.m.u.) and the charge in elementary charge units (e).

The instrument consists of 3 main parts (a) an ionization source, (b) a mass analyzer, and (c) a detector. The spectrometer used in this work is operated in the residual gas analysis (RGA) mode, where neutral species from the sample are ionized by electron ionization (EI), as shown below.



The molecular ion ($M^{\cdot+}$) formed from Equation xxx is a radical cation with an odd number of electrons and therefore, would normally undergo fragmentation into a radical (R) and an even ion (EE) with an even number of electrons or a molecule (N) and an odd ion (OE), as shown by equations 2.2 and 2.3. Each primary ion produced from the molecular ion can undergo further fragmentations and so on.



The ions that are generated are then separated by means of a quadrupole mass analyzer. The separation is based on the stability of the ion trajectories in the oscillating electric fields applied to two pairs of parallel metal rods.

MS is widely used in plasma diagnostics to detect specific phenomena and identify the chemical composition and structure of molecules in many fields like physics, biology, chemistry. Despite its many benefits, an important limitation of MS when operating in RGA mode is that neutral species when subjected to ionization can undergo extensive fragmentation even at low electron kinetic energies. Therefore, MS should be used in conjunction with other diagnostic tools such as FTIR.

The mass spectrometer used in this work was a Hiden EQP 1000 quadrupole mass spectrometer (QMS) from Hiden Analytical. This device is a combined mass spectrometer and energy analyzer. This allows recording either a mass spectrum with a given and fixed kinetic energy for the ions, or to analyze the energy distribution of ions for one given mass.

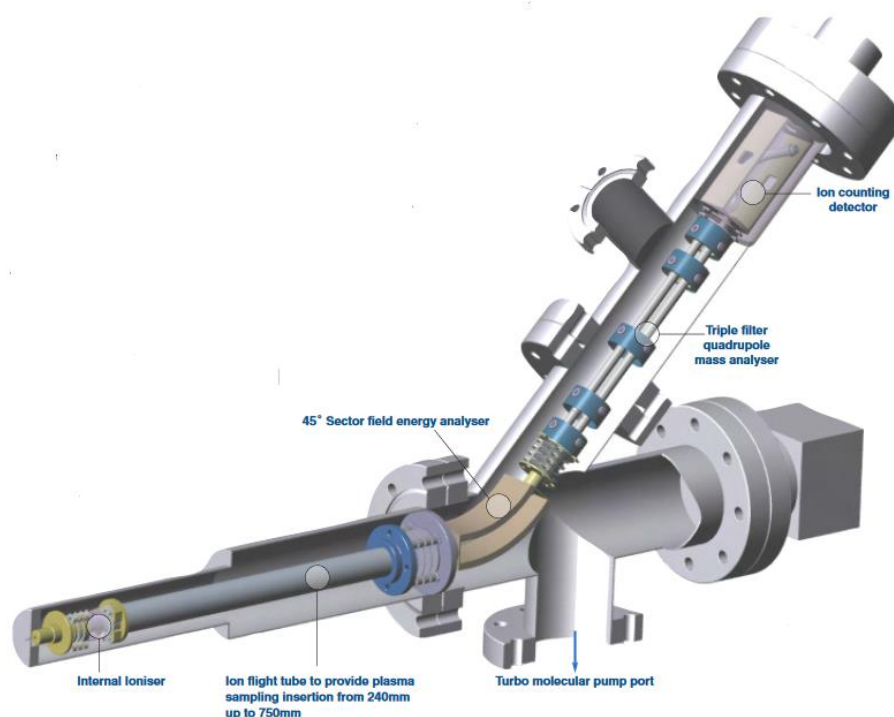


Figure 2.4 Scheme of the section view of a Hiden EQP 1000 quadrupole mass spectrometer. The picture originates from the device's user manual.

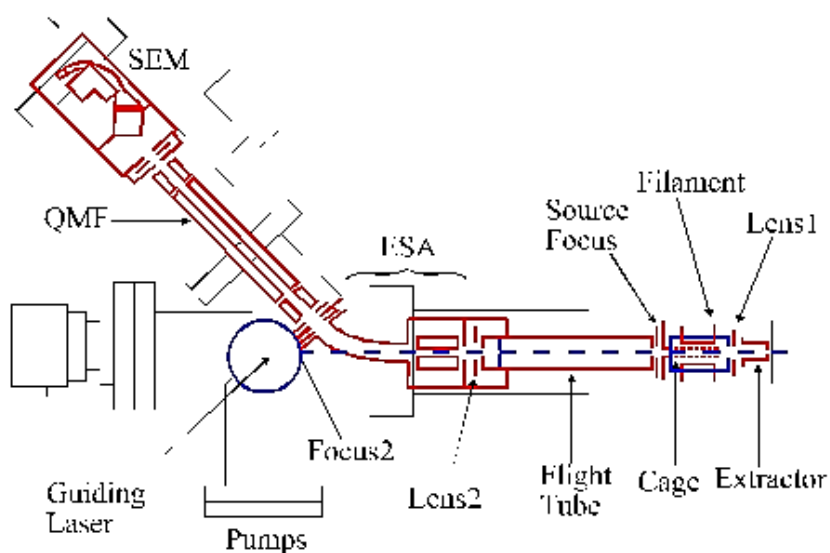


Figure 2.5 Scheme of the Hiden EQP 1000 quadrupole mass spectrometer used in this Ph.D.

2.3 Microwave interferometry

Microwave interferometry of plasma is a technique based on the investigation of the dielectric properties of a medium by employing electromagnetic waves. Since the dielectric constant of plasma depends on the chosen plasma parameters. The measure of the propagation characteristics of microwave radiation through the plasma allows determining the value of the electron density. The technique measures the phase shift of microwave radiation, which is produced by the plasma, in the primary transmission path of the interferometer compared to a wave that is taken as a reference by the interferometer. In low pressure plasmas, the phase shift measured is a function of the plasma density.

The device used was an MWI 2650 from Miwitron, which works at 26.5GHz. It can measure electron densities between 1×10^9 and 3×10^{12} cm.

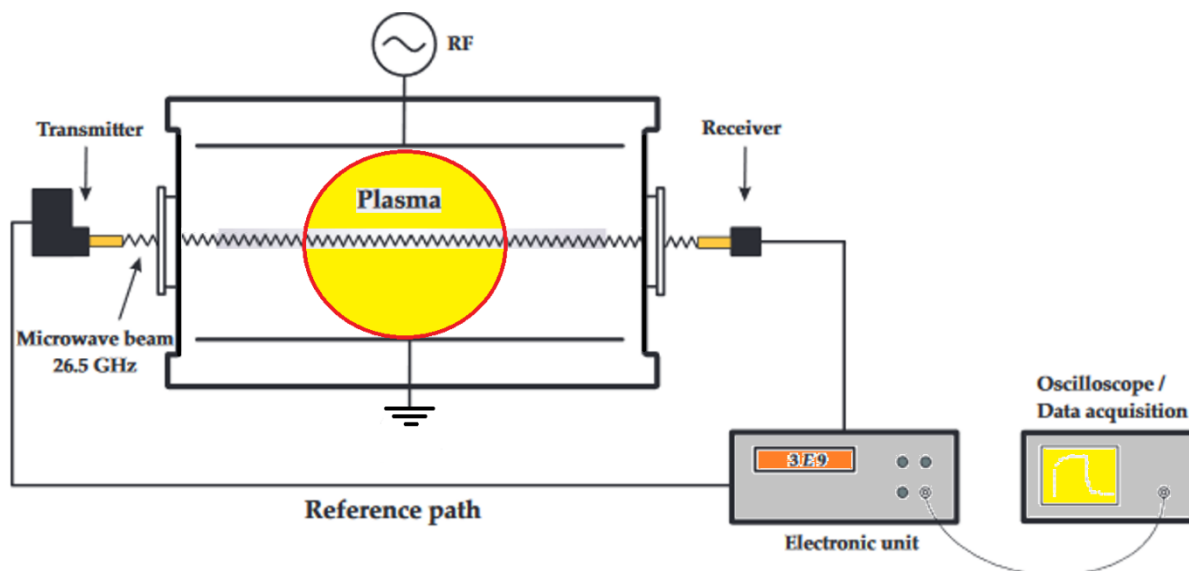


Figure 2.6 Scheme of microwave interferometry set-up for electron density measures adapted from [1].

2.4 Fourier Transform Infra-red spectroscopy

FTIR spectroscopy is a useful technique to extract structural information of molecules present in a solid, liquid, or gaseous sample. When a sample is irradiated with an infrared beam, vibrating molecules in the sample will absorb energy from the beam and excite to a higher vibrational level. The transmitted or absorbed light is measured by a detector as a function of the wavenumber. This method is effective only towards molecules that are IR active, i.e. the vibration of the molecule must produce a change in the dipole moment.

The working principle of an FTIR is based on an interferometer, which measures the interference pattern of two light beams. The most common type of interferometer used is a Michelson interferometer, as shown in figure 2.7. An infrared light beam is passed through a beamsplitter after reflecting from a collimating mirror, which is used to make the light rays parallel. As the name suggests, the beamsplitter splits the beam into two which are made to reflect normally from two mirrors. One of the mirrors is fixed and the other is allowed to move in the direction shown in figure 2.7. The difference in the distance of the two mirrors from the beamsplitter is called optical path difference, δ . As the two beams travel back to the beamsplitter, they superpose to form an interference pattern whose intensity is measured by the detector as a function of δ , to produce an interferogram, i.e. a plot of intensity (arbitrary units, a.u.) vs δ (cm). This interferogram is then Fourier transformed to give an IR spectrum, which is a plot of intensity (a.u.) vs wavenumber (cm^{-1}).

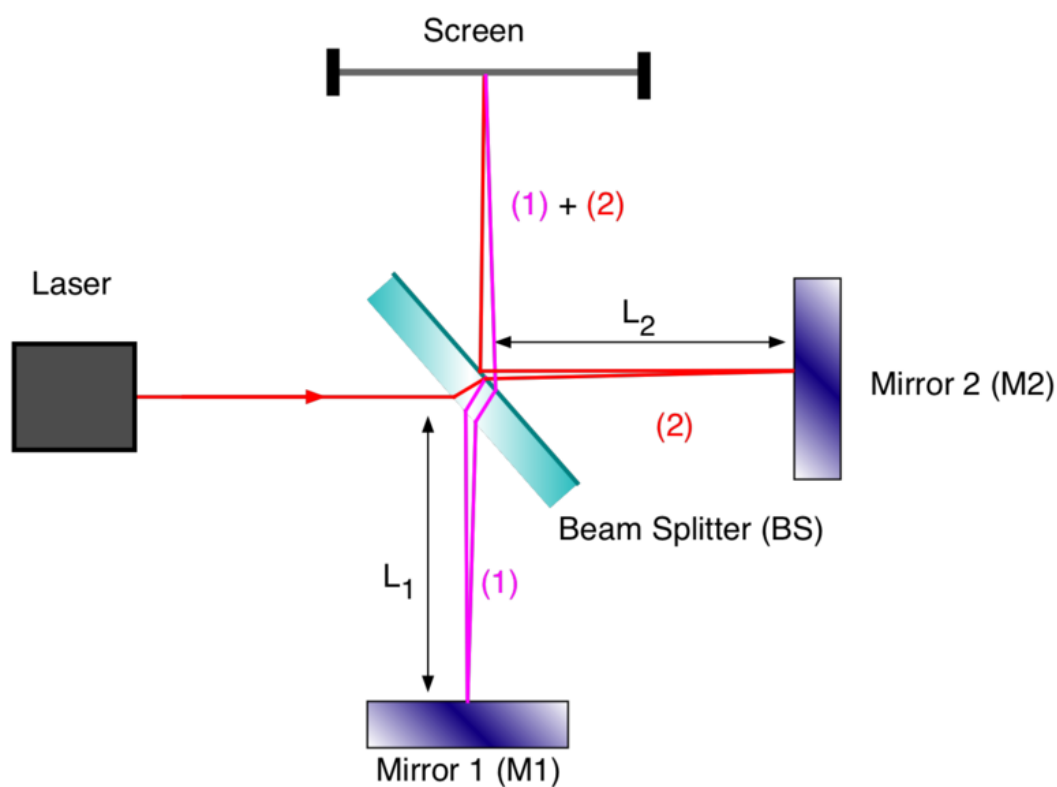


Figure 2.7 Scheme of Michelson interferometer implemented into the FTIR spectrometer.

FTIR spectra can be plotted either in absorbance units or percent transmittance (%T). Absorbance can be calculated by using the following equation:

$$A = \log \left(\frac{I_0}{I} \right) \text{ (equation 2.4)}$$

where A is the absorbance, I_0 is the intensity of the background spectrum and I is the intensity

of the sample spectrum. Absorbance is related to concentration by Beer's law,

$$A = \epsilon lc \text{ (equation 2.5)}$$

Where ϵ is absorptivity, l is the path length and c is the concentration. The height or area of a peak in the absorbance spectrum is proportional to the concentration of the corresponding molecules in the sample which can be calculated by Beer's law. FTIR is useful in quantitative and qualitative analysis of the plasma phase as well as plasma polymer films where monomer dissociation, new species formation, and powder formation can be detected. It appears to be a promising tool especially in plasma diagnostics owing to its non-intrusiveness (unlike MS) allowing for an in-situ picture of the plasma phase chemistry and the rapidity of measurement allowing for spectral acquisitions with high signal-to-noise ratios.

The spectrometer used in this work is a Vertex 70 from Bruker. A specific optical set-up using a white cell and golden mirrors was designed together with Bruker to lead IR light inside the vacuum chamber. In-situ FTIR spectroscopy can therefore be performed inside the reactor either in gas mixtures or in plasmas. In this configuration, the infrared light crosses the plasma volume 22 times.

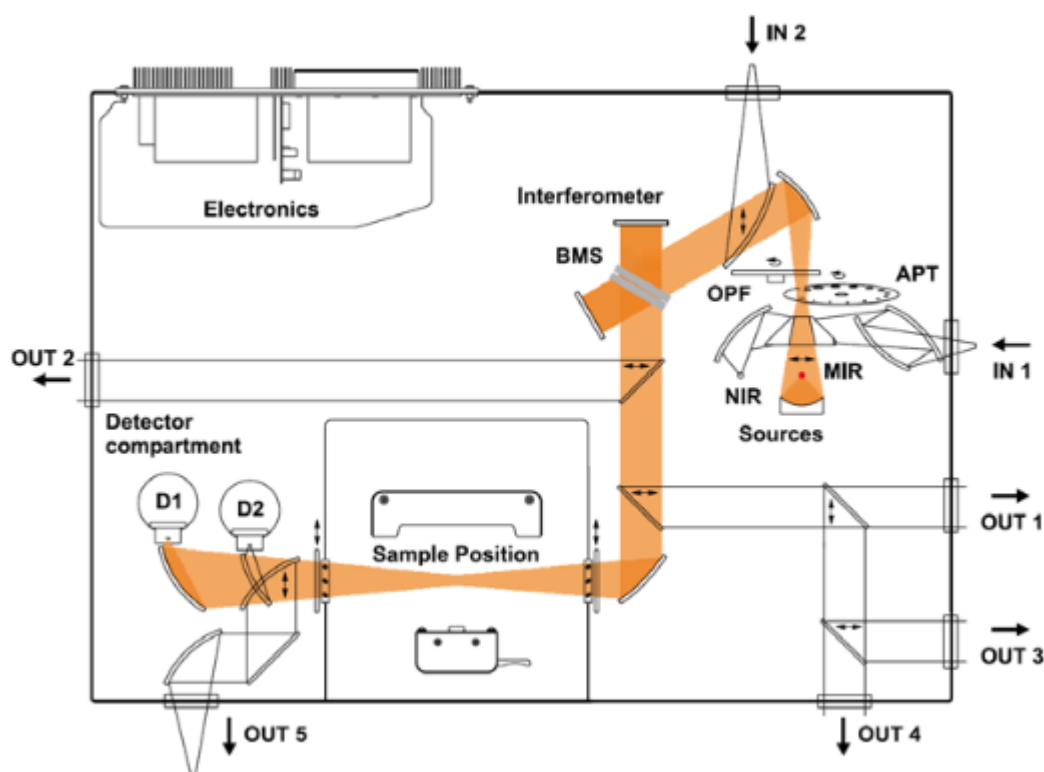


Figure 2.8 Scheme of Vertex 70 FTIR spectrometer by Bruker. The interferometer used in this instrument is a Michelson interferometer.

Besides measurements performed in the vacuum chamber (in-situ), the FTIR spectrometer was also largely used to carry out material analysis of polyaniline thin films synthesized by plasma.

2.5 Laser Light scattering imaging

Laser light scattering (also known as Mie scattering), is a technique in which a laser beam passes through a dispersed particulate sample, large particles scatter light at small angles and small particles scatter light at large angles relative to the laser beam. Particle size is then determined from the measured variation in the intensity of scattered light as a function of scattering angle, using the Mie theory of light scattering [2]–[4].

The extinction cross-section σ_{ext} is defined as the sum of the total cross-section for scattering and absorption σ_{sca} and σ_{abs} assuming that the incident light is either scattered or absorbed:

$$\sigma_{ext} = \sigma_{sca} + \sigma_{abs} \text{ (equation 2.6)}$$

both cross-sections depend on the α coefficient defined as size parameter:

$$\alpha = \frac{2\pi r_d}{\lambda} \text{ (equation 2.7)}$$

Where r_d is the particle size,

$$\sigma_{sca} \approx \frac{2\lambda^2}{3\pi} \alpha^6 \text{ (equation 2.8)}$$

$$\sigma_{abs} \approx \frac{-\lambda^2}{\pi} \alpha^3 \text{ (equation 2.9)}$$

The extinction is strongly dominated by the absorption process due to the α^3 dependence compared to the scattering dependence α^6 , but for this case assuming that the particle can be considered perfectly dielectric and then the value of the imaginary part of the refractive index is very low, the absorption contribution can be considered negligible and thus we can resume:

$$\sigma_{ext} \approx \sigma_{sca} \propto \frac{r_d^6}{\lambda^4} \text{ (equation 2.10)}$$

For this reason, the extinction measures are quite sensitive to the dust size as the scattering measures and thus difficult to measure for very small dust size.

In the Mie scattering the dimension of the dust size is comparable to the laser wavelength ($0.1\lambda < r_d < 20\lambda$) and the scattering starts when the particle size is about 100 nm diameter when using a green laser with $\lambda = 532 \text{ nm}$.

2.6 Scanning electron microscopy

Electron microscopy is a technique that exploits the interaction between a beam of electrons and atoms that make up the sample under examination and allows to obtain images with very

high magnifications exceeding the resolution limit of optical microscopy, being able in some cases to reach resolutions at the atomic level.

In general, when an object is observed, it is not possible to resolve two points whose distance is less than the wavelength (λ) of the probe used and optical microscopy has as its physical limit the λ of light (in the order of hundreds of nm in the visible range). Since the electron microscope are used electrons (which compared to photons have a λ of about three orders of magnitude lower) the resolution limit of the scanning microscope is much higher, in the order of nanometers.

The SEM also provides images with a greater depth of field and, if it is equipped with an EDX detector, to obtain compositional information about the sample under examination (elemental analysis).

In the SEM the electron beam generated by the source (in this case a field emission gun) and accelerated through the column scans the surface of the sample. At each point of the scan, the interaction between beam and sample produces signals that are exploited by the detectors in the SEM to generate images or perform elemental analysis. The signals most often used are:

- Backscattered electrons (BSE) arise as a result of elastic interaction between the electrons of the beam and nuclei of the atoms constituting the sample.

- Secondary electrons (SE) are emitted from the material upon impact with the electrons in the beam. Since this is an inelastic interaction, in which some energy is lost, the secondary electrons have significantly lower energy than the backscattered ones. Only the SE near the surface electrons of the beam (in the range of a few tens of nm) are able to emerge from the sample and reach the detector. The image obtained by exploiting the secondary electron detector (SED) is an image that does not return compositional information but has more surface detail and is thus useful for topographic analysis.

- X-rays have characteristic energy and allow the identification of the elements that constitute the sample, both from a qualitative and semi-quantitative point of view.

The SEM used in this Ph.D. was a Supra 40 from Zeiss, equipped with an In-Lens detector (High efficiency), an SE2 detector (Everhart-Thornley Secondary Electron Detector), an EDX module, and a SEEF module which allows making a positive polarization of the sample, in order to associate the low voltage resolution of the In-Lens detector to chemical information. This technique was mainly used to investigate the surface and the morphology of the deposited plasma polymeric films.

2.7 Ellipsometry

Spectroscopic ellipsometry is a technique that calculates the change in the polarization state of a light beam after being reflected obliquely from a thin film sample. Ellipsometry uses a model-based approach to determine thin film, interface, and surface roughness thicknesses, as well as optical properties for thin films ranging in thickness from a few Angstroms to several tens of microns.

Spectroscopic ellipsometry measures two angles defined ψ and Δ , both of which describe the output elliptical polarization state after a linearly polarized beam is reflected obliquely off of a thin film sample.

The parameters ψ and Δ are related to the complex Fresnel reflection coefficients. After the collection of those two parameters is necessary, in order to measure the thickness and the optical parameters, to build up a model which reflects the film structure of the thin film analyzed.

Need to be pointed out that this technique does not measure directly the thickness or the optical parameters associated with the film. In fact, in order to determine thin film thickness and/or optical properties, a model-based approach must be used.

Since is a technique nondestructive and noninvasive can be employed easily for analysis of different kinds of materials and characterization of a range of thin-film properties including layer thickness, surface roughness thickness, interface thickness, optical constants, composition, bandgap, composition, crystallinity, grading, anisotropy, and uniformity by depth and area. The ellipsometer used in this Ph.D. was a Horiba Uvisel 1 used for the analysis of thickness and refractive index of polymer thin films.

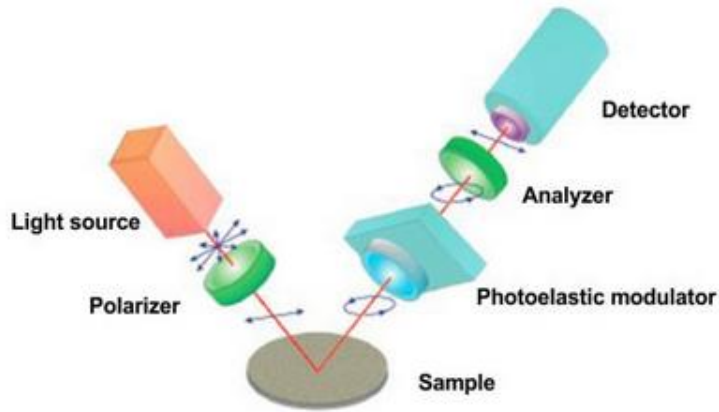


Figure 2.9 Optical set-up of the UVISSEL ellipsometer from Horiba.

2.8 Quartz microbalance

The Quartz Crystal deposition Monitor (QCM) utilizes the piezoelectric sensitivity of a quartz crystal, which is used as a monitor system, to the added mass. The QCM uses mass sensitivity to control the deposition rate and final thickness of a deposition process under vacuum.

When a voltage is applied across the faces of a properly shaped piezoelectric crystal, the crystal is distorted and changes shape in proportion to the applied voltage. At certain discrete frequencies of applied voltage, a condition of sharp electro-mechanical resonance is encountered.

When a mass is deposited to the face of a resonating quartz crystal, the frequency of these resonances is reduced. This change in frequency is very repeatable and is precisely understood for specific oscillating modes of the quartz. The oscillation frequency of quartz depends first on its structure (i.e. its shape and its chemical composition, for example, our quartz are covered with a layer of gold) and then on the weight of the particles (lm, nanoparticles, etc...) which are deposited on it during the plasma. The quartz used has an oscillation frequency of about 6 MHz without any deposit. With the deposit, which will start to form after the ignition of the plasma, this frequency will decrease. Thus, by measuring the frequency difference, the instrument can give the weight of what is deposited on the quartz.

The dependence between the oscillation frequency difference and the thickness is expressed by the following equation:

$$T_f = \left(\frac{N_{at} d_q}{\pi d_f F_c Z} \right) \arctan \left(Z \tan \left(\frac{\pi(F_q - F_c)}{F_q} \right) \right) \text{ (equation 2.11)}$$

With T_f the thickness of the deposit, $N_{at} = 166100\text{Hz}$ the frequency constant of quartz cut AT, $d_q = 2.649 \text{ g/cm}^3$ the density of the quartz, d_f the density of the deposit, Z the acoustic impedance ratio, F_q the starting frequency and F_c the frequency with deposit.

For thin deposits and therefore small variations in frequency (of the order of 2% and less of the initial frequency of quartz), equation 2.11 can be rewritten using a limited development. We will thus have:

$$T_f = \frac{N_{at}d_q(F_q - F_c)}{d_f F_q^2} \text{ (equation 2.12)}$$

This simplification will be very useful later to calculate the thicknesses of deposits without going through the calculation of the software of the microbalance.

The relation was formulated in an equation in 1959 by Günter Sauerbrey. The equation is a linear relationship between the resonance frequency of an oscillating quartz crystal and mass changes. In this case, the mass has been converted into film thickness by knowing the density. The model assumes that the deposited layer can be approximated to be a part of the oscillating crystal itself, which means that the crystal will now have the thickness $h + \Delta h$ [5].

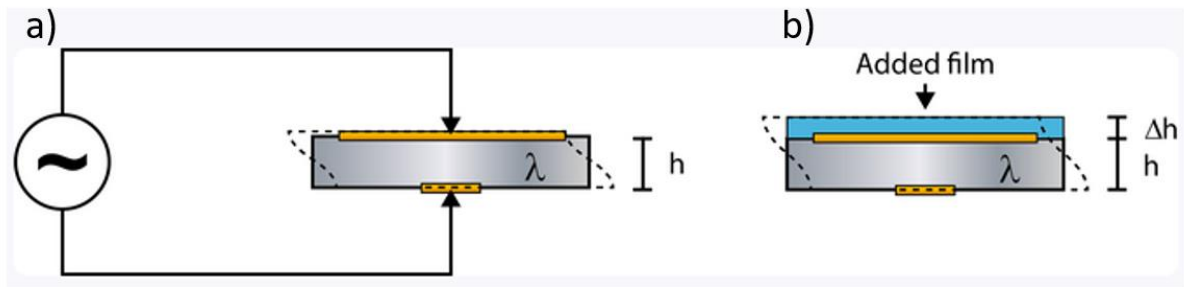


Figure 2.10 Scheme of a quartz crystal, of thickness h and mass m , excited to resonance by the application of an alternating voltage (a) and (b) oscillating crystal with added mass. After the deposition, the thickness is $h + \Delta h$ and the mass is $m + \Delta m$.

The Sauerbrey equation is valid under the following three conditions: (1) the added mass is small compared to the mass of the crystal itself, (2) the added mass is rigidly adsorbed, and (3) the mass is evenly distributed over the active area of the crystal. This equation has been used and is still being used in several industries for monitoring the rate and thickness of metal deposition under the vacuum or gas phase.

2.9 X-Ray Photoelectron spectroscopy

X-ray photoelectron spectroscopy is a technique based on the photoelectric effect: radiation in

the X-field ($10^{-12} \leq \lambda \leq 10^{-8}$ m) strikes a solid surface causing electrons to be emitted outward (photoelectrons). In its simplest configuration, an XPS spectrometer consists of a primary radiation source (usually produced by the interaction between electrons that are emitted from a cathode and are accelerated towards an Mg or Al anode), a sample holder, and an electron analyzer. To avoid any possible interference to the analysis, these instruments operate in the ultra-high vacuum range ($P < 10^{-9}$ mbar).

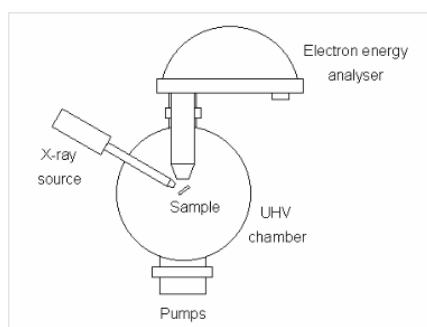


Figure 2.11 Scheme of a basic XPS set-up.

The X-rays produced by the source interact with the sample generating photoelectrons, i.e. electrons coming from the inner shells of the atoms, but also the valence ones.

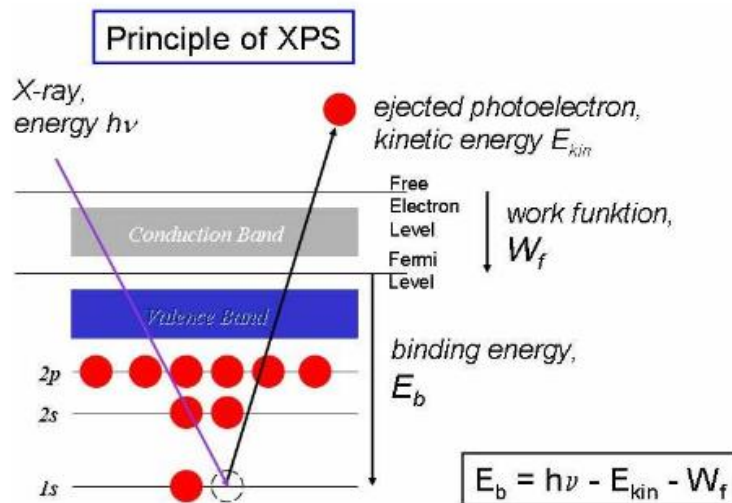


Figure 2.12 Scheme of photoemission process: an electron from the inner shell 1s is ejected due to the interaction of X-ray photo with the material.

The analyzer allows discriminating the kinetic energy associated with these electrons, providing as output a spectrum that reports the signal intensity (number of electrons counted per second) against the kinetic energy of the electrons. This energy depends on the energy of the incident photons (primary radiation, $\nu = hE$) and the binding energy of the electrons of the atom (Binding

Energy, BE). It is possible to relate these quantities through the equation 2.13:

$$BE = h\nu - E_{kinetic} \text{ (equation 2.13)}$$

This technique has been performed to determine the elemental composition of the samples and to identify the chemical bonds.

2.10 NEXAFS (Near edge x-ray absorption fine structure) Spectroscopy

NEXAFS spectroscopy is a technique quite similar to XPS spectroscopy and allows to obtain information regarding the elemental composition and bond structure of analyzed samples. This technique uses a synchrotron source, which allows using of tunable and polarizes X-rays to photoemission spectroscopy (XPS) technique, where the photon energy is fixed and the electron intensity is measured as a function of electron kinetic energy, in NEXAFS the X-ray energy is scanned and the absorbed x-ray intensity is measured. The photon energies are collected in total electron yield (TEY) when the absorbed x-ray intensity is not measured directly but rather the photoelectrons that are originated by the absorbed x-rays in the very first 1-2 nm of sample depth. X-rays are absorbed through excitations of core electrons to empty states above the vacuum or Fermi level. The photon energy can be expressed also in partial electron yield when all-electron originating from photo-emission are collected. In both cases, this technique as XPS allows obtaining information regarding only the surface structure of the material analyzed (around 5 nm).

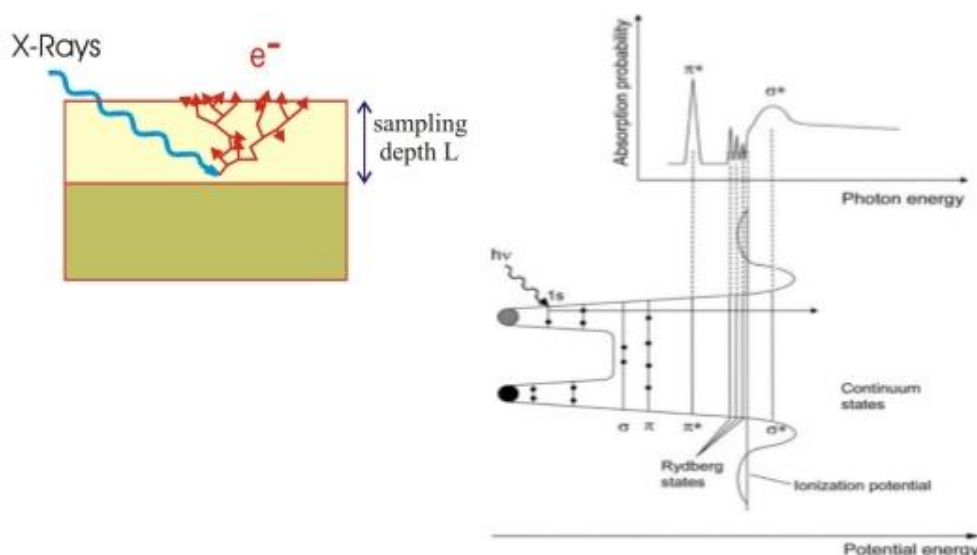


Figure 2.13 Scheme of potential (bottom) with the corresponding NEXAFS spectrum (top) for a diatomic molecular group [6], [7].

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Chapter 3

3.1 Introduction

The focus of this chapter is to study the basic properties of pPANI deposition using argon/aniline RF plasmas. The first step is to fix some experimental parameters which will be used as reference parameters throughout this section. Then, the deposition of thin-films is performed on reference substrates (here intrinsic silicon) to carry out material diagnostics and analyze the polymer structure (using FTIR, XPS, and NEXAFS), the film roughness (AFM and SEM microscopy), and some key processing information such as the growth speed or the deposition homogeneity.

When an argon/aniline plasma is ignited, some of the reactive species created in the discharge will reach the electrodes and the walls of the vacuum chamber all along the process and contribute there to the growth of thin films. This is the basis for plasma deposition of pPANI thin-films, which only requires fixing a given sample on one of these surfaces. Because of the specific design of the vacuum chamber (electrode diameter = 12cm, electrode wall distance = 24 cm), the interactions with the walls are substantially reduced, and pPANI deposition will happen mostly on the electrodes – or at least the growth speed there is much greater. For this reason, most of the films in this study will be deposited on substrates placed on the electrodes. Chapter 3 will deal with the study of plasma polymerization of polyaniline in different gas mixtures.

3.2 Plasma polymerization

Plasma polymerization as already said in chapter 1 is a technique, which allows the synthesis of different products such as thin films or nanoparticles.

The process starts with the electron impact dissociation of the parent molecules (in our case the aniline monomer) which results in the production of a great variety of different fragments like neutrals, radicals, and positive and negative ions [1]–[5]. All those species formed inside the plasma can react with each other in subsequent polymerization processes, which can occur both in the plasma volume and on surfaces exposed to the plasma. These reactions lead to the formation of the main products of plasma polymerization: thin film and nanoparticles.

The details of each plasma process strongly depend on the experimental parameters, which are chosen before the experiment. One important example is the pulsing of the plasma which can be used, if the pulse parameters are properly chosen, to partially avoid and block the formation

of nanoparticles in the plasma volume. One of the main differences between a continuously operated plasma and a pulsed plasma concerns the role of negative ions which are believed to play an important role in the formation of nanoparticles. In a continuously operated plasma, the negative ions stay confined in the plasma volume due to the positive plasma potential (positive with respect to the walls surrounding the plasmas). In the plasma off phase of a pulsed plasma, however, the negative ions can escape from the discharge [1], [6] (if the plasma off time is long enough) interrupting in this way those polymerization reactions which are potentially driven by the negative ions.

Due to the potentially great number of different species and reactions involved in the plasma process is it easy to understand that plasma polymerization is a very complex process. A better understanding of the role the different types of species (neutral radicals, positive and negative ions) play in the polymerization process is therefore essential to control the resulting products be it nanoparticles or thin films.

The main contribution of this Ph.D. work concerns the production of polymeric thin films originating from argon/ aniline gas mixtures but also from pure aniline and to study how it is possible to modify the properties of the thin films in a controlled way.

The plasma deposition is performed with a capacitively coupled plasma. The discharge is operated in a pulsed mode with a pulse frequency of 25 Hz to have a dust-free process:-

The deposition of the films is performed on two different types of substrates undoped and doped silicon wafers with a thickness of 300 μm .

The standard parameters chosen for the deposition are given in table 1:

Power (W)	Pressure (mbar)	Gas mixture	Duty Cycle	Pulse frequency (Hz)
1-15 W	0.18 mbar	Argon 20 sccm Aniline 1 sccm	0.5 (20 ms on/40 ms tot cycle)	f=25 Hz

3.3 FTIR analysis of aniline plasma

In this section, some fundamental phenomena of reactive plasmas and the time scales associated with these phenomena are illustrated using some experimental results from in-situ infrared spectroscopy.

Figure 3.1 shows first an in-situ infrared spectrum of pure aniline (at a pressure of 0.18 mbar) that was recorded before the plasma was switched on. The aniline used in all experiments is from Sigma Aldrich (reagent purity >99.5%). The infrared spectrum of aniline was measured at room temperature with a Bruker Vertex 70 series Infra-Red spectrometer equipped with an MCT detector (cooled with liquid nitrogen) which allowed a frequency range from 500 cm^{-1} to 4000 cm^{-1} . For all spectra, a resolution of 0.2 cm^{-1} was chosen.

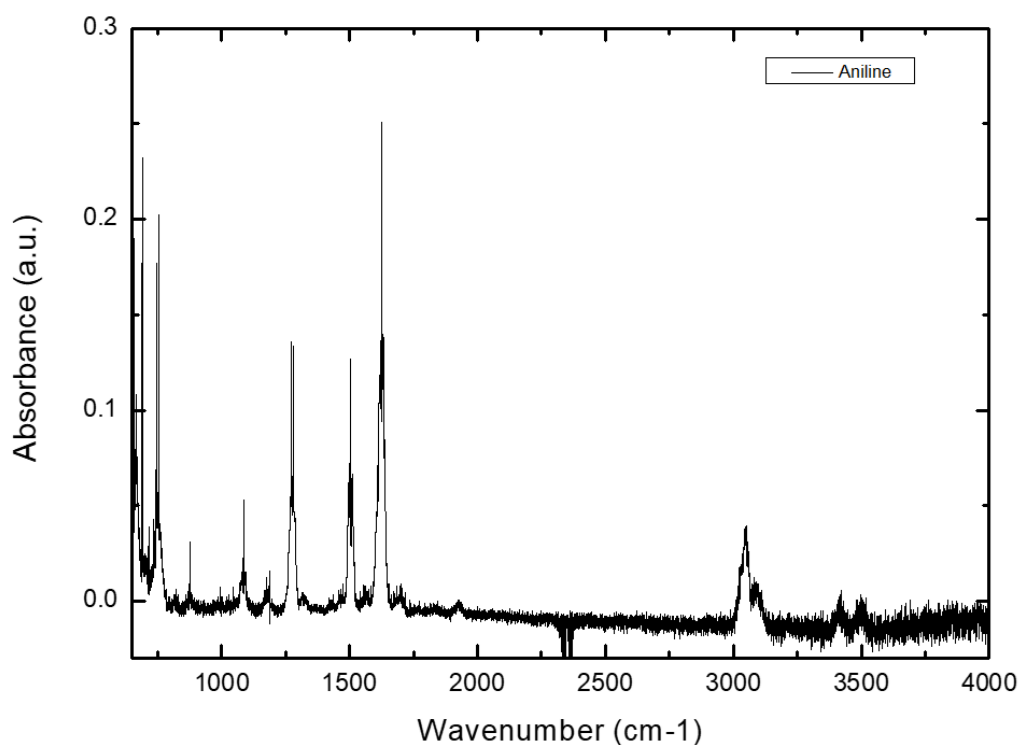


Figure 3.1 In situ FTIR spectrum of aniline recorded with a resolution of 0.2 cm^{-1} .

The peak around 3400 and 3100 cm^{-1} can be attributed to N-H stretching vibration. The peak observed at 3050 cm^{-1} indicates the presence of C-H stretching vibration that occurred on the benzenoid ring. The band between 1650 cm^{-1} and 1580 cm^{-1} refers to N-H bending and this peak is visible only in primary amine like aniline. The peak between 1335 and 1250 cm^{-1} refers to the C-N stretch (aromatic amines) while peaks in the range between 1250 cm^{-1} and 1020 cm^{-1} can be attributed to the C-N stretch of aliphatic amines vibrational contribution. Several peaks

appear in the range between 650 cm^{-1} and 950 cm^{-1} and include the contribution of C=C stretching of the aromatic ring (monosubstituted ring), ortho, meta, and para-substituted ring, and N-H wag [7]–[9].

In order to monitor the temporal evolution of the spectra, once the plasma is switched on an acquisition routine was created for the rapid scan execution, which allowed to collect of a spectrum every 12 seconds with a resolution of 0.2 cm^{-1} .

The temporal evolution of the FTIR signal during the operation of the plasma is illustrated in figure 3.2. Figure 3.2 (a) shows again the FTIR spectrum of the pure aniline i.e., it was measured before the discharge switched on. The spectrum in figure 3.2 (b) was measured about 90 seconds after the discharge was ignited. The plasma was operated with a power of 5W under the standard conditions given in table 1. The most significant difference between the two spectra concerns the overall decrease of absorbance in figure 3.2 (b). This is of course related to the decrease of the aniline concentration caused by the fragmentation of the monomer due to electron impact dissociation. The time scales involved in this process are more clearly visible in figure 3.3 which shows the temporal evolution of the absorbance of the peak at 1620 cm^{-1} referring to N-H bending. In the first 90 sec after switching on the plasma (at $t = 0$) the intensity of the peak is decreasing by almost a factor of two.

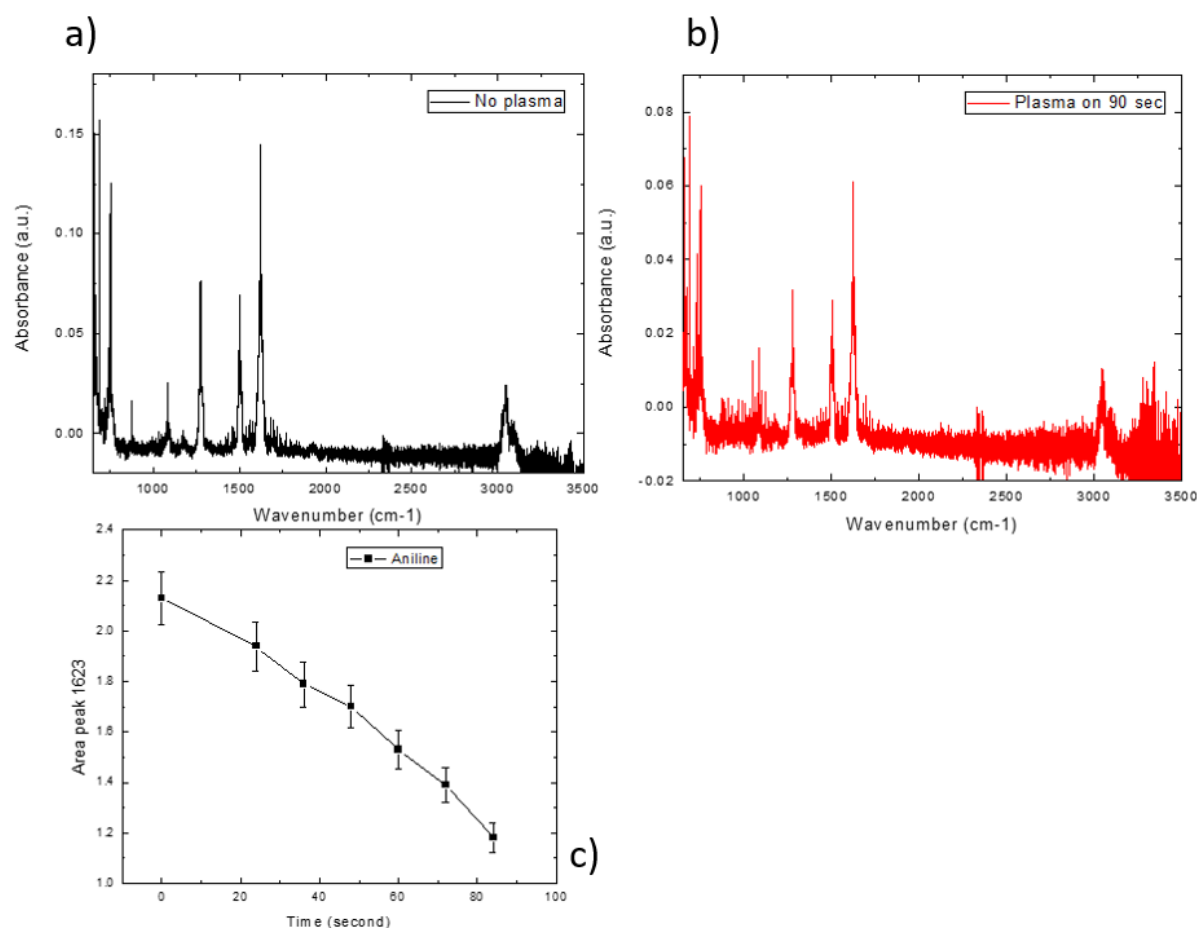


Figure 3.2 Aniline in situ FTIR spectra of aniline before (a) and after plasma (b), and evolution of aniline peak at 1623 cm⁻¹ in function of time (c).

After acquiring the spectrum, at $t = 90$ s the plasma is switched off and several spectra were acquired after 1 minute, 3 minutes, 5 minutes, and 7 minutes. The recovery of the monomer concentration happens quite fast in the first 30 sec after the plasma is switched off and then slowly goes up until it reaches the original concentration values after approximately 7 min. At this time there is a balance between the loss of aniline due to pumping and the increase of aniline due to the continuous injection of fresh aniline from the source. An important finding from this measurement concerns the time scales of our plasma process. In contrast to the plasma parameters for noble gas discharges, which typically level up in a very short time (micro to milliseconds), we are dealing here with time scales that are in the range of several minutes.

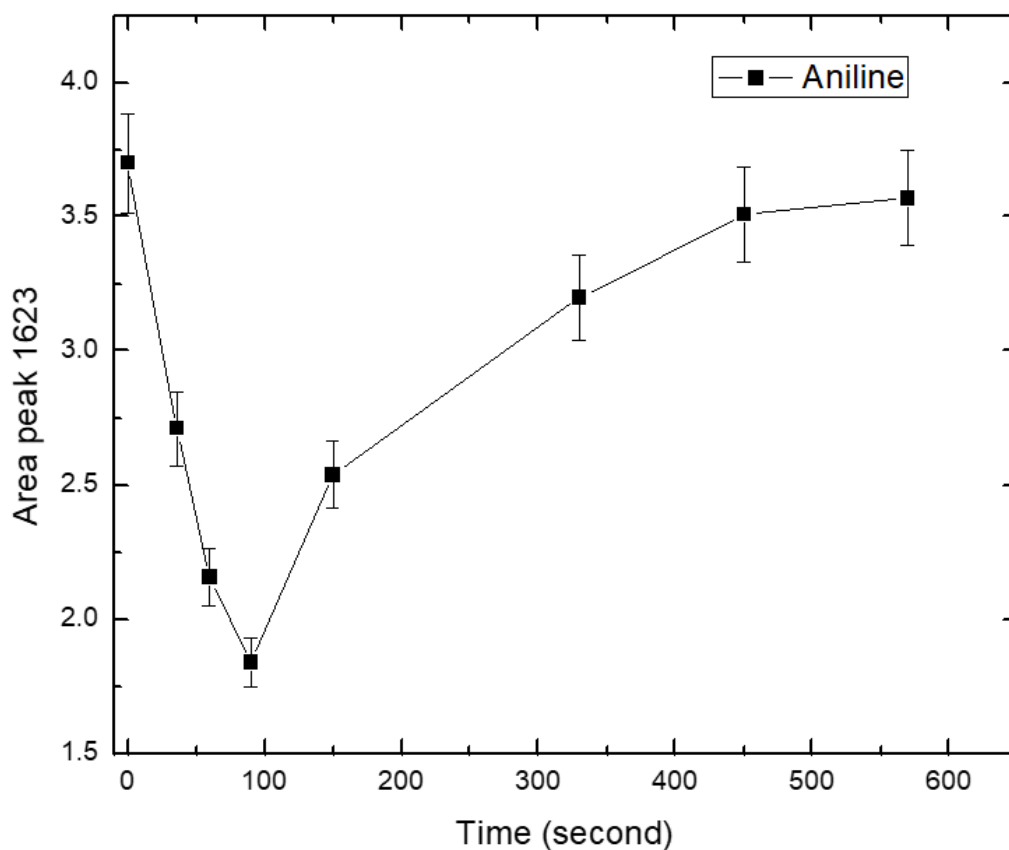


Figure 3.3 Aniline recovery after switching off plasma in function of the time.

Another phenomenon relevant for the understanding of reactive plasmas is illustrated in figure 3.4 (a-d). The figures each show a section of the entire spectrum. Figures *a* and *b* display a wavenumber interval from 600 to 700 cm^{-1} and figures *c* and *d* an interval from 700 to 750 cm^{-1} . The figures on the left each show a spectrum that was recorded before the plasma was ignited the figures on the right shows' spectra measured 90 seconds after the discharge was switched on.

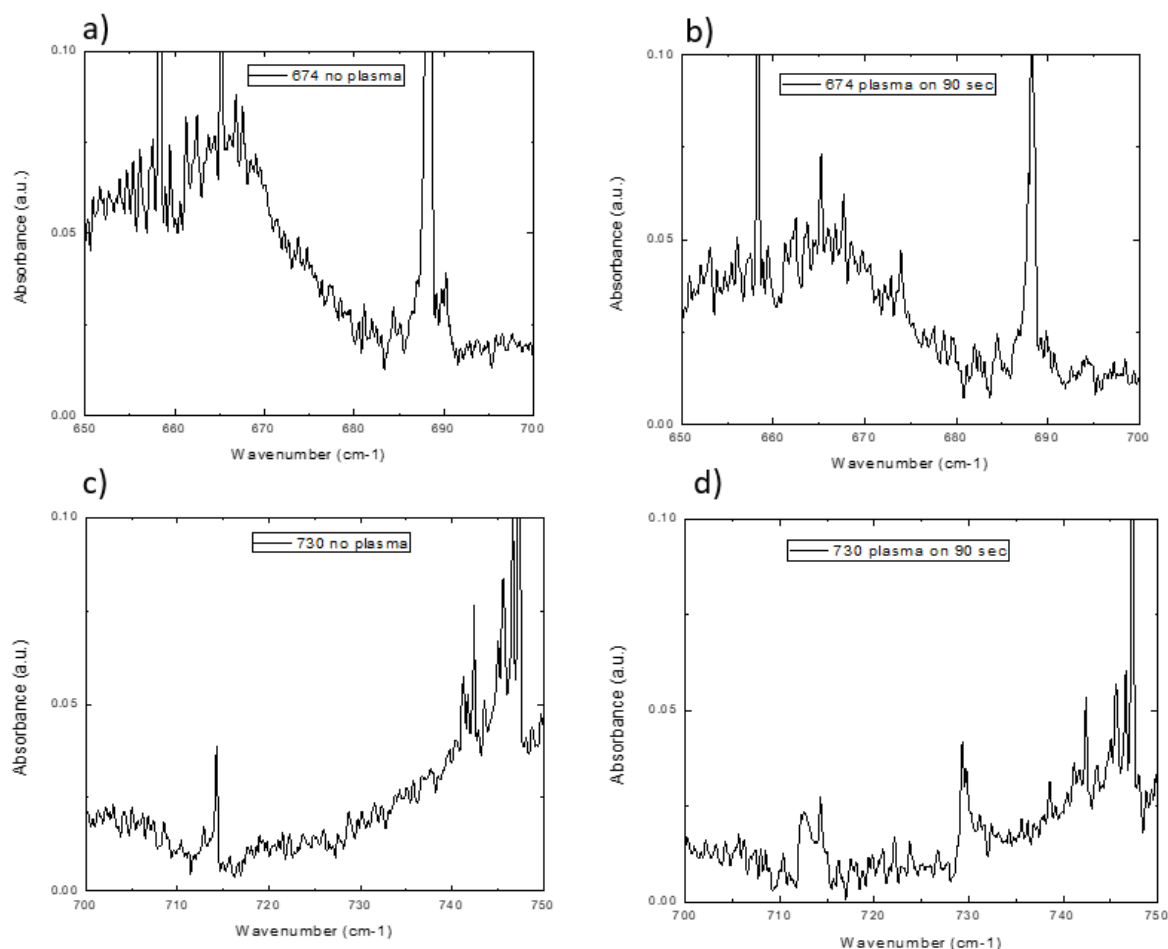


Figure 3.4 Evolution of peaks at 674 cm^{-1} (a and b) and 730 cm^{-1} (c and d).

The graphs in figure 3.4 show the rise of two new peaks of interest at 674 cm^{-1} and 730 cm^{-1} that could be attributed to benzene and toluene (NIST Chemistry WebBook). In the initial spectra (left side), there is no presence in the spectra of both of these peaks. This can be explained by the fact that the species that contribute to those peaks are not present in the initial gas and are formed only when the plasma is switched on. Figure 3.5 shows the temporal evolution of the absorbance at 674 cm^{-1} .

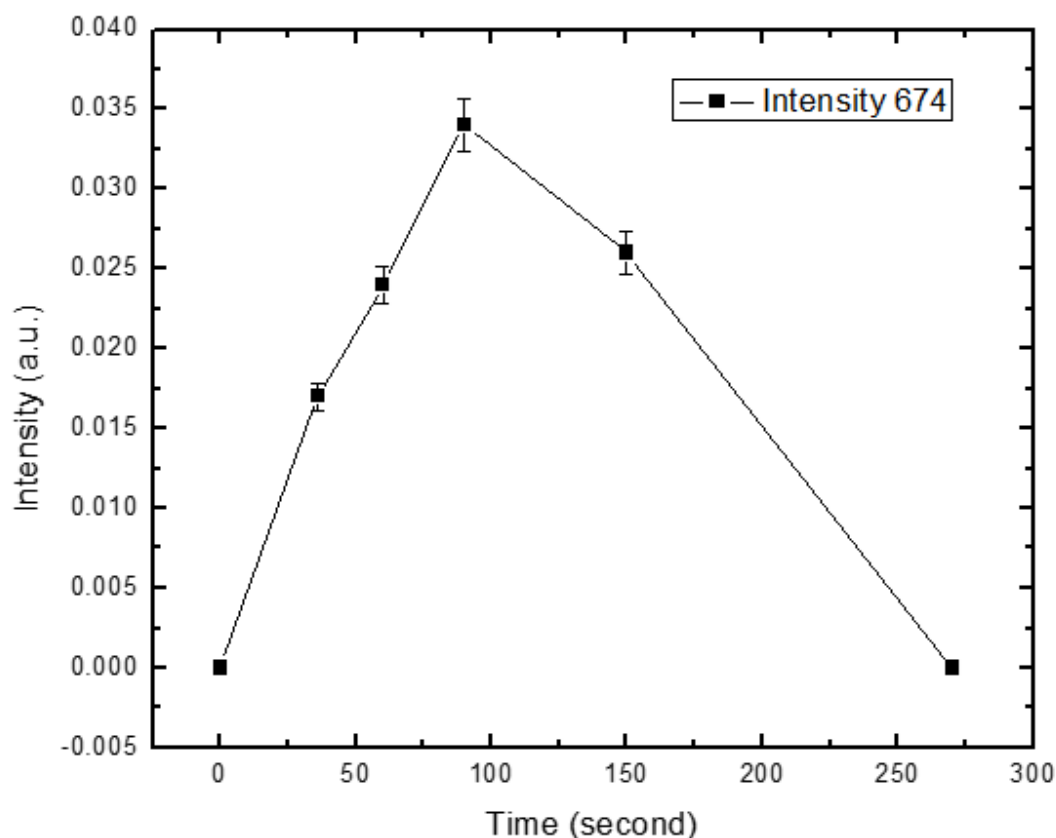


Figure 3.5 Evolution of peak at 674 cm^{-1} before and after plasma.

The absorbance is equal to 0 in the starting mixture and starts to increase when the plasma is switched on. After around 90 seconds the plasma is switched off and new spectra are acquired. The absorbance is slightly reduced until we reach 150 sec (60 sec after plasma off) and at 270 sec (180 sec after plasma off) the absorbance returns to 0 like in the initial spectra acquired before the plasma. This experiment confirms that the species that contribute to this peak are formed only when the plasma process is running - due to the fragmentation of the aniline monomer and due to the creation of new species. When the plasma is switched off it is disappearing due to pumping losses. A comparison between figures 3.7 and 3.8 also shows that the time scales for the destruction of the monomer due to electron impact disassociation and the loss of species due to pumping are in the same order of magnitude.

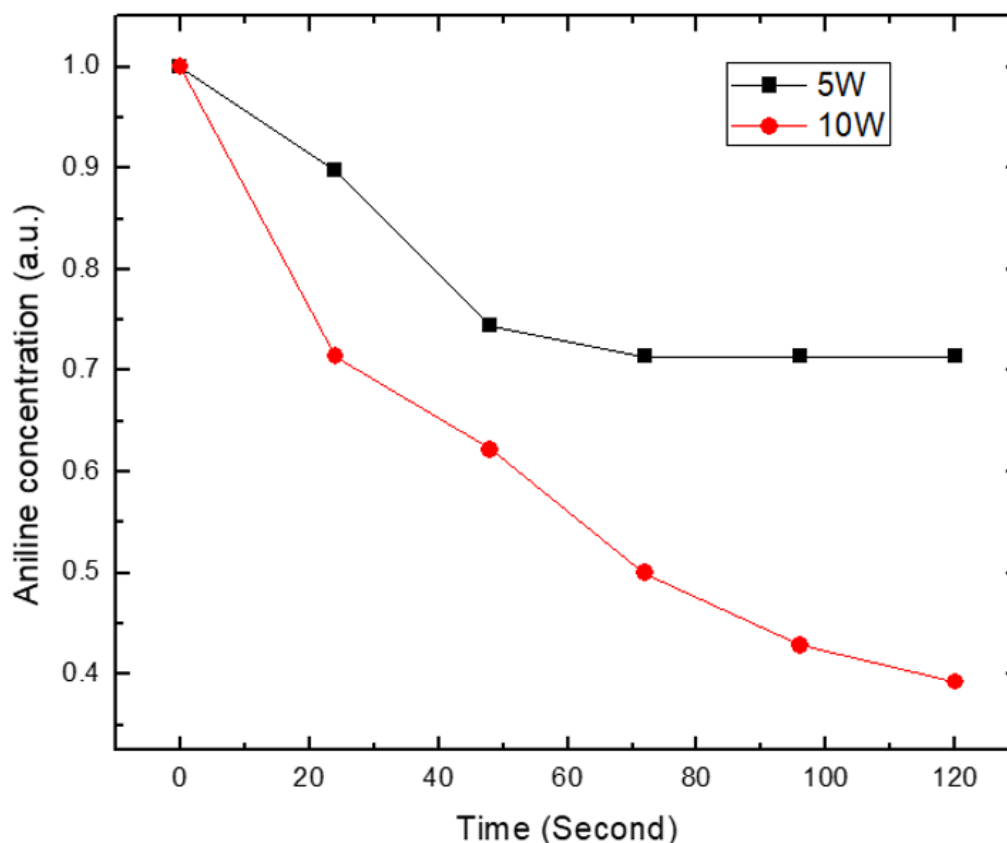


Figure 3.6 Aniline depletion as a function of time for 2 different powers.

The time scales involved in the plasma process of course depend on the plasma parameter and therefore on the external discharge parameter. This is illustrated in figure 3.6 which shows the decrease of the aniline concentration over time for two different powers applied to the discharge: 5 and 10 Watt. The results confirm the intuitively clear idea that a higher power – resulting in a higher electron density- will lead to a faster depletion of the monomer. However, it is not only the power or electron density that influence the temporal evolution of the different species, there are also other factors that play an important role such as gas mixture ratio or the pumping speed. Figure 3.7 shows the temporal evolution of the FTIR signal recorded at several different wavenumbers (corresponding to Benzene at 674 cm^{-1} , Toluene at 729 cm^{-1} , Ethylene at 966 cm^{-1} , Aliphatic CH at 2944 cm^{-1}). In contrast to figure 3.6 the measurement here was performed in a gas with an input flow of 2 sccm Ar and 1 sccm aniline at a pressure of 0.18 mbar. The results show that the decrease of the absorbance at 1504 cm^{-1} (aniline) is much slower than in the previous case.

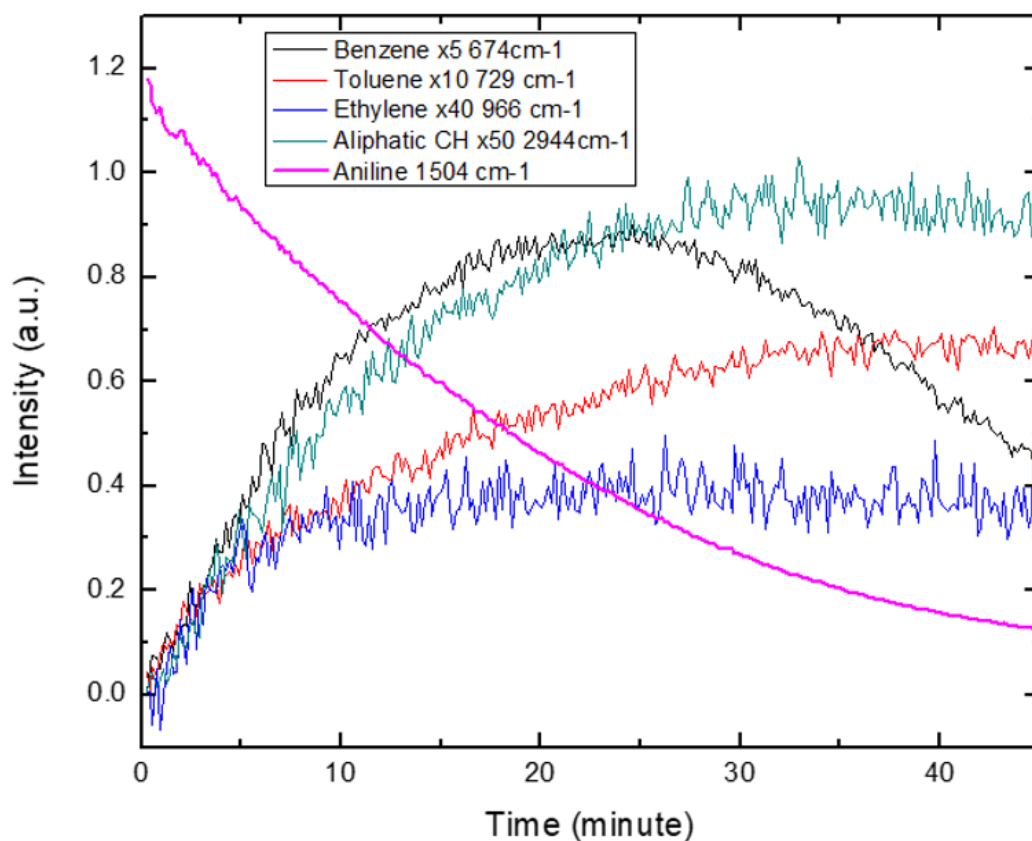


Figure 3.7 Evolution of species produced in a discharge operating in Ar/aniline mixture (2:1 sccm).

The increase of the absorbance at the other wavenumbers – indicating the build-up of new molecules- occurs also on a much slower timescale. Moreover, the temporal evolution of each of those species is different since some of them may be produced directly from the original monomer (such as benzene) while others might require further multi-step polymerization processes to be produced. Figure 3.8 shows the results of a similar experiment. However, in this experiment, the gas flow was doubled (4 sccm Ar and 2 sccm aniline) while the pressure was kept constant at 0.18 mbar (by increasing the pumping speed).

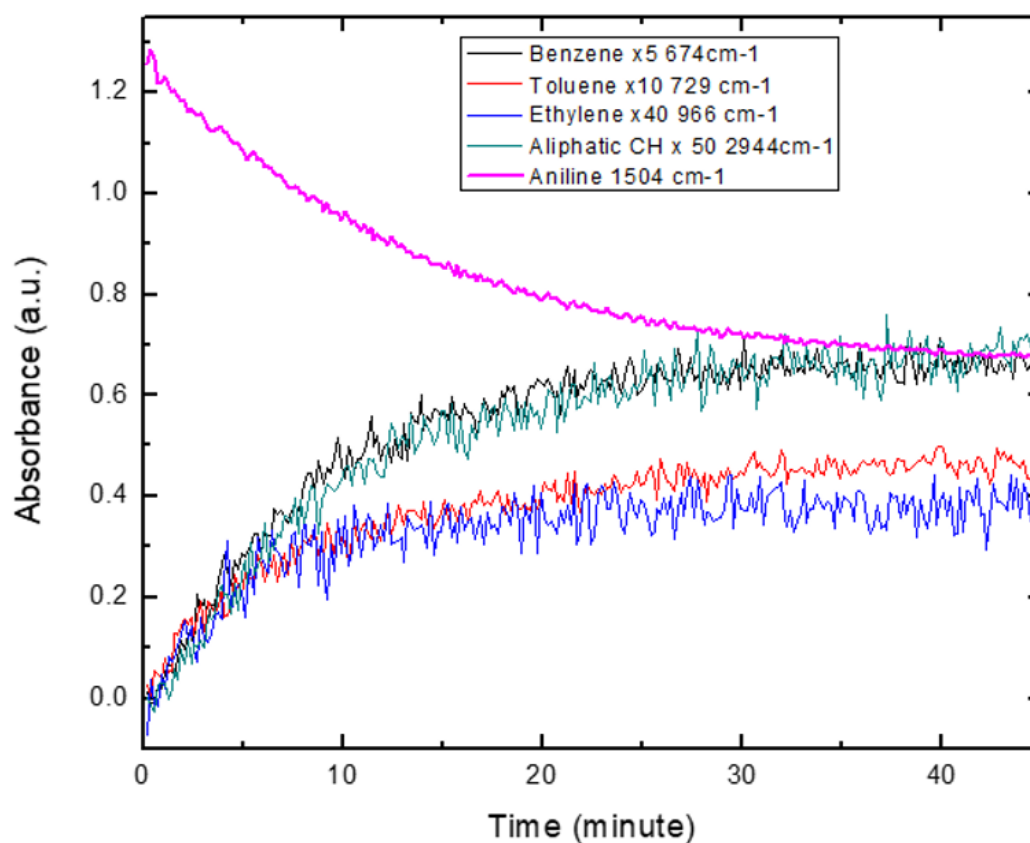


Figure 3.8 Evolution of species produced in a discharge operating in Ar/aniline mixture (4:2 sccm).

The results show that even though the pressure was kept constant the time scales of the temporal evolution of the signals are affected by the variation of gas flow and pumping speed.

Before looking at these timescales from a more theoretical point of view, another topic will be briefly discussed: the formation of nanoparticles.

Figure 3.9 shows 4 FTIR spectra measured at 4 different times. In this experiment, the plasma was running in a **continuous mode** with a power of 10 W (i.e. a power doubled compared to the previous experiments). In addition to the overall decrease in extinction as the plasma on-time progresses, another phenomenon can be observed: the broadening of the peaks.

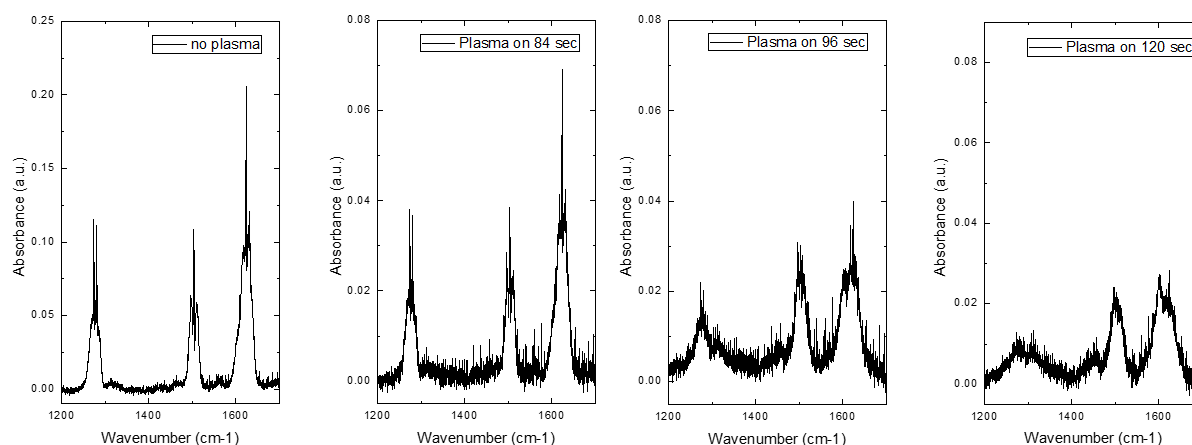


Figure 3.9 Evolution of FTIR spectra in function of plasma on time.

This is illustrated more clearly in figure y which shows the temporal evolution of the full width half maximum (FWHM) of the peak at 1623 cm^{-1} . The width of the peak remains approximately constant for the first 80 seconds after the plasma is switched on. After 80 seconds, the peak width increases by almost a factor of two at 96 and 120 seconds.

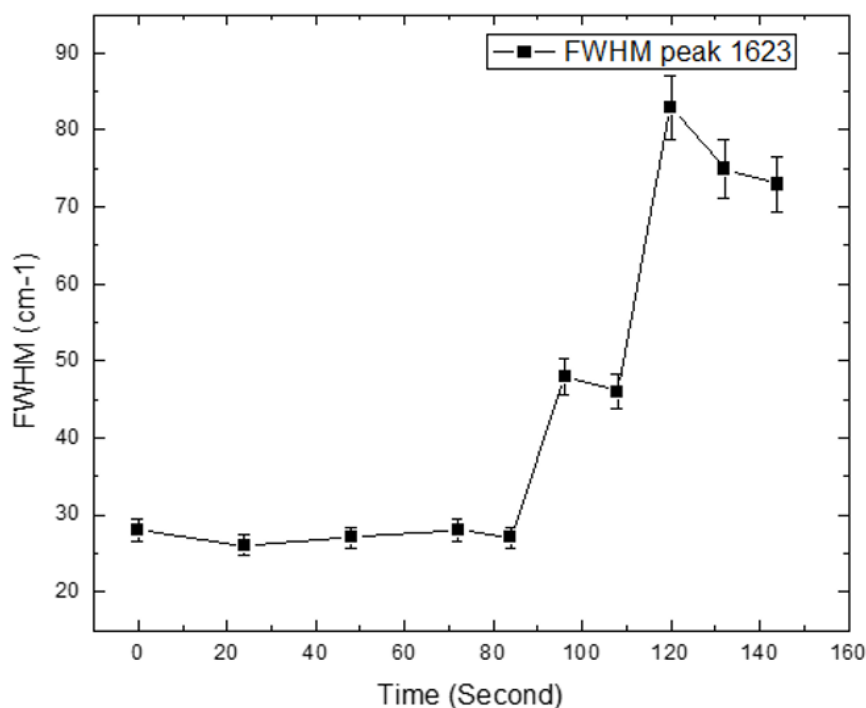


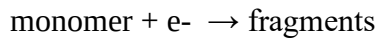
Figure 3.10 Full width half maximum evolution of peak at 1623 cm^{-1} .

This effect can be may be explained by the formation of nanoparticles in the plasma volume illustrating once again the complexity of reactive plasmas.

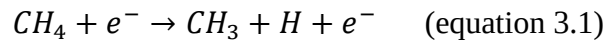
3.4 Theoretical model

In order to better understand the time scales involved in reactive plasma processes, a small theoretical model will be discussed in this paragraph.

As described in the introduction of this chapter the plasma process starts with the fragmentation of the chosen monomer molecule due to electron impact. The hot electrons present in the plasma possess enough kinetic energy to fragment the monomer resulting in the formation of different species such as radicals, neutrals, positive and negative ions. i.e. the starting reaction can be written as:



Even for the case of a rather simple monomer as methane the collision of electrons with a methane molecule can result in a great number of different reactions as e.g.

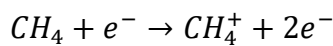
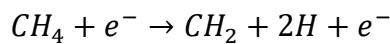
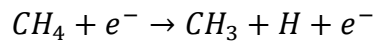


The concentration of the monomer n_{mon} as a function of time is described by the following simple differential equation:

$$\frac{dn_{mon}}{dt} = -n_e n_{mon} R_c \quad (\text{equation 3.2})$$

where n_e is the electron density and R_c is the rate coefficient of the reaction that is considered.

For simplicity, we assumed before that only one reaction can occur. In reality, more reactions have to be considered in the process as e.g.



.....

The differential equation which describes the process becomes, therefore:

$$\frac{dn_{CH_4}}{dt} = -n_e n_{CH_4} (R_{CH_4 \rightarrow CH_3} + R_{CH_4 \rightarrow CH_2} + R_{CH_4 \rightarrow CH_4^+} + \dots) \quad (\text{equation 3.3})$$

wherein the destruction of the monomer all possible reactions with their respective rate coefficients have to be taken into account.

The solution of the differential equation is:

$$n_{mon} = C e^{-(kt)} \quad (\text{equation 3.4})$$

where $k = n_e * (R_1 + R_2 + R_3 + \dots)$ and $C = n_{0_{mon}}$ is the starting concentration of the monomer.

In order to better understand the “real process,” we need to take into account also the continued introduction of new monomer molecules and also the losses due to pumping. By adding those factors, the differential equation becomes:

$$\frac{dn_{mon}}{dt} = -n_e n_{mon} R_c + F - n_{mon} * R_p \quad (\text{equation 3.5})$$

Here F represents the injected gas flow expressed (in $m^{-3} \cdot s^{-1}$) and R_p indicates the pumping frequency defined as $P_{freq} [s^{-1}] = P_{speed} / V_{chamber}$

The differential equation that describes the process has thus the simple form:

$$\frac{dn}{dt} = -kn + F \quad (\text{equation 3.7})$$

Where $k = n_e R_c(Te) + P_{freq} = k_{plasma} + P_{freq}$ which include both the contribution of the destruction of monomer due to electron impact and losses due to pumping. The solution of the equation is :

$$n = n_0 e^{-kt} - \frac{F}{k} [e^{-kt} - 1] \quad (\text{equation 3.8})$$

In order to estimate the starting quantity of the monomer (n_0) at the beginning of the process when there is no plasma we have $k_{plasma} = 0$ and we assume that the density of the monomer is constant. So the equation is simplified and we obtain:

$$\frac{dn}{dt} = -P_{freq} * n + F = 0 \quad (\text{equation 3.9})$$

which gives:

$$n_0 = \frac{F}{P_{freq}} \text{ (equation 3.10)}$$

In order to calculate the parameters used in this model, we used experimental values. The value of F was calculated from the known injected monomer flow in sccm (standard cubic centimeters) and converted into ($\text{m}^3 \cdot \text{s}^{-1}$) through the following formula:

$$F[\text{m}^3 \cdot \text{s}^{-1}] = \text{aniline input [in sccm]} \cdot (4,47\text{E}17) / \text{chamber volume } [\text{m}^3] \text{ (equation 3.12)}$$

The value of the pumping frequency was estimated starting from the calculation of the pumping speed, given by:

$$P_{\text{speed}} \left[\frac{\text{l}}{\text{s}} \right] = \text{Flow[sccm]} * 1/59.2 / P[\text{mbar}] \text{ (equation 3.13)}$$

and then calculating the pumping frequency as:

$$P_{freq} [\text{s}^{-1}] = P_{\text{speed}} / V_{\text{chamber}} [\text{liter}] \text{ (equation 3.14)}$$

In contrast to the values of pumping frequency and gas flows the value of $k_{\text{plasma}} = n_e R_c(Te)$ is not known a priori. Figure 3.12 shows the temporal evolution of the monomer density for different values of k_{plasma} . We assume here that the value of k_{plasma} is approximate of the same order of magnitude as the pumping frequency calculated from the experimental values. The label $n_e \cdot 1$ in figure x corresponds to the case where $k_{\text{plasma}} = P_{\text{freq}}$, the label $n_e \cdot 2$ corresponds to the case where $k_{\text{plasma}} = 2 \cdot P_{\text{freq}}$, and so on.

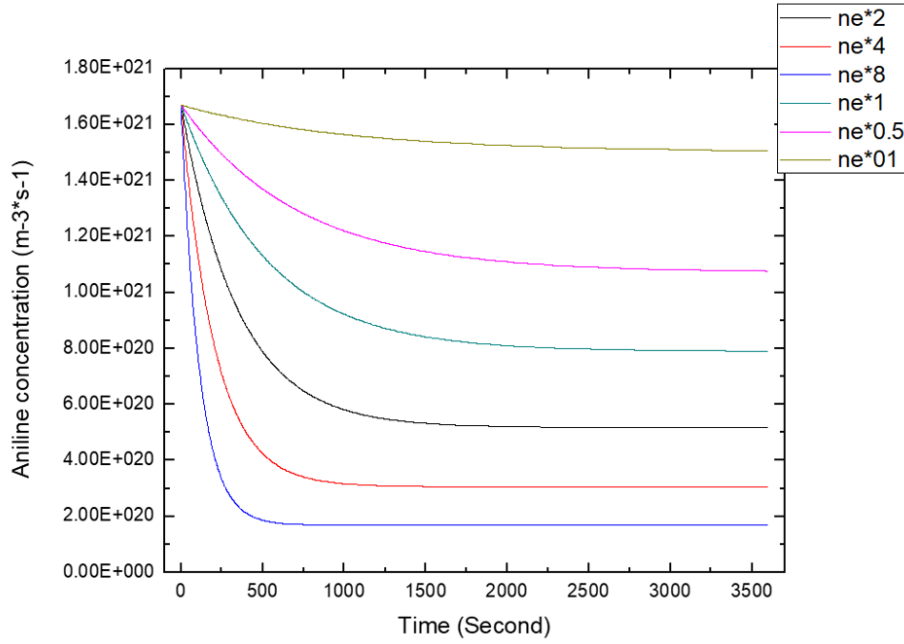


Figure 3.11 shows the influence of k_{plasma} on the temporal evolution of the aniline concentration.

Figure 3.11 clearly shows that the depletion of the (aniline) monomer in time strongly depends on the value of the k_{plasma} . The larger the value of k_{plasma} the faster is the depletion of aniline. For $t \rightarrow \infty$ the value of the aniline concentration will reach the stationary value given by:

$$n = \frac{F}{k} \text{ (equation 3.15)}$$

which depends on the injected flow F and the destruction of monomer due to electron impact and due to losses due to pumping expressed by k . However, the ratio $\frac{n_0}{n_{inf}} = \frac{k_{plasma} + P_r}{P_r}$ does not depend on the injected monomer flow F .

Another important factor (in particular from an experimental point of view) concerns the ratio of the gas flow F to the pumping frequency P_r . Although the initial monomer concentration depends exclusively on the ratio of these two parameters, the development of the monomer density over time depends on both parameters individually. This is illustrated in figure 3.12 which shows the temporal evolution of the monomer density for different values of F and P_r but for a constant ratio of both parameters. The figure shows that with higher values of the pumping frequency and thus with higher values of the gas flow F the decrease of the monomer density over time is less pronounced as was also observed in figure 3.12.

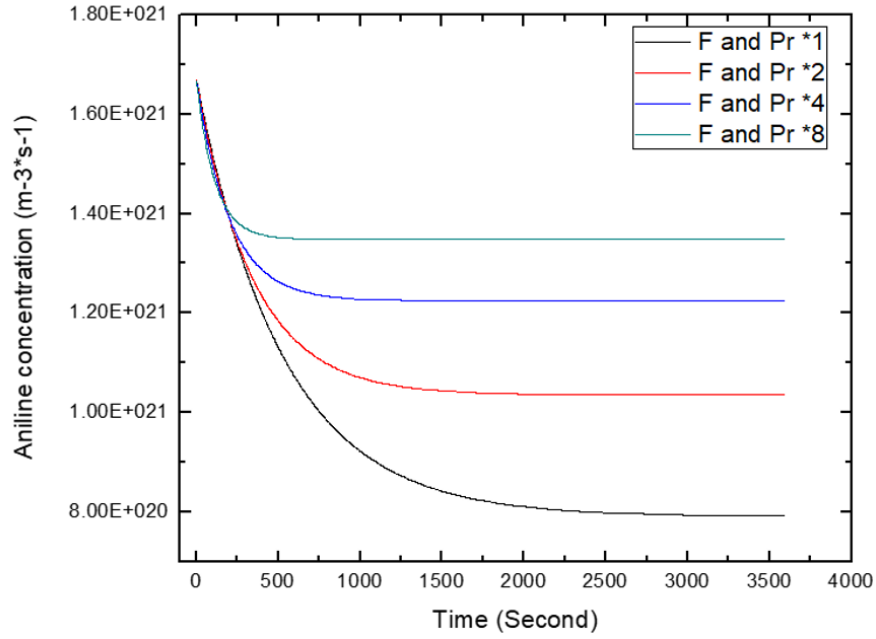


Figure 3.12 Temporal evolution of aniline for different flows and pumping frequencies.

The solution (eq. 3.7) of the differential (eq. 3.8) implies that the plasma parameter namely electron density and electron temperature remain constant during the whole process.

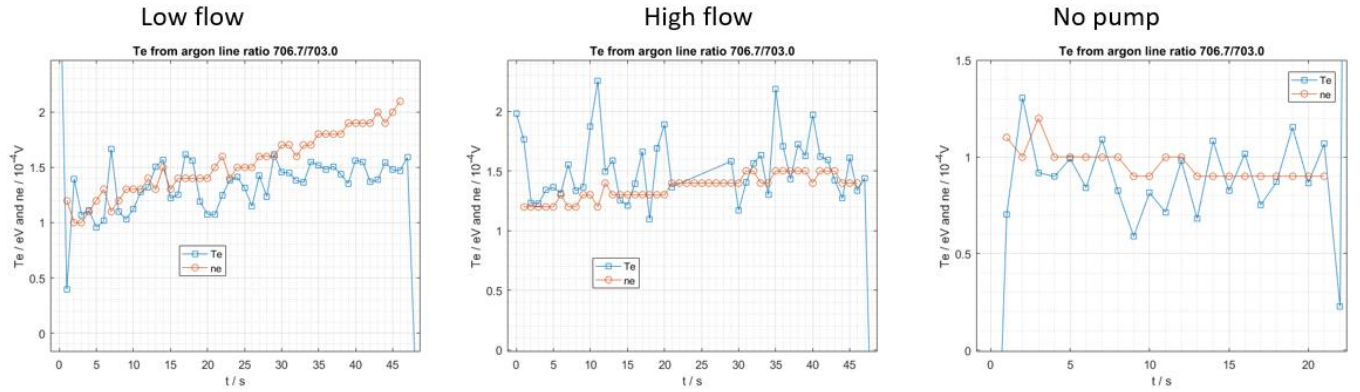


Figure 3.13 Electron density and electron temperature estimation for three different experiments.

To check the validity of this assumption both parameters were measured during the experiments shown previously in figures 3.7 and 3.8. The measurements were performed by means of OES (optical emission spectroscopy) and microwave interferometry. The electron temperature has been estimated from the line ratio of the Ar lines at 703 nm/706.7 nm [10] measured with OES. The estimated electron temperature for the two experiments is approximately constant within

the margin of the noise level and ranges between 1 and 2 eV depending on the experimental parameters and especially on the gas mixture. The same holds for the electron density which stays approximately constant for the experiments of high flow and increases slightly for the case of low flow.

3.5 POLYANILINE THIN FILM DEPOSITION

3.5.1 Introduction

The focus of this chapter is the synthesis and the analysis of thin films of plasma polymerized aniline (pPani) synthesized from Ar/Aniline mixtures employing a capacitively coupled RF plasma. The choice of experimental parameters (gas mixing ratio and pulsing frequency) is based on the final product desired, for this reason, a pulsed plasma is preferred rather than a CW plasma to minimize and avoid the formation of nanoparticles within the plasma volume and to avoid in this way the contamination of the substrate with nanoparticles[1].

The deposition is carried out on different kinds of reference substrates, in this work mainly on intrinsic and extrinsic silicon wafers with a thickness of 300 μm to perform material analysis techniques and analyze the polymer structure and composition (employing FTIR, NEXAFS, and XPS) and the thickness through ellipsometry.

The deposition is carried out in a mixture of Ar and Aniline with a ratio of 20:1 (20 sccm Ar/1 sccm Aniline). The pressure is stabilized to 0.18 mbar before each process to increase the reproducibility. The input average power applied varies in the range between 2 and 10 W and the pulsing applied is $f=25\text{Hz}$ with a duty cycle $DC=0.5$ (20 ms on time/40 ms tot cycle). The deposition time process was chosen according to the desired thickness of the film.

The deposited films appear from a macroscopic point of view quite uniform and homogeneous. Depending on the thickness and the properties of the film deposited the color of the film can change.

3.5.2 FTIR and NEXAFS analysis of plasma polymerized polyaniline thin films

To evaluate the film composition, ex-situ FTIR and NEXAFS spectroscopy were performed on samples deposited on intrinsic silicon wafers. The thickness of the films is around 200 nm.

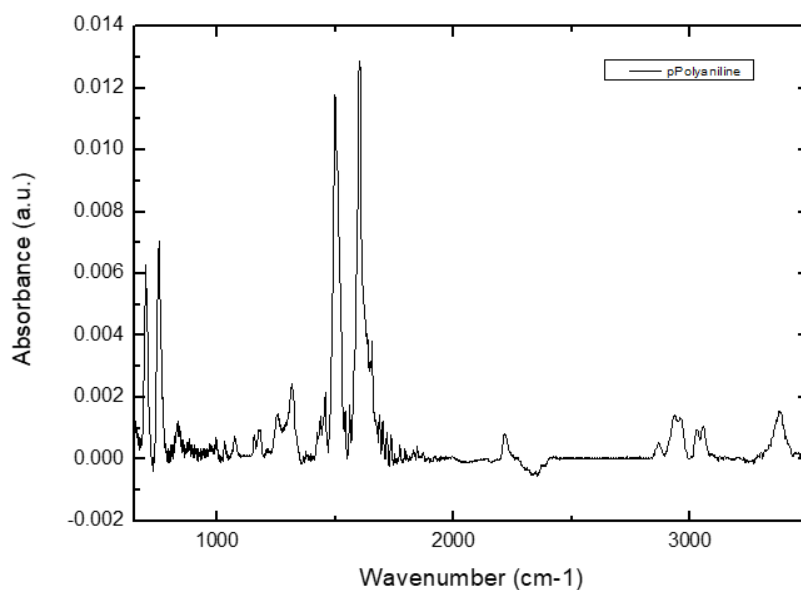


Figure 3.14 FTIR ex-situ spectra of plasma polymerized polyaniline.

The infra-red spectrum of the deposited films is quite complex (see figure 3.14) and the main features are shown in the following table:

Bond Vibration	Wavenumber (cm ⁻¹)
N-H vibration and deformation	3325/3379
Unsaturated C-H stretching	3020/3060
Saturated C-H aliphatic vibration	2920/2960 (or 2800-3080)
C≡N stretching	2212-2215
C=O stretching of ketone	1684-1673
Alkenes (non aromatic) C=C stretching	1600 & 1670
N-H vibration and deformation	1633
C=C stretching of quinoid rings	1589-1600
C=C stretching of benzenoid rings	1496-1500
C=C stretching of benzenoid rings	1403
C-N stretching (QBQ)	1370-1376
C=C interactions	1316
C-N stretching of aromatic ring (aromatic amine)	1306-1317
C-C interactions	1173
Electronic like absorption of N=Q=N	1165
C-C stretching of the alkyl chain	1100

Monosubstituted benzene ring	730-770 & 690-710
Ortho disubstituted aromatic ring	735-770
Meta disubstituted aromatic ring	690-710 & 750-810 & 880
Para disubstituted aromatic ring	800-840

In the spectrum shown in figure 3.14, the main prominent peaks resulting in the strongest IR absorption features are the peak at 1600 cm^{-1} related to the C=C stretching of the quinoid ring and the peak at around 1500 cm^{-1} related to the C=C stretching of the benzenoid ring. The presence of both of those two structures indicates a structure close to the emeraldine or leucoemeraldine like (half reduced and half oxidized polymeric chains) [11]–[13]. Other important features to be considered are the peaks at 3379 cm^{-1} related to the N-H vibration, at 3020 cm^{-1} related to the aromatic C-H stretching contribution, and at 2930 cm^{-1} attributed to aliphatic C-H stretching. A particular case is the peak at around 2220 cm^{-1} which is attributed to the $\text{C}\equiv\text{N}$ structure (nitrile groups) which is not visible in the polyaniline spectrum synthesized with conventional methods such as chemical or electrochemical synthesis but is usually present in plasma polymerized polyaniline.

The analog case is the peak at 1451 cm^{-1} which is attributed to C-H deformation.

NEXAFS spectroscopy is a complementary technique to FTIR and provides valuable information about the composition and the type of bonds in the material. The main features for the C-K edge (figure 3.15 a) and N-K edge (figure 3.15 b) are shown in the following tables:

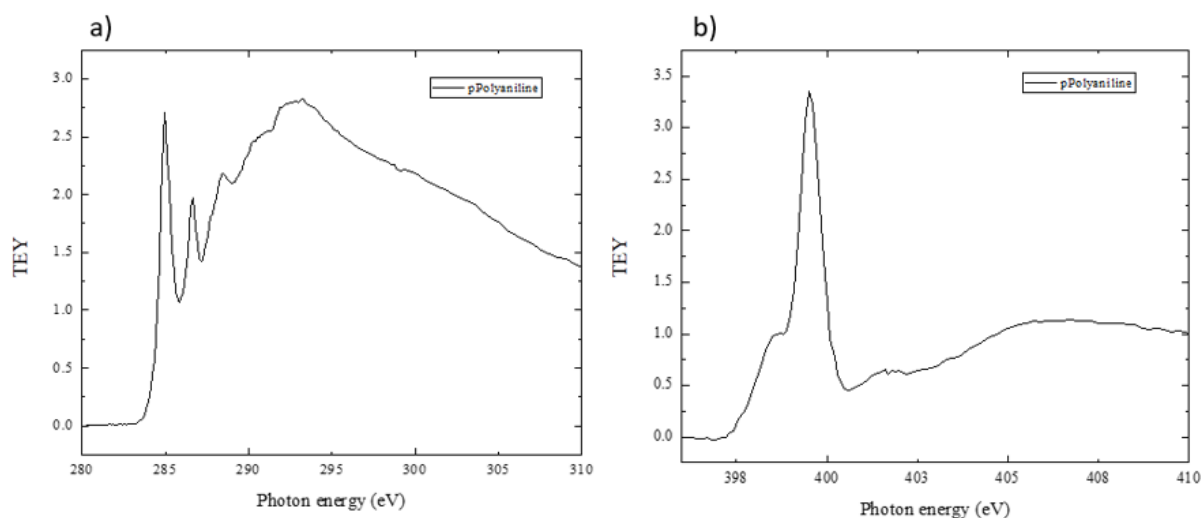


Figure 3.15 NEXAFS C-K edge (a) and N-K edge (b) spectra of plasma polymerized polyaniline.

C K Edge	
Bond	Photon Energy (eV)
π^* resonance of C=C (aromatic)	284.9 – 285.5
π^* resonance of C $\equiv$ N / C=N	286.7
σ^* resonance of C-H	287.4
π^* resonance of C=O	288.8
σ^* resonance of C-N	290
σ^* resonance of C-C	291.7
σ^* resonance of C-C	293.2
σ^* resonance of C-O	294.3
σ^* resonance of C-C	295.8
σ^* resonance of C-O / C-C	298
σ^* resonance of C=C	303.2
σ^* resonance of C=C/C=O	310.3

N K Edge	
Bond	Photon Energy (eV)
π^* resonance of N=C	398.8
π^* resonance of N $\equiv$ C	399.7
σ^* resonance of N-H	402.6
σ^* resonance of N-C	405.4
σ^* resonance of N-C	408
σ^* resonance of N=C	411.1
σ^* resonance of N $\equiv$ C	423.3

The NEXAFS spectra confirm the presence of characteristics groups present in the FTIR spectrum.

As in the case of the FTIR spectrum, in the NEXAFS spectrum, the main prominent peak located at 285 eV is attributed to the π^* resonance of C=C in aromatic rings. Other important contributions usually found in polyaniline are C-C, C-N, C=N, and C-H in the case of C-K edge spectra and the N-H (imine), N-H₂ (amine), and C $\equiv$ N (nitrile) in the case of N-K edge spectra.

3.6 Plasma enhanced chemical vapor deposition of polyaniline

Once the deposition procedure was established and after checking that the thin films are polyaniline-like, the next step of work was to study possibilities to control the properties of the films in a controlled way. There are two ways how to control the thin film deposition process. The first one is to focus the attention on the production of reactive species in the plasma by acting directly on the experimental parameter (varying input power, pressure, gas mixture ratio). The second way is to control the flux of species impinging onto the surfaces.

As described in the introduction of chapter 3, plasma deposition is a rather complex process that starts with the electron impact dissociation of the monomer leading to a cascade of reactions (dissociation and polymerization processes) resulting in the formation of a great variety of different species. Those species that are reaching surfaces exposed to the plasma will influence the properties and the composition of deposited films.

It has to be highlighted that not all the species formed inside the plasma effect interact in the same ways with the surfaces. Neutrals (radicals, atoms, and molecules) can easily reach the surfaces in contact with the plasma and then contribute to the surface reactions according to their sticking coefficient for example.

However, positive and negative ions act differently. Positive ions are accelerated in the plasma sheath region and are thus responsible for an additional energy input into the surface [14]–[16]. Even chemical inert noble gas ions can therefore influence the deposition process e.g. by activating the surface [17]–[21].

The negative ions on the other hand are mostly confined within the plasma volume due to the positive plasma potential. However, in pulsed plasma, the negative ions can leave the plasma volume during the plasma off times (according to the pulsing frequency applied) and can then directly contribute to surface reactions [22], [23].

To control which species will reach the surfaces new filtering method was employed.

3.6.1 Deposition process assisted by filtering method

To study and control the flux of species toward the substrate a custom “channeled” electrode, designed to use a ground electrode, has been realized.

Figure 3.16 shows a sketch of the “channel electrode” which is used to control, to a certain extent, the flux of species reaching the substrate. The electrode consists of a metal plate, characterized by its thickness l and by holes/channels, which are drilled into the metal plate, characterized by their diameter d .

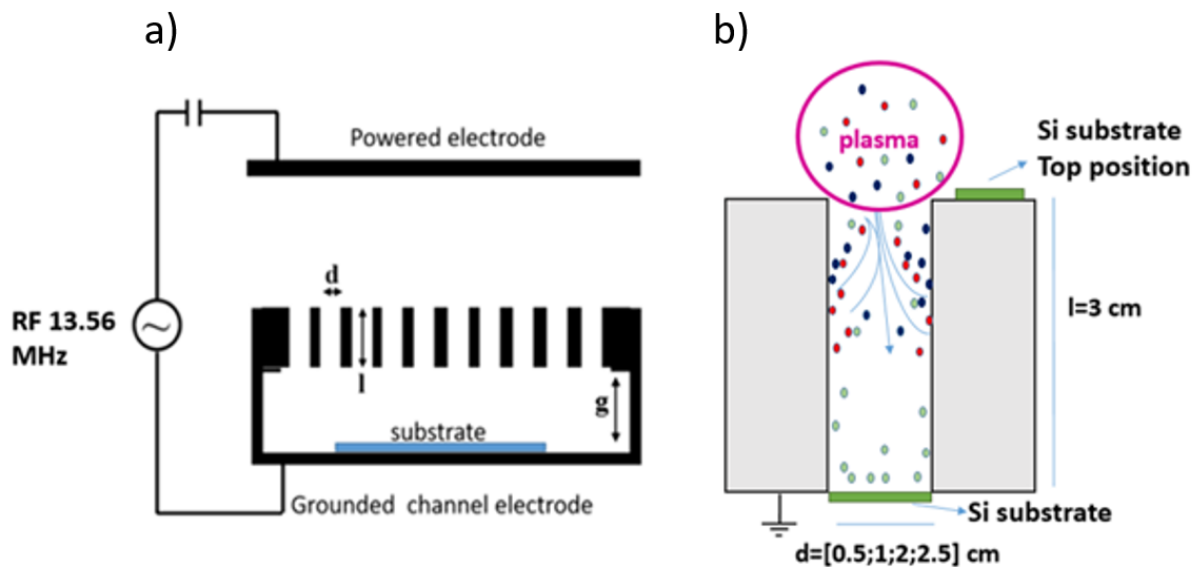


Figure 3.16 a) General scheme of the channel electrode and b) magnification of a single channel. The substrates are positioned directly below the holes (distance between sample and electrode $g = 0$ cm). In the experiment presented here, the metal plate with a thickness of $l=3$ cm has only 4 holes/channels with diameters of 0.5, 1, 2, and 2.5 cm. To evaluate the effect of the holes, one reference wafer is placed on top of the metal plate during the experiments.

It was shown in [24] that structured electrodes can have a tremendous influence on the electron heating dynamics and charge carrier density profiles in capacitively coupled radio frequency plasmas (above and inside the electrode structures). The investigations carried out in [24] were performed in neon. In the present case, the situation is more complex due to the reactive nature of the used gas mixture. In this case, the sticking of reactive species to the sidewalls of the hole could add an additional filtering effect: species with a high sticking coefficient will have smaller probabilities to reach the bottom of the hole and can thus not contribute there to the growth of the film. The filter effect can be controlled by the aspect ratio of hole diameter d to plate thickness l . To guarantee a homogeneous film deposition the substrate can be separated from the holes by a certain distance g . In the present experiment, the metal plate has a thickness of $l=3$ cm and features only 4 holes but with different diameters ($d= 0.5$ cm, 1.0 cm, 2.0 cm, and 2.5 cm). The silicon wafers are attached to the metal plate directly beneath these holes ($g=0$ cm) (Figure 3.17).

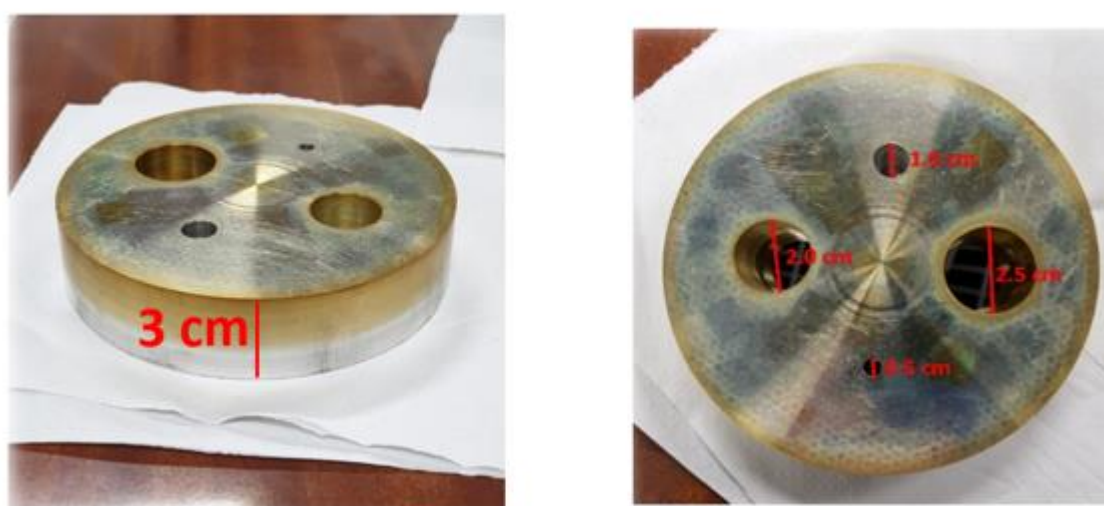


Figure 3.17 Picture of the electrode used to control the flux of reactive species.

Figure 3.18 shows the ex-situ FTIR spectra of thin films from samples placed beneath the different holes. The spectrum in black refers to the sample placed on top of the electrode (see figure 3.16 b).

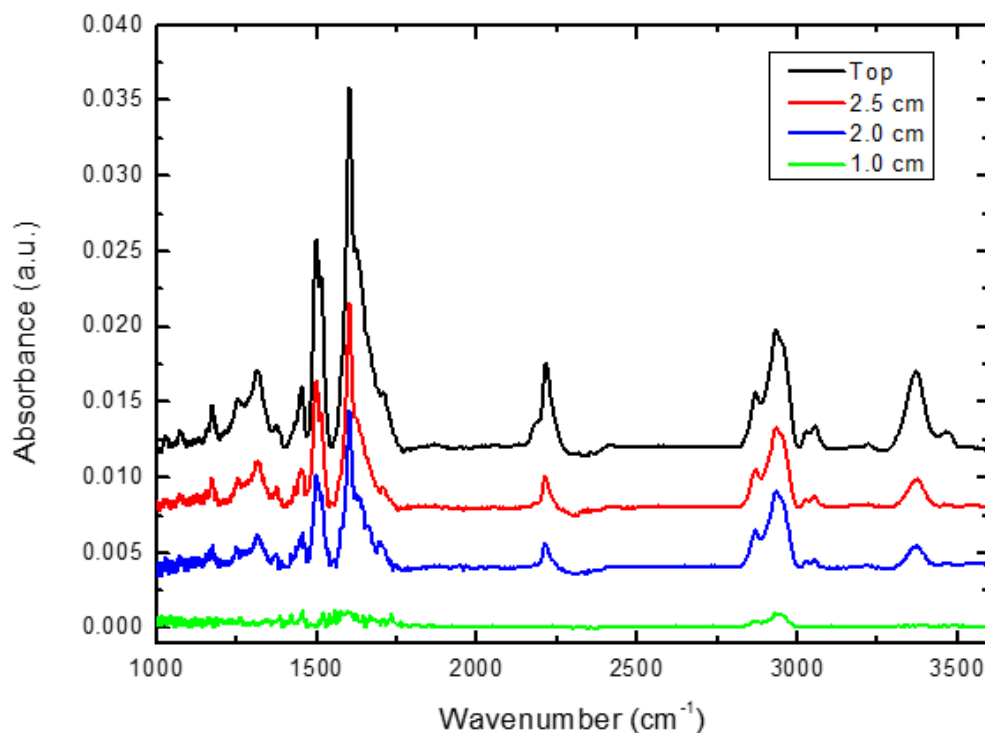


Figure 3.18 Ex-situ FTIR spectra of samples placed in different positions during the growth process. The black line shows the spectrum of the sample placed on top of the electrode. The red, blue, and green lines show spectra of samples placed under the holes with 2.5 cm, 2 cm, and 1 cm diameter, respectively.

The band around 3362 cm^{-1} can be associated with N-H vibrations [25]–[29]. The next two bands around 3020 cm^{-1} and 2930 cm^{-1} can be referred to C-H stretching modes in aromatic structures [29]–[31] or to C-H stretching modes related to aliphatic compounds [25], [27], [30], [31]. The peak around 2217 cm^{-1} can be attributed to C $\equiv$ N bonds [30]–[32]. At 1496 and 1600 cm^{-1} the typical absorption peaks for C=C stretching of benzenoid and quinoid rings are observed [25], [26], [30], [33], [34]. The bands at 1173 cm^{-1} and at 1316 cm^{-1} arise from C-C and C=C interactions and C-N stretching [27], [34]. The band at 1451 cm^{-1} can be attributed to C-H deformation [6].

The spectra in red, blue, and green in figure 3.18 represent the spectra of films from samples that are placed under the different holes of the structured electrode. Compared to the sample placed on top of the electrode, these spectra exhibit an overall decrease in absorbance. This reduction is the stronger, the smaller the size of the hole under which the sample is placed. It can be explained by a decrease in film thickness of the corresponding samples. The growth rate, measured by means of ellipsometry and profilometry, reduces from 4.0 nm/min for the sample

placed on top to 0.25 nm/min for the sample placed under the 1 cm hole.

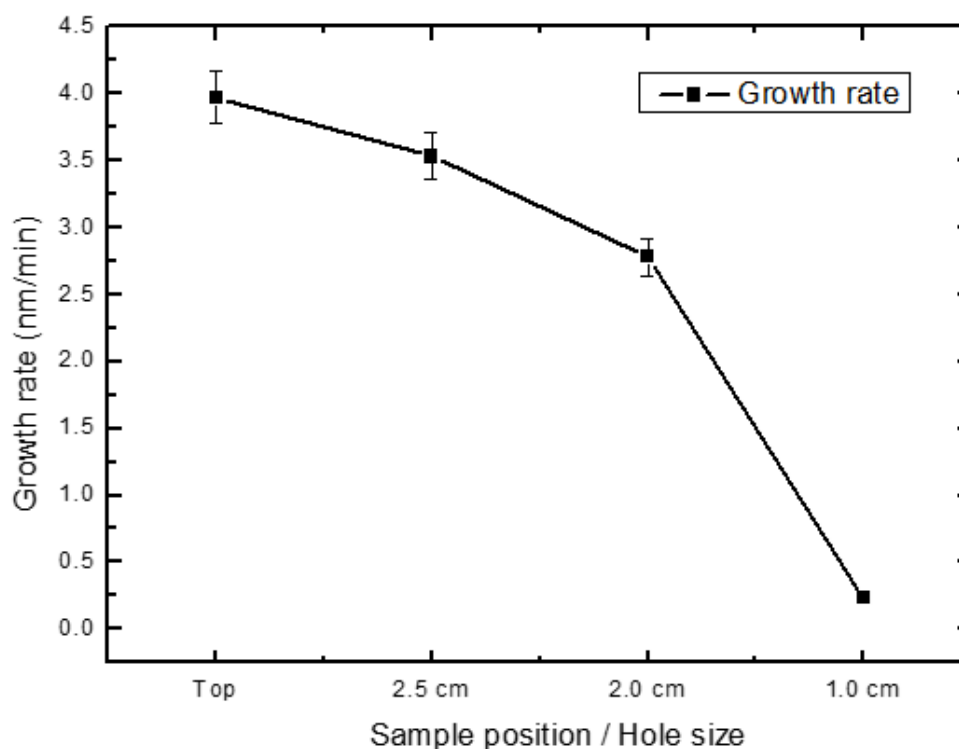


Figure 3.19 Growth rate for samples placed at different positions (on top of the electrode and under holes with different diameters). The thickness was determined by ex-situ ellipsometry (Horiba UVisel 1).

Besides the overall decrease of the absorbance, the relative intensities of the individual bands with respect to each other are also changing. The peaks referred to benzenoid (1496 cm^{-1}), quinoid (1600 cm^{-1}), $\text{C}\equiv\text{N}$ (2217 cm^{-1}), and C-H (2930 cm^{-1}) show a rather similar relative decrease – when going from the top to the bottom in figure 3.18. In comparison, the decrease in absorbance at 2930 cm^{-1} (C-H stretching) is much less pronounced (figure 3.20). These results show that, besides the growth rate, also the chemical structure of the thin films is altered depending on the size of the hole.

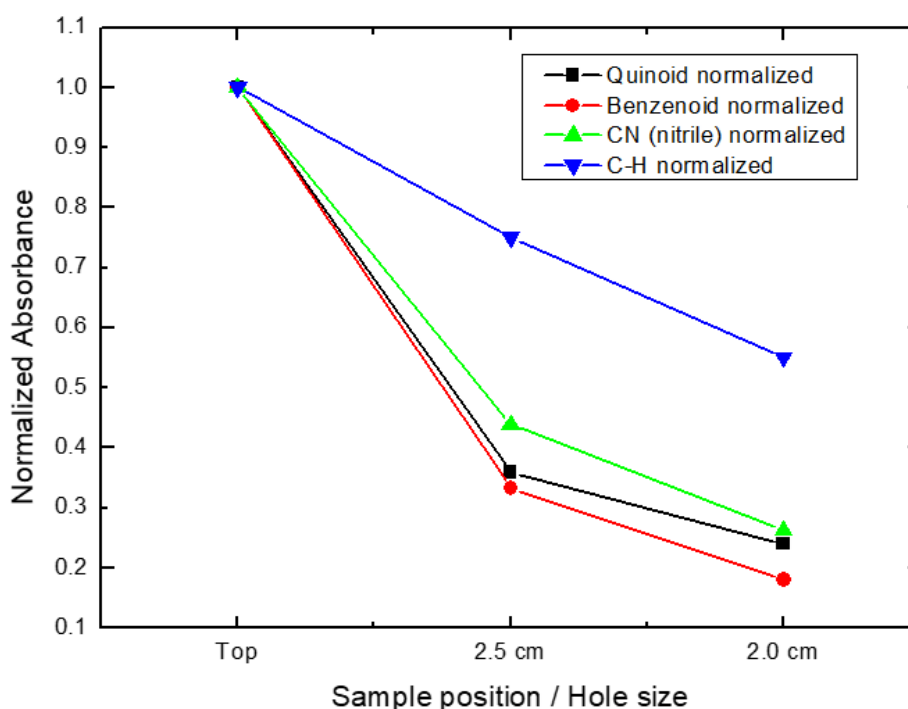


Figure 3.20 Normalized absorbance of the quinoid (black line), benzenoid (red line), $C\equiv N$ (green line), and C-H (blue) bands for different sample positions. All bands have been normalized to the intensity of the sample placed on top of the electrode.

This is confirmed by the NEXAFS spectra of the C K-edge and N K-edge shown in Figures 3.21 a) and b). The spectra are acquired in total electron yield (TEY) mode. After the acquisition, the spectra are normalized to the photon flux by division through the transmission spectrum obtained on a freshly sputtered Au sample. NEXAFS is particularly suitable to study systems with conjugated π -electron systems. In NEXAFS, changes in unsaturation are directly reflected in changes in intensities of the respective π^* -resonances observed at the K-edge for each element.

The C K-edge spectrum of the sample placed on the top (black) shows a sharp resonant feature at 285 eV (A) which is attributed to the $C\ 1s \rightarrow \pi^*$ resonance of $C=C$ bonds in aromatic systems [22], [35]–[39]. This resonance is typical for sp^2 hybridized carbon atoms in e.g. aromatic compounds and allows to assess the degree of unsaturation in carbonaceous compounds. The second resonance peak localized at around 286.8 eV (B) can be attributed to the $C\ 1s \rightarrow \pi^*$ transition of carbon atoms bound to nitrogen [22], [35]–[39]. Around 287.7 eV (C) is a small resonance indicating the presence of Rydberg states of C-H. The fourth resonance around 288.5 eV (D) can be related to the $C\ 1s \rightarrow \pi^*$ resonance transition of $C=O$ [40], [41]. The broad bands above 290 eV are due to the $C\ 1s \rightarrow \sigma^*$ transitions of different bonding environments (C-C, C-

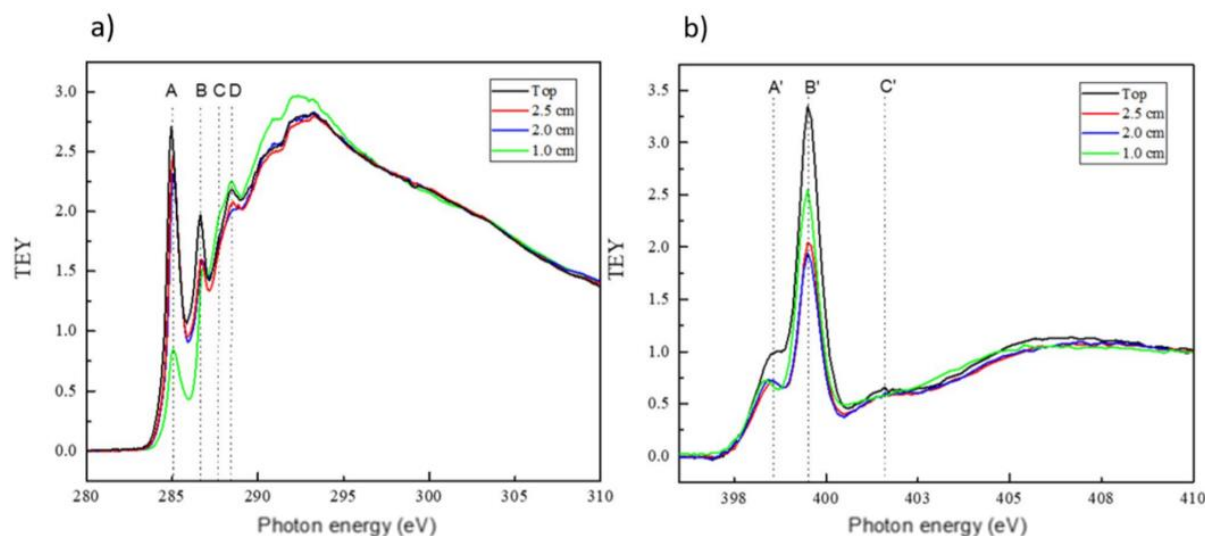


Figure 3.21 a) NEXAFS C K-edge and b) N K-edge spectra of thin films deposited on silicon samples placed in different positions : the black line shows the spectrum of the sample placed on top of the electrode, the red, blue, and green lines show the spectra of the samples placed below the holes with diameters of 2.5 cm, 2.0 cm, and 1.0 cm, respectively.

Figure 3.21 shows that a reduction of the hole size leads to a strong decrease of the resonance peak at 285 eV. This indicates a loss of the aromatic character and is in agreement with the FTIR spectra in figure 3.18. The by far lowest intensity of this resonance appears for the sample placed under the 1 cm hole, where also the FTIR spectrum shows the almost complete disappearance of the aromatic structure. Correspondingly, the σ^* resonances around 294 eV display the highest intensity for the sample placed under the smallest hole. As expected, for these resonances the intensity is increasing with decreasing hole size. The Rydberg states, localized around 287.7 eV and indicating the contribution of C-H in the material, can be related to the FTIR peak around 2930 cm^{-1} corresponding to aliphatic C-H. In agreement with the FTIR results the resonance peak at 287.7 eV is the strongest for the sample placed below the 1 cm hole.

No clear trend can be stated on the other hand for the resonance around 286.8 eV due to multiple contributions of many carbon-nitrogen species in the material, e.g. imine, nitrile, and amine which have to be further analyzed in the N K-edge. Here, figure 3.21 b), the resonance near 398.6 eV (A') corresponds most likely to the $\text{N } 1s \rightarrow \pi^*$ resonance of imine-like N-species [35], [42], [43] while the intense resonant feature around 399.6 eV (B') can be attributed to the N

$1s \rightarrow \pi^*$ transition of nitrile groups ($-C \equiv N$). The less intense peak around 401.8 eV (C') is due to the N $1s \rightarrow \pi^*$ transition of amine. While the small amine resonance peak at 401.8 eV is observed for the samples placed on top and in the 2.5 and 2.0 cm holes, the sample placed in the smallest hole of 1 cm does not show any significant presence of this feature. However, the identification of the peaks is non-trivial due to several possible resonances originating from nitrile groups [43].

3.6.2 Control of ion components

In principle, the filtering effects of the holes concern both, neutral radicals and ions. To study the contributions of ions to the deposition process, a stainless-steel grid with a transparency of 47% is placed on top of the grounded structured electrode. This grid acts as an electrode restricting the plasma to regions above the hole while allowing the flux of radicals to reach the substrate [44]: i.e., the grid preferentially blocks the contribution of the ions while it allows about 50% (equal to the transparency of the grid) of the radicals to pass it. (In the following experiment, the effect of the grid is only investigated for the hole with the largest diameter, 2.5 cm).

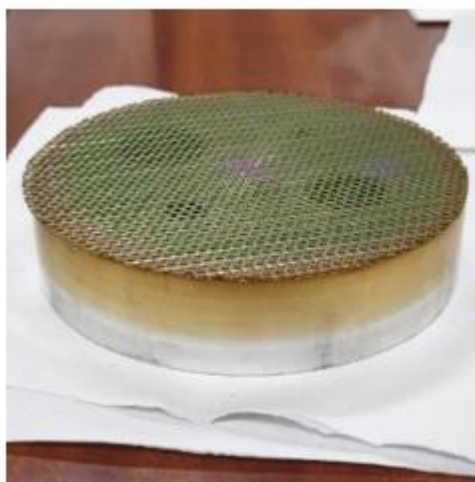


Figure 3.22 Picture of the electrode with stainless steel mesh on top of it.

The most obvious effect of the grid concerns the growth rate of the deposited films. The value of the growth rate exhibits a reduction by a factor higher than 10 when a grid is placed on the top of the electrode. The thickness measured goes from 210 nm to around 18 nm for the sample placed in the hole of 2.5 cm diameter before and after placing the grid on top of the electrode.

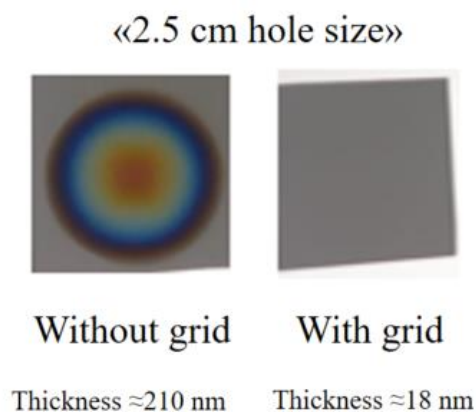


Figure 3.23 Photos of samples placed in the same hole (2.5 cm diameter) before and after placing the grid to filter the ion component.

NEXAFS C K-edge and N K-edge spectra in figure 3.25 a) and b) show that also the film composition is affected by the presence of the grid.

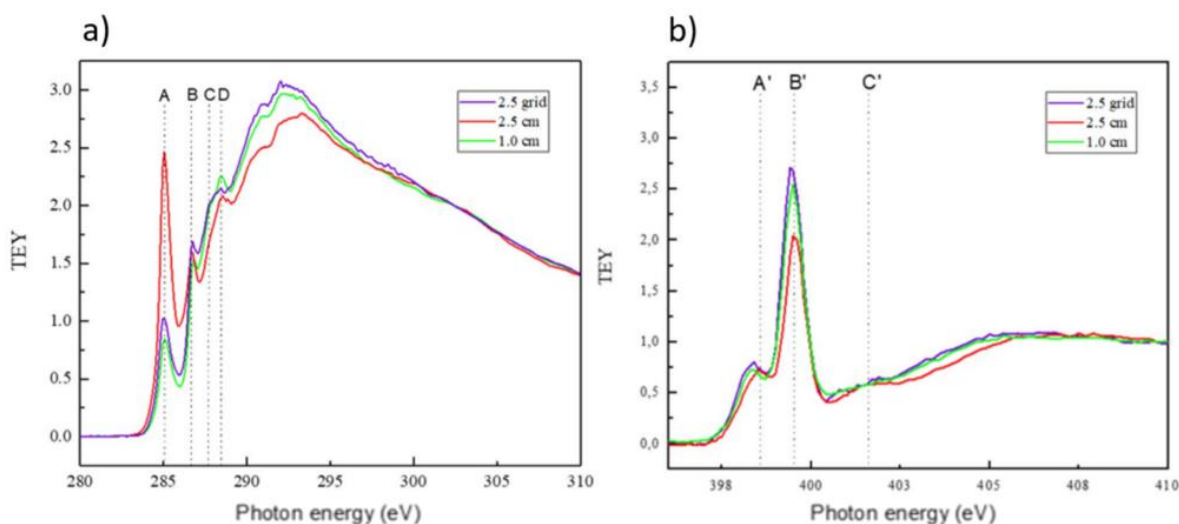


Figure 3.24 In a) NEXAFS C K-edge and in b) N K-edge spectra of samples placed under the 2.5 cm hole which is either covered with a grid (purple) or uncovered (red). The green line shows the spectrum of the sample placed under the hole of 1.0 cm diameter for comparison.

In figure 3.24 a) the sample placed under the 2.5 cm hole with grid (purple line) shows a much smaller resonance intensity at 285 eV than the sample under the same 2.5 cm hole without grid (red line). This indicates a notable decrease in the aromatic character of the film which comes along with an increase of the intensity of the σ^* resonances around 294 eV underlining the stronger aliphatic feature of the film. It is worth mentioning that the sample placed under the 2.5 cm hole with grid shows a similar behavior as the sample placed under the 1 cm hole without

grid (green line in figure 3.24).

A similar trend can be observed for the N K-edge in figure 3.24 b). The spectra of the sample placed under the 1 cm hole and the sample placed under the grid exhibit again a quite comparable behavior.

The results presented in figure 3.24 and the fact that the growth rate is substantially reduced due to the presence of the grid suggest that the ionic component plays an important role in the deposition process. Two possible mechanisms could explain the experimental findings: either the ions directly contribute to the growth of the film and are responsible for most of the film growth (figure 3.25 a) (see e.g. the discussion in [4], [19], [45], [46]) or they activate the surface by creating dangling bonds which can then act as reaction sites either for the aniline molecule itself or for radicals created in the plasma (figure 3.25 b). The latter, better known from plasma etching, is referred to as an ion-neutral synergistic effect [47].

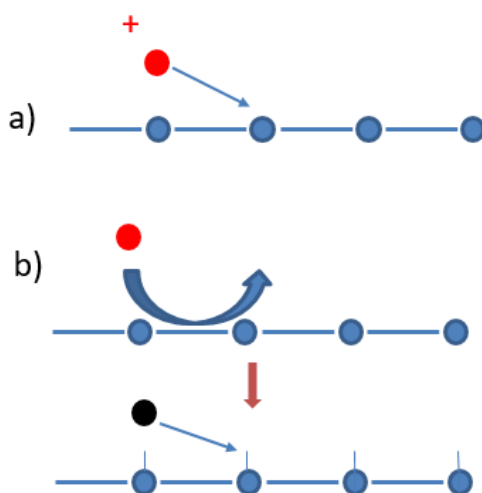


Figure 3.25 Sketch of a possible explanation of the two mechanisms of action of ion during plasma deposition. In a) ion supported growth while in b) ion-assisted deposition.

Mass spectroscopy has been performed to measure the aniline mass spectrum during the experiment. In figure 3.26, we observe the positive ion mass spectrum measured in Ar/aniline mixture. The highest signal measured is for the aniline ion with mass 93 amu.

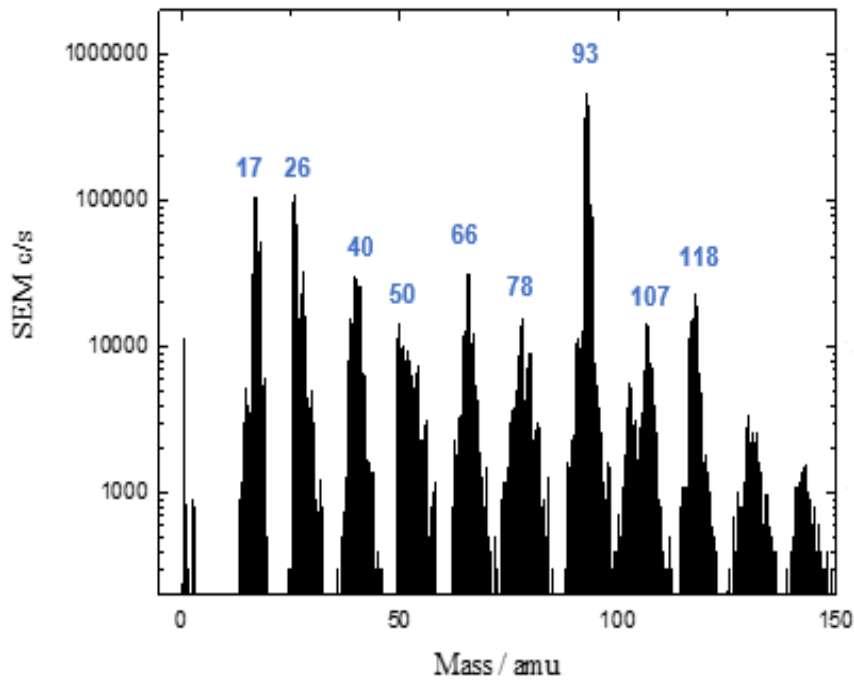


Figure 3.26 Positive Ion mass spectrum measure in Ar/aniline mixture (20:1 sccm).

In principle, the ion flux to the substrate -which consists mainly of positive aniline ions with a mass of 93 amu could be sufficiently high in our discharge to support the first mechanism. (Although the argon concentration is much larger than the aniline concentration in our experiment mass spectrometer measurements of positive ions [1] show that the most abundant positive ion in our case is the aniline ion with a mass of 93 amu. (This can be explained by the fact that aniline has a much smaller ionization potential (7.7 eV) than argon (15.7 eV)). Measurements performed by means of microwave interferometry give a value of $5 \times 10^{15} \text{ m}^{-3}$ for the electron density. Taking this value, assuming an electron temperature even as low as 1 eV and applying the rather simple Bohm formula [19]:

$$\Gamma_i = 0.61 \cdot n_i \sqrt{\frac{kT_e}{M_i}} \text{ (equation 3.16)}$$

gives a time-averaged ion flux of about $\Gamma_i = 1.5 \times 10^{18} \text{ ions / (m}^2\text{s)}$. Assuming a mass density even as large as 2 g/cm^3 for the deposited thin films and a sticking coefficient of 1 results in a -purely ion supported-growth rate of about 8 nm/min which is about 2 times higher than the measured growth rate. (A discussion about the sticking coefficient of positive ions can be found e.g. in [19], [20]). Even as this is twice the value of the observed growth rate it is important to stress, that this simple estimation does not rule out, that the ion-induced surface activation (the second mechanism discussed above) does not play a role in the growth of our films.

Summary

This experimental chapter aimed to control the flux of different species towards the surface and contribute there to the properties of plasma deposited thin films. This is achieved by using a particular “channel electrode” design that is easy to implement in any given reactor for either scientific or industrial purposes. As a case study, the deposition from an aniline/argon plasma was investigated.

The material characterization by means of FTIR and NEXAFS spectra shows that this electrode design effectively allows tuning the chemistry of the deposited material from highly aromatic to the aliphatic character. A similar result is observed by covering the electrode with a stainless-steel grid, which is used to reduce preferentially the positive ion flux arriving on the substrate. This demonstrates the important role of positive ions in the deposition process in our particular setup and chemistry, affecting not only the deposition rate but also the composition of the deposited films.

It has to be mentioned, however, that the composition and magnitude of the neutral and ion fluxes for given chemistry strongly depend on the discharge parameters. In particular, neutral radicals with a smaller sticking coefficient might be prone to losses due to pumping (a loss channel that depends on the pumping speed and the actual volume of the process chamber and the plasma) and to losses due to electron impact fragmentation (a loss channel depending on electron temperature, electron density and residence time). Consequently, the role of neutral radicals and vice versa the role of the positive ions in the deposition process may strongly depend on the parameters and may therefore vary in different experiments.

3.7 Improved control on deposition processes

3.7.1 Introduction

In the introduction of chapter 3, it has been stated that there are two ways to tune the properties and the composition of films deposited through PECVD. From the previous experiments, we have concluded that the filtering system (the channeled electrode) -independently from the mechanism involved in the process- works and allows to tune the properties of the deposited films by acting directly on the reactive species which travel towards the substrate. Moreover, the system can be applied to any type of chemistry and the experimental condition play a crucial role.

The next step is a mixed approach that concerns both, the control of the formation of reactive species formed inside the plasma by acting on the experimental parameters (power, pressure, gas mixture, and pulsing) and also the control of the species flux arriving at the substrate by employing different electrode systems designed by our research group.

The change in the experimental parameters is summarized in the following table 2:

Experiment protocol	Gas mixture	Power	Duty Cycle	Pressure	Pumping system
Old	Ar 20 sccm/ Aniline 1 sccm	10W	0.5 (20 ms/40 ms)	0.18 mbar	On
New	Aniline 1 sccm	4W	0.25 (10 ms/40 ms)	0.18 mbar	Off

The main changes in the experimental conditions are the working mixture, which passes from an Ar/aniline mixture to pure aniline, and the choice to work without a pumping system during the deposition i.e. the pumping speed was zero resulting in a pressure that is increasing during the experiment.

The main reason behind the choice to work in pure aniline is based on previous studies which proved that a higher aniline concentration leads to a higher retention of the monomer original structure. The reason for this is the electron temperature in pure aniline is smaller than in argon/aniline mixture thus resulting in a milder plasma. The main visible difference between argon/aniline plasmas pure aniline plasmas concerns their color and their brightness (see figure 3.27).

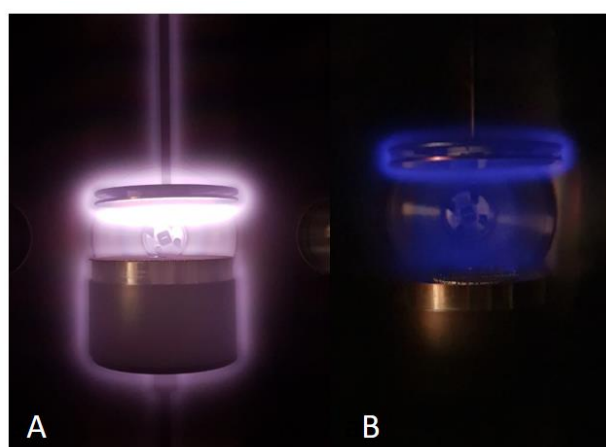


Figure 3.27 Photos of plasma in different mixtures at pressure 0.18 mbar with a power of 5W. In A plasma is running in Ar/aniline (20:1 sccm) while in B plasma is running in pure aniline

(1 sccm).

In particular, the plasma in figure 3.27 b is barely visible with naked eyes (visible only with a camera) because the plasma emits mainly in the UV range.

3.7.2 Effects of new deposition protocol

By employing the new deposition protocol, the results obtained from the deposition processes were completely different compared to the ones obtained previously. The deposition time process is set arbitrarily to 40 minutes during the first experiments. The films obtained through plasma polymerization were analyzed again by means of ex-situ FTIR and NEXAFS.

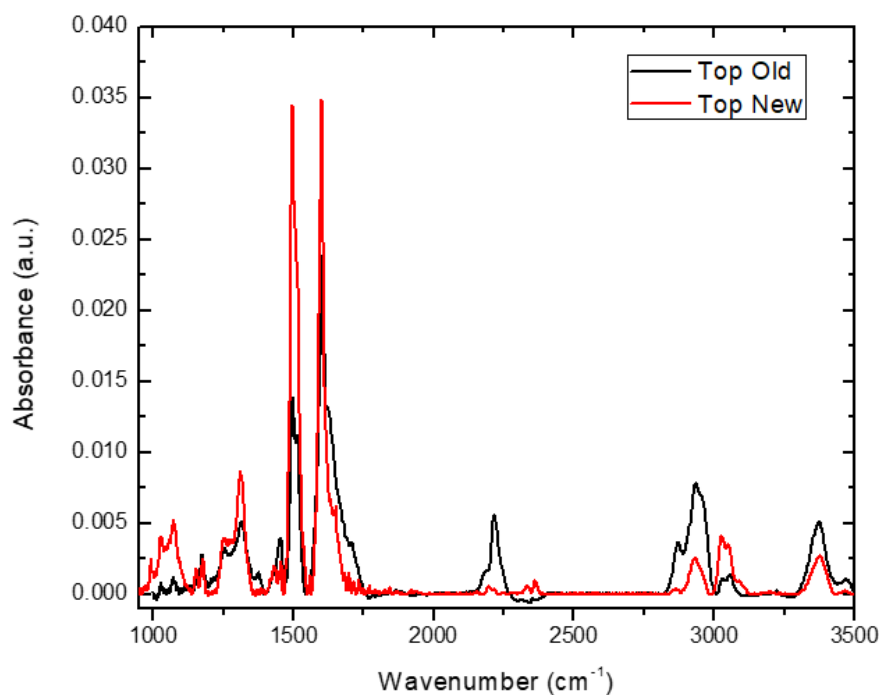


Figure 3.28 Ex-situ FTIR spectra comparison of polyaniline deposited on top of the electrode with old and new deposition protocol.

Figure 3.28 shows the comparison of ex-situ FTIR spectra of samples placed on top of the electrodes for the old and the new deposition protocol. The difference in the peak ratios indicates that the composition of the film is changed. In particular, the change in the ratio between benzenoid (1496 cm^{-1}) and quinoid (1600 cm^{-1}) peaks could indicate the production of polyaniline more emeraldine-like (half oxidized form). Moreover, one can observe a change in the ratio of the peak at 2930 cm^{-1} and 3050 cm^{-1} referring to aliphatic and aromatic C-H

respectively. The new film shows a higher aromatic character compared to the sample produced in an argon/aniline mixture. The ratio of aliphatic C-H to aromatic C-H changes from a value of 4:1 for the case of the old procedure to a value of 1:2 for the new one. It has to be highlighted also that the intensity of the peak at 2220 cm^{-1} referring to nitriles groups ($\text{C}\equiv\text{N}$) (considered as a mere by-product of the plasma polymerization process) is greatly reduced.

The second effect of the new deposition concerns the morphology/surface structure of the films deposited in the holes of the structured electrodes (see figure 3.29).

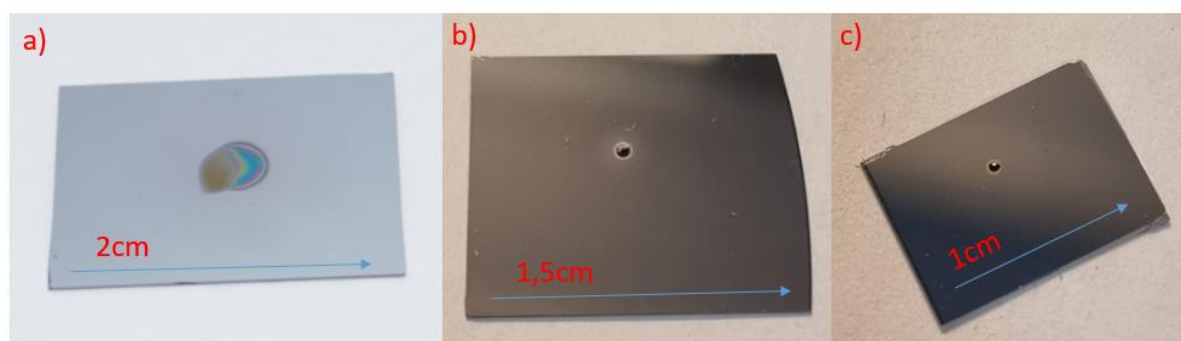


Figure 3.29 Pictures of samples deposited in the different holes: a) in the 2 cm, b) in the 1 cm, and c) in the 0.5 cm hole sizes.

Before discussing this morphology in more details, it has to be stressed that these “structures” emerge only with the new deposition procedure which involves the use of pure aniline and the absence of a pump output flow. Moreover, these structures are present only when the deposition time is larger than 40 minutes. For deposition times smaller than 40 minutes all samples besides the one on top appeared to be blank. It was also essential that the plasma is continuously on. This was shown in the following three experiments. In the first experiment, the plasma was operated for 10 minutes. Then the plasma was switched off and the chamber was evacuated to a pressure of 10^{-6} mbar. After that, the chamber was refilled again with aniline and the plasma was switched on. This procedure was repeated 4 times resulting in a total deposition time of 40 minutes. Two other experiments were performed according to a similar procedure:

- 2x20 min with an evacuation of the chamber and a subsequent refill with aniline after each step (total deposition time $t=40$ min)
- 4x10 min with an evacuation of the chamber and a subsequent refill to a pressure it was supposed to be in the 1x40 min experiment (to analyze if the deposition was an effect of the pressure increase).

None of these experiments gave similar results to the 1x40 min experiment, all samples besides

the one on top appeared to be blank.

These experiments show that a certain amount of time (>30 min) is necessary to build up and accumulate reactive species in the volume between the two electrodes. In order to verify the effect of the pumping on the deposition pattern a similar experiment with the same experimental condition has been performed but this time with the pumping system on (resulting in a stable pressure of 0.18 mbar). The resulting samples (in the holes) did not present any sign of the new structures meaning that the absence of the pumping system is crucial.

The films deposited in the 2 cm, 1 cm, and 0.5 cm holes have been analyzed through SEM and optical microscope imaging.

For the sample of 2 cm (figure 3.30) the diameter of the film is approximately 0.5 cm with an average thickness measured of $\approx 1.7 \mu\text{m}$ for 40 min of deposition.

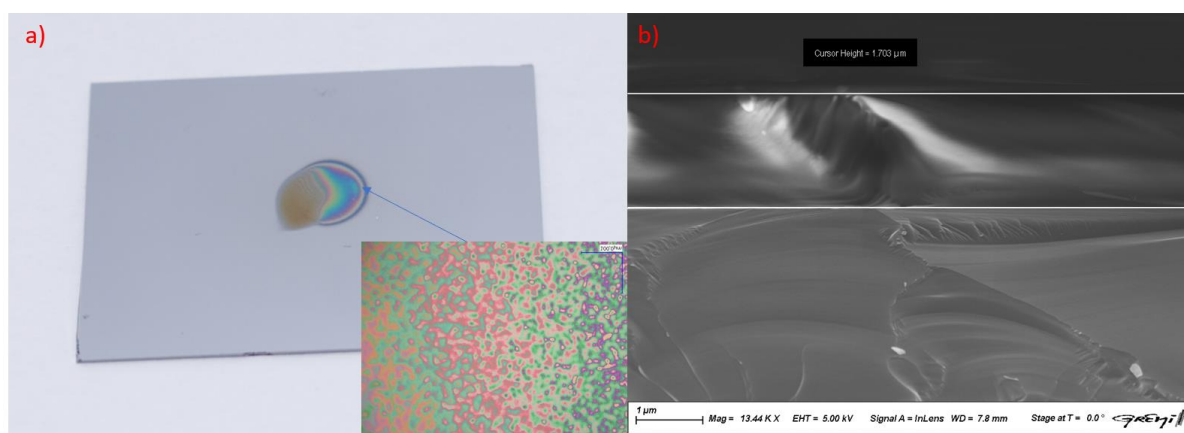


Figure 3.30 Photo, optical microscope a), and SEM picture b) of the sample deposited in 2 cm hole size.

This sample appears macroscopically inhomogeneous, the circular pattern can be divided into two halves in which the deposition is different, on the first half (golden left part in the picture) the deposition is quite uniform while on the second half (rainbow right part in the picture) the deposition is inhomogeneous and consists of several layers with different thicknesses, as shown in the optical microscope picture in the top right corner.

Regarding the sample deposited in the 1 cm hole, the deposition pattern is completely different: it mainly consists of a circular “blob” with a diameter of $\approx 800 \mu\text{m}$ (figure 3.31).

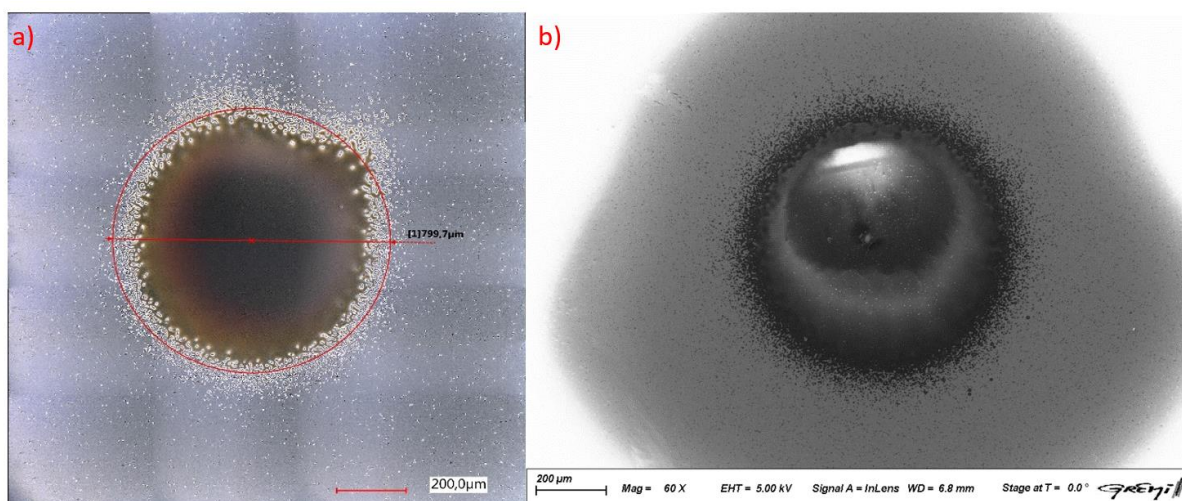


Figure 3.31 Optical microscope a), and SEM picture b) of the sample deposited in 1 cm hole size.

For the same deposition time (40 min) the average (maximal) thickness of this *blob* is around $\approx 5 \mu\text{m}$. The thickness decreases when moving from the center outwards.

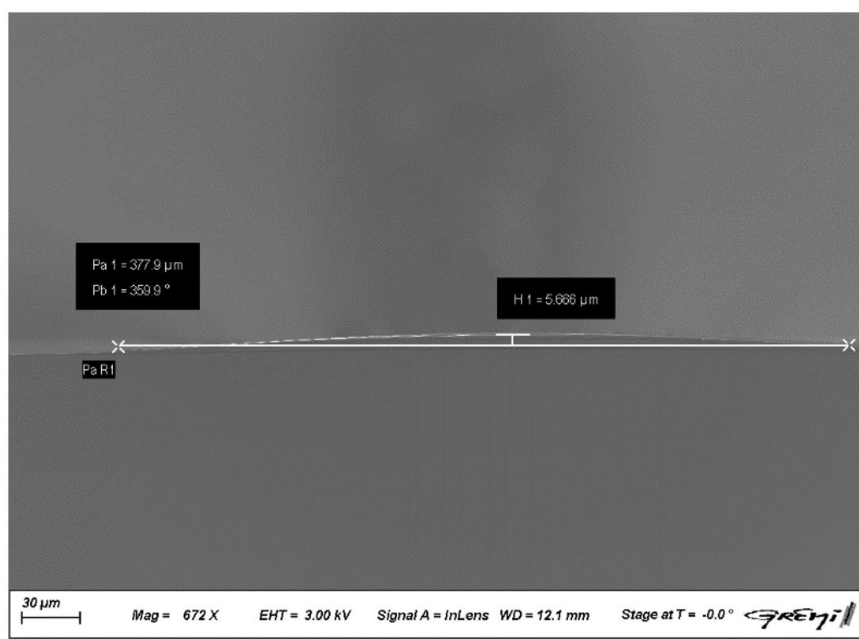


Figure 3.32 SEM image of the sample deposited in the 1 cm hole. The deposition thickness is not homogeneous and at the center, it measures a thickness of $5.6 \mu\text{m}$.

The sample deposited in the 0.5 cm hole shown in figure 3.33, has a structure quite similar to the sample in the 1 cm hole size. The differences concern the dimension and the thickness of the main blob which has here a lateral dimension of $\approx 400 \mu\text{m}$ and (maximal) thickness of around

$\approx 9 \mu\text{m}$.

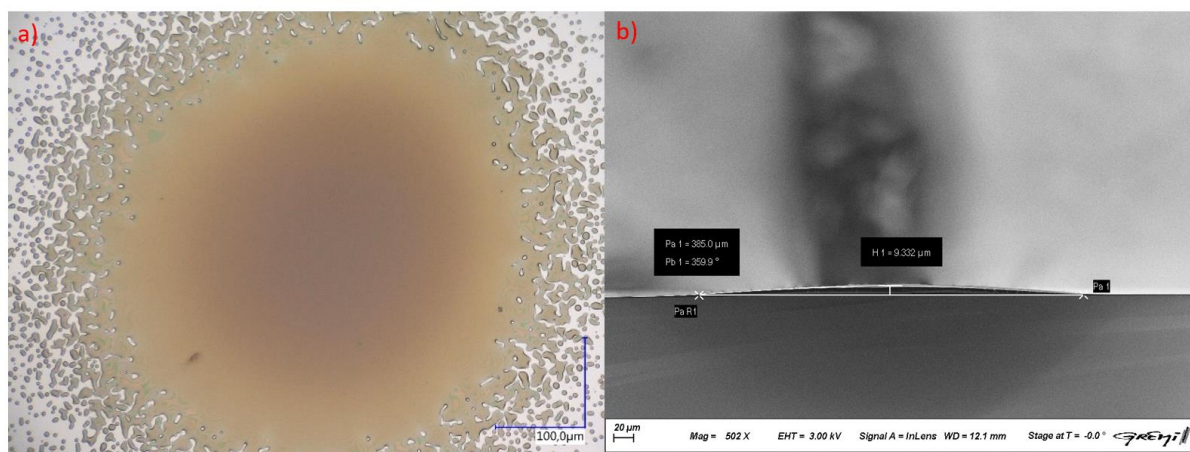


Figure 3.33 Optical microscope a), and SEM picture b) of the sample deposited in 0.5 cm hole size.

Both samples (deposited in the 1 cm and the 0.5 cm hole) show a circular area, a “corona” that surrounds the main deposition structure (the blob). This region is mostly made by the same units that form the “blob” at the center but with a reduced surface density.

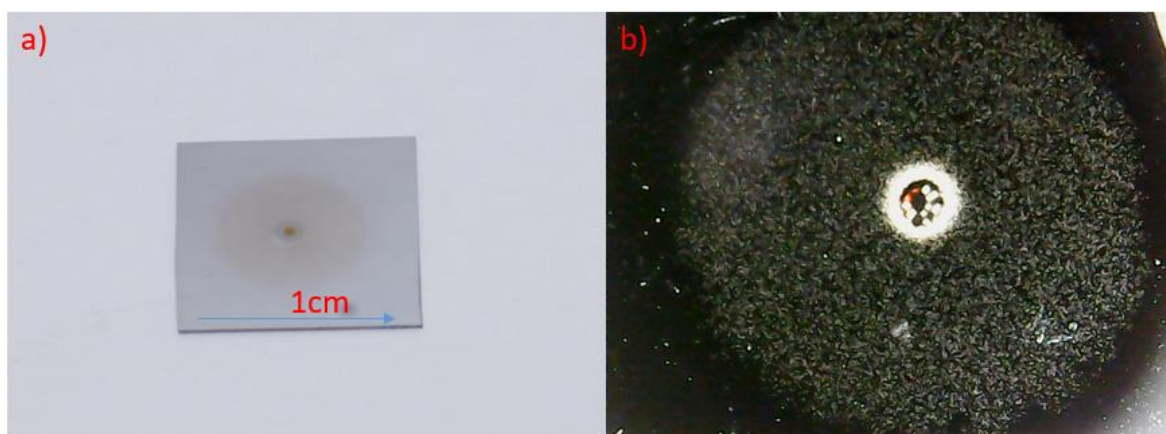


Figure 3.34 In a) photo of the sample with the visible corona around the centered blob and b) image of the corona region taken with a microscopic camera.

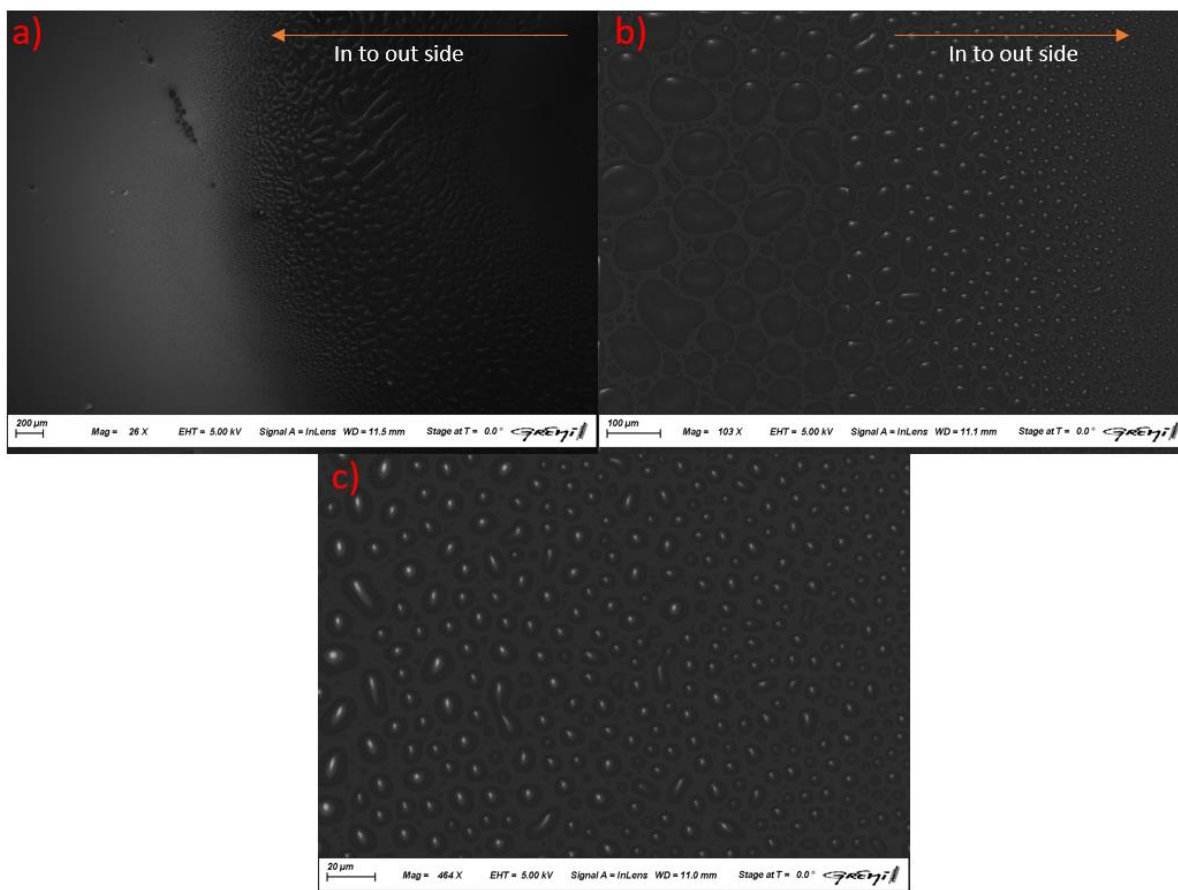


Figure 3.35 SEM images of the blob structure in the 1 cm sample. Moving from the inner side to the outer side (a and b) the unit structures (that resembles “droplets”) decrease in dimension and in density. In c) are shown the units far from the center region (blob) where they form a lower density deposition region around the central structure, named “corona region”.

3.7.3 Material characterization of produced films

The spectrum of the film on top has been compared with the sample in the holes to investigate if the change in the morphology corresponds to a change in the composition.

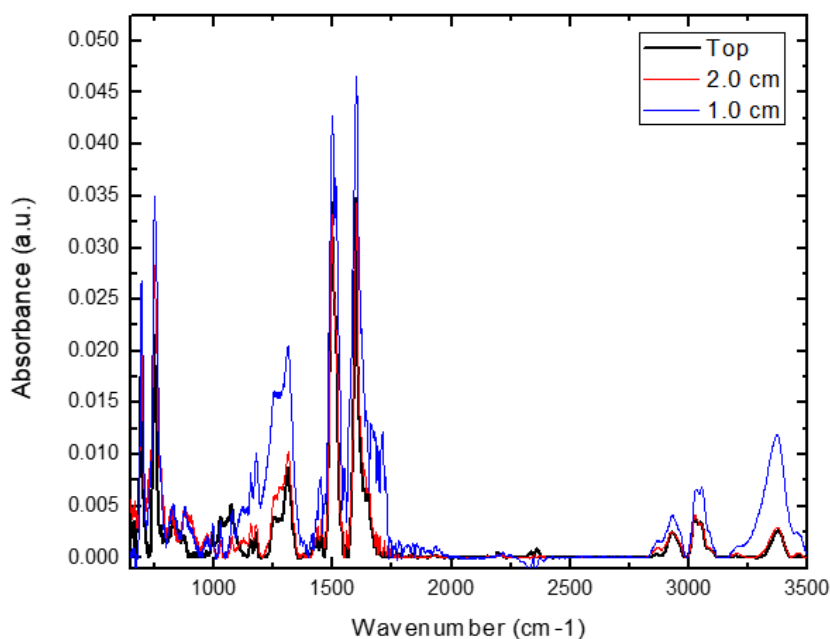


Figure 3.36 *Ex-situ FTIR spectra of samples placed in different positions during the growth process. The black line shows the spectrum of the sample placed on top of the electrode. The red and blue lines show spectra of samples placed under the holes with 2 cm, and 1 cm diameter, respectively.*

The sample deposited in the hole of 1 cm (blue line) shows broader peaks compared to the “2 cm” sample and the “top sample”. Moreover, the ratio of the peaks indicates a change in the film composition: the “1 cm sample” shows a higher content of unsaturated carbon as can be seen from the high intense peak at 1310 cm^{-1} but a lower amount of aromatic compounds (lower ratio benzenoid to quinoid). Important is also the higher amount of N-H as can be seen from the major increase of the N-H stretching at 3370 cm^{-1} .

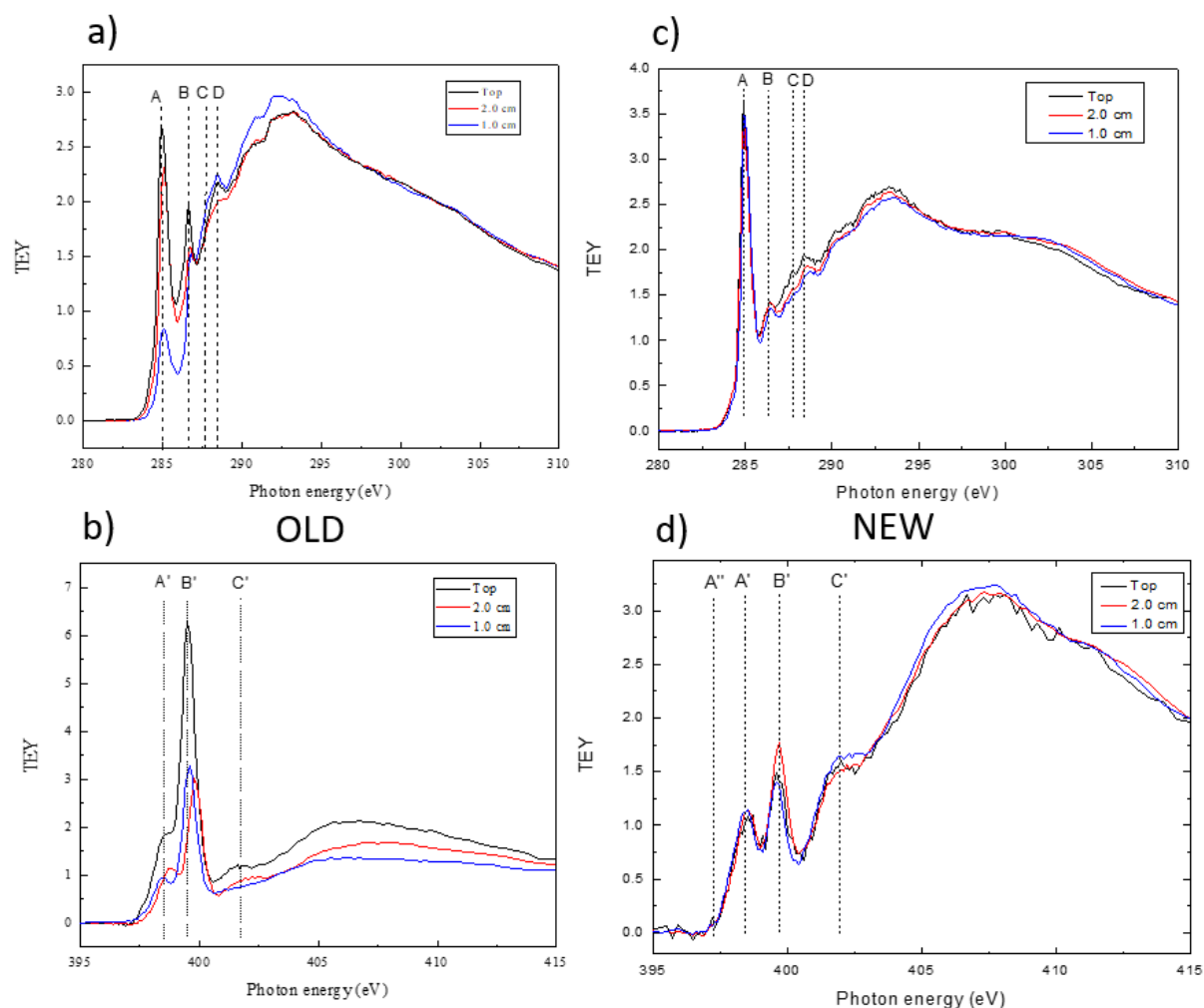


Figure 3.37 NEXAFS C K edge and N K edge comparison of samples deposited through the structured electrode with the old (a and b) and the new deposition protocol (c and d).

Figure 3.37 shows a comparison of the NEXAFS C K edge and the N K edge spectra between the old and new deposition experiments (for the samples deposited in holes with different sizes). Firstly, by comparing the two C K edge spectra (old and new) one can observe an increase of the peak A located at 285 eV meaning that the aromatic character of the material is notably increased while the other peaks related to carbon bonded to nitrogen (B) at 286.6 eV, Rydberg (C) at 287.7 eV and carbon bonded to oxygen (D) at 288.5 eV are reduced. The reduction of the Rydberg peak C is related to the reduced presence of defects in the material. Concerning the N K edge, the new samples exhibit a remarkable reduction of the peak B' at 399.6 eV, (associated to nitrile groups and thus to unwanted by- products of the plasma polymerization process), compared to the peaks A' at 398.6 eV and C' at 401.8 eV which are related to imine and amino nitrogen groups in the polyaniline structure. For the first time, it was observed also the presence of a new peak A'' at 397.4 eV associated in the literature with a splitting of the π^*

resonance of imine nitrogen due to a mesomeric conjugation effect.[35], [38]. This peak is generally observed in the emeraldine form of polyaniline. Regarding the filtering effect exerted by the holes of the structured electrode, minimal differences in both the C K edge and the N K edge have been observed - comparing the spectrum of the sample on top and the ones in the holes. The main effect is a small reduction of the σ^* system intensity by reducing the hole size.

3.7.4 Negative and positive ions mass spectra

Figure 3.38 b) shows a mass spectrum of positive ions measured about 15 minutes after the plasma was switched on. The dominant peak is again the peak at mass 93. The dominant peak in the mass spectrum of negative ions (figure 3.38 a)) is at mass 90. The situation is thus similar to the one that was discussed in more detail in [22]. What is more interesting in this context, however, is the temporal evolution of the mass spectra and the information contained in this temporal evolution.

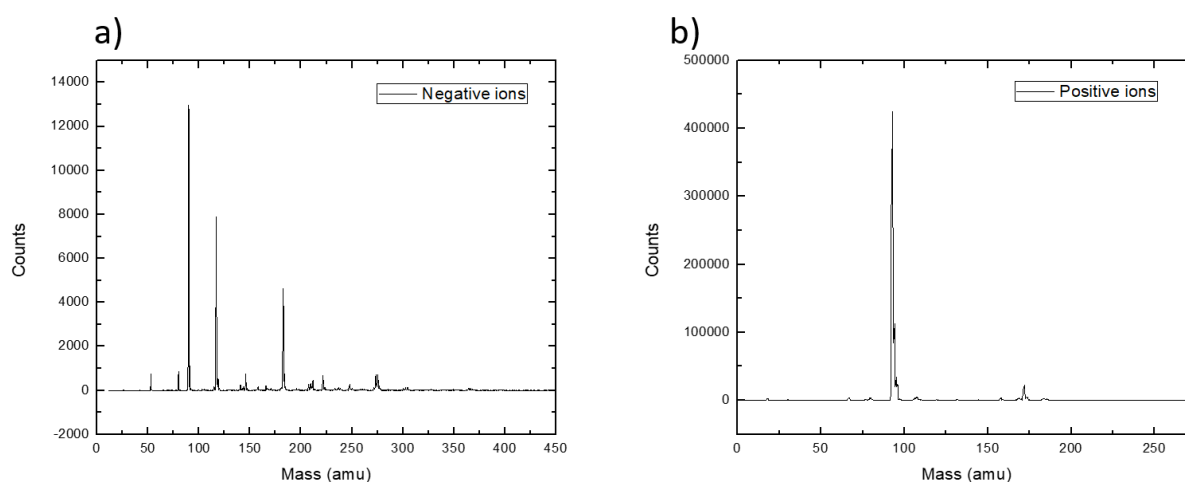


Figure 3.38 Negative (a) and positive (b) ion mass spectra of pure aniline plasma (1 sccm).

To study this in more detail a mass spectrum was recorded every 8 minutes over a period of about 45 minutes. Instead of showing each of these spectra individually, Figure 3.39 shows count rates summed over different mass ranges as a function of time. In the first curve (white dots), in each spectrum (measured every 8 minutes), the counts were summed up over all masses (from $m = 1$ amu to $m = 475$), in the second curve (blue dots) all masses with $m > 93$ amu were summed up and in the third curve (red triangles) all masses in the range $89 \text{ amu} < m < 93 \text{ amu}$. The figure clearly shows:

(i) Masses greater than the mass of the monomer contribute significantly to the total negative ion flux. This is especially true when considering the mass flux (e.g., the number of carbon

atoms) and also considering that the mass spectrometer is less sensitive to higher masses.

(ii) the integrated signals, especially those for higher masses, increase throughout the whole measurement. This shows that it indeed takes a long time for some species to form, which could explain the rather long timescales of the experiment (40 minutes).

Figure 3.38.2 b) shows the equivalent of figure 3.38.2 a), for positive ions. As is the case in the previous figure, the curves increase throughout the experiment, however:

(i) the masses higher than the mass of the original monomer do not contribute as significantly to the total flux, as it is the case for the negative ions.

(ii) the increase over time is by far not as strong as it was for the negative ions.

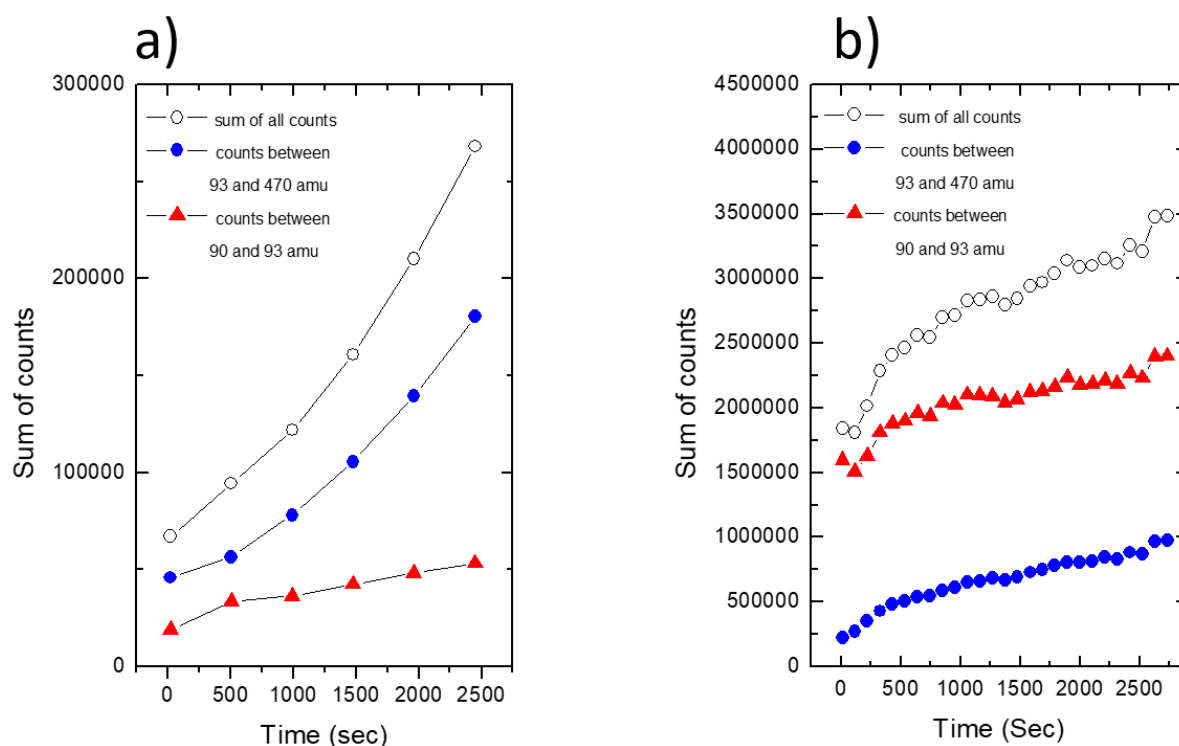


Figure 3.39 Sum of counts for masses in the negative a) and positive b) mass spectra of aniline in function of time.

3.8 Duty cycle study

All the new experiments have been performed with a reduced Duty Cycle compared to the old experiments performed in the Ar/aniline mixture. The Duty Cycle is defined as the ratio between the plasma-on time divided by the width of the period:

$$DC = \frac{T_{on}}{T_{tot}} \text{ (equation 3.17)}$$

In the case of the old deposition protocol, the Duty Cycle was set to 0.5 (20 ms on/40 ms total cycle time). In the new experiment, since the aim was the deposition of polyaniline films that could keep a structure closer to the original monomer structure and at the same time do not produce nanoparticles, a smaller Duty Cycle was chosen: - (10 ms on/40 ms tot cycle) DC 0.125
Several other duty cycles were also tested:

- (5 ms on/40 ms tot cycle) DC = 0.125

In the case of (5 ms on/40 ms tot cycle), DC = 0.125 problems were found in keeping the discharge on; moreover, after the deposition process, the samples placed in the holes (0.5, 1, and 2 cm) remained blank (after 40 minutes) without any sign of deposition on it.

- (7.5 ms on/40 ms tot cycle) DC = 0.187

In the case of (7.5 ms on/40 ms tot cycle), DC = 0.187 the samples placed in the holes were showing deposition signs but the morphology of the deposited film was not fully formed as shown in figure 3.40. The “blob” structure has a lower density and dimension compared to the one obtained with a DC of 0.25.

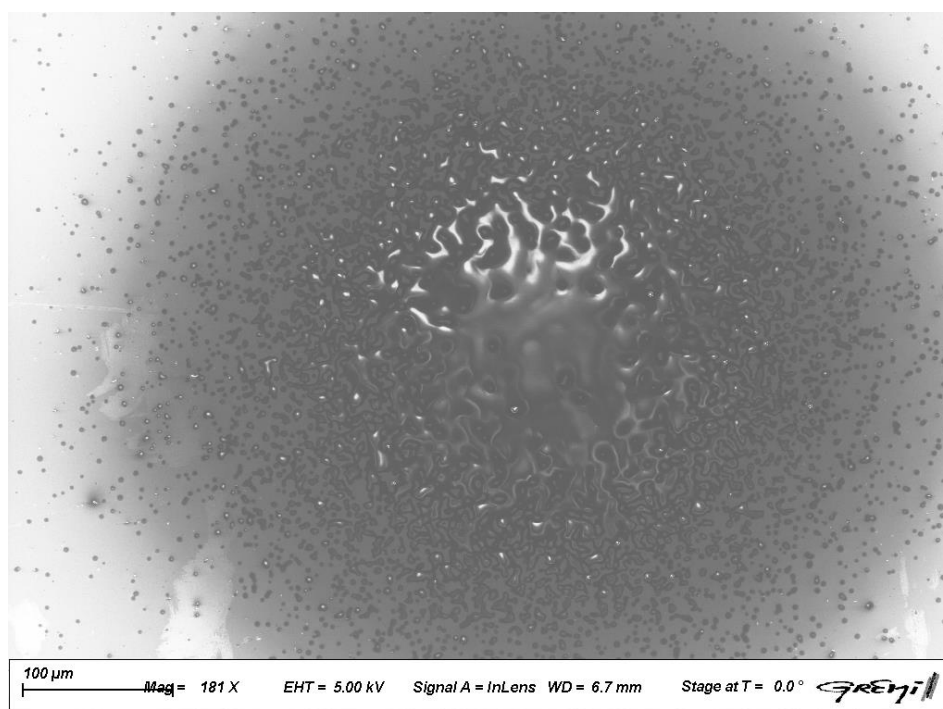


Figure 3.40 SEM picture of the bubble structure of the sample deposited in the 1 cm hole.

- (10 ms on/40 ms tot cycle) DC 0.25

Conventional results

- (15 ms on/40 ms tot cycle) DC = 0.375

For this case, the deposition was similar to the case of DC= 0.187 but the SEM picture highlighted also the presence of dust particles with a dimension of micrometer size, embedded in the polyaniline structure (figure 3.41).

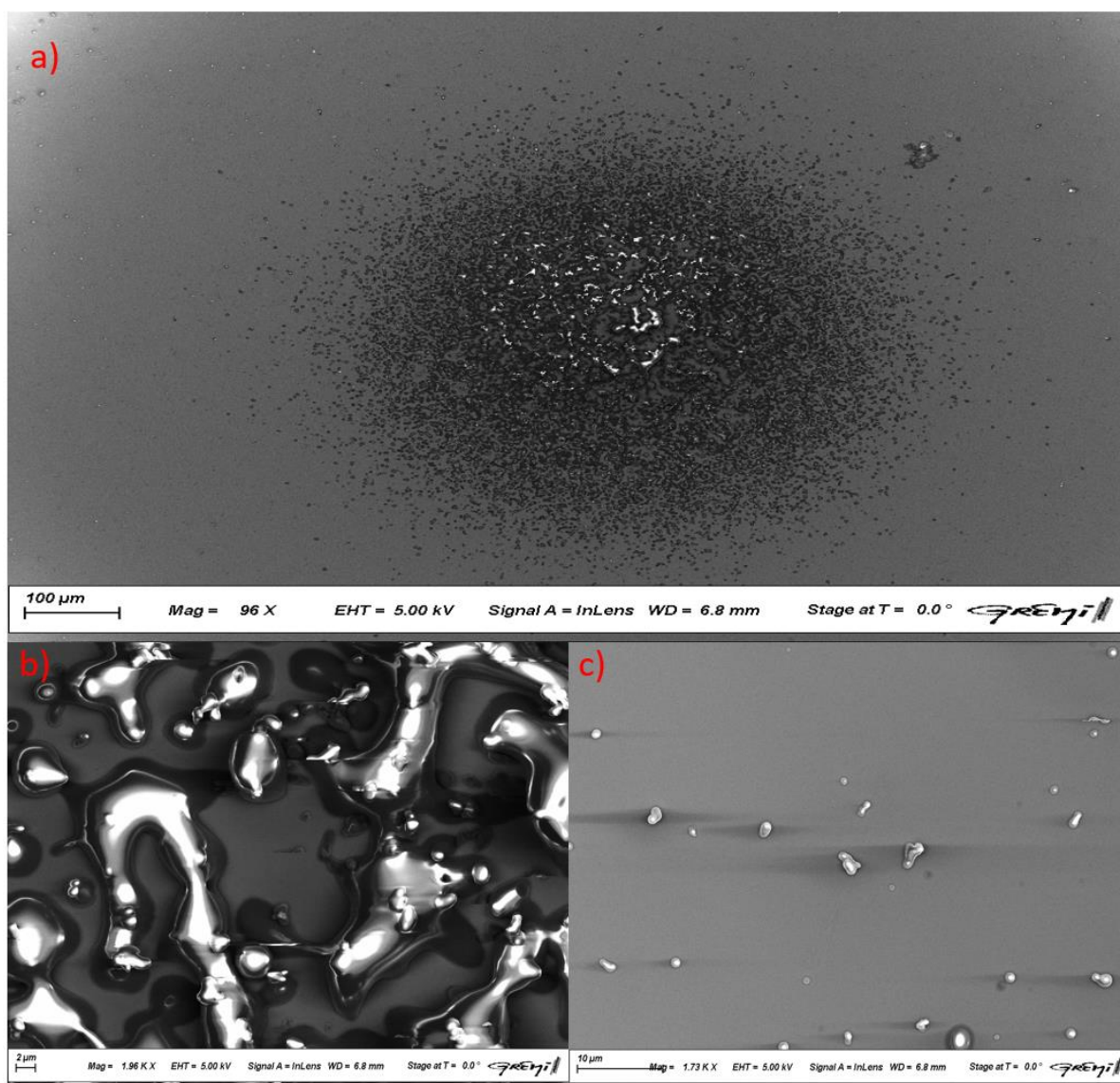


Figure 3.41 SEM picture of sample deposited in 1cm hole with DC of 0.375.

Summary

The change in the deposition protocol with the choice of the new experimental parameter (Power, Duty Cycle, pumping speed, and particular the gas mixture) led to a new kind of deposition that differs strongly from the old deposition experiments performed in Ar/aniline

plasmas with their harsher plasma conditions. According to the FTIR and NEXAFS spectra, the quality of the deposited films has been strongly improved with a great reduction of the nitrile peak at 2225 cm^{-1} . Moreover, seen from the peak ratio in the FTIR spectra, the polyaniline structure of the deposited films is much closer to the emeraldine structure while the structure of the polyaniline of the older experiments was closer to the leucoemeraldine one.

3.9 The effect of external electric fields on deposition process – the “cup” electrode

To study the effects of external electric fields on the deposition process a new electrode the “cup electrode” (figure 3.42) has been developed. The electrode resembles the channel and has a diameter of 9 cm and a height of 5 cm.

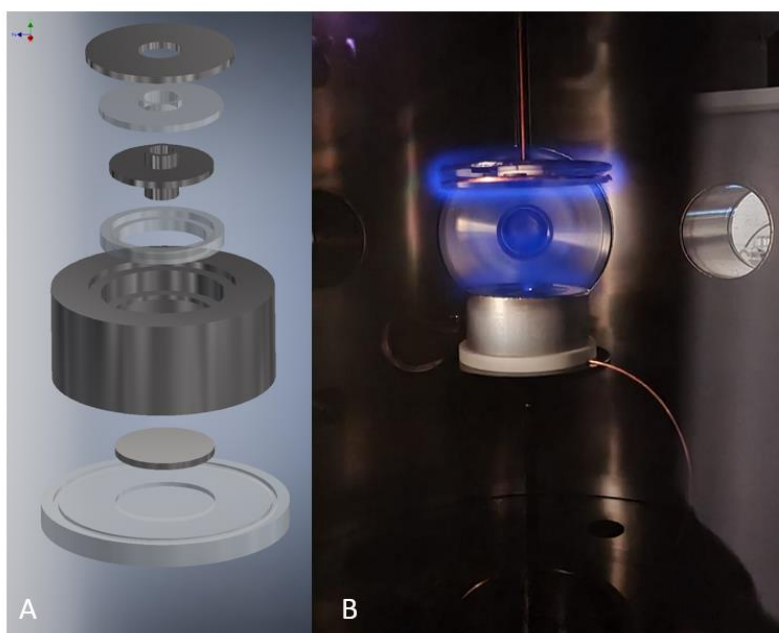


Figure 3.42 A) cup electrode design with the different parts composing it, B) cup electrode used in aniline plasma deposition.

In contrast to the channel electrode, the cup electrode consists of several parts made of stainless steel which can be replaced with a correspondent ceramic part to separate them in case the user wants to bias some parts of the electrode. This electrode was mainly designed to study the effect of charged species during the deposition and to repulse or attract them by biasing the electrode or the samples themselves.

For the current set up the electrode is placed on a ceramic plate, but is connected via a cable

with the grounded electrode on which it is placed.

On top of the electrode is a hole of 1 cm size with a channel of a length of 3 cm. The silicon sample is placed on a glass substrate above the ceramic plate and the channel part of the electrode is placed right above the sample position. In this one, we obtain a system analog to the channel structured electrode used in the previous paragraph to filter species during the deposition.

3.9.1 Deposition experiments with cross voltage applying

In the first series of experiments the silicon substrates were placed on a glass substrate and were pinched at the extremity with two crocodiles connected to a voltage generator (figure 3.43). The idea behind this system is to influence the movement of charged species right above/on the substrate surface.

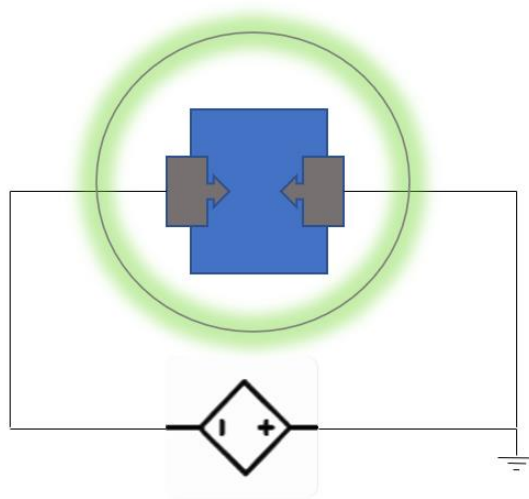


Figure 3.43 Top view scheme of the experimental set-up.

Different voltages have been applied through the silicon substrate and the morphology has been analyzed with optical and SEM imaging.

- For an applied voltage across the sample equal to $V_{appl}=0V$

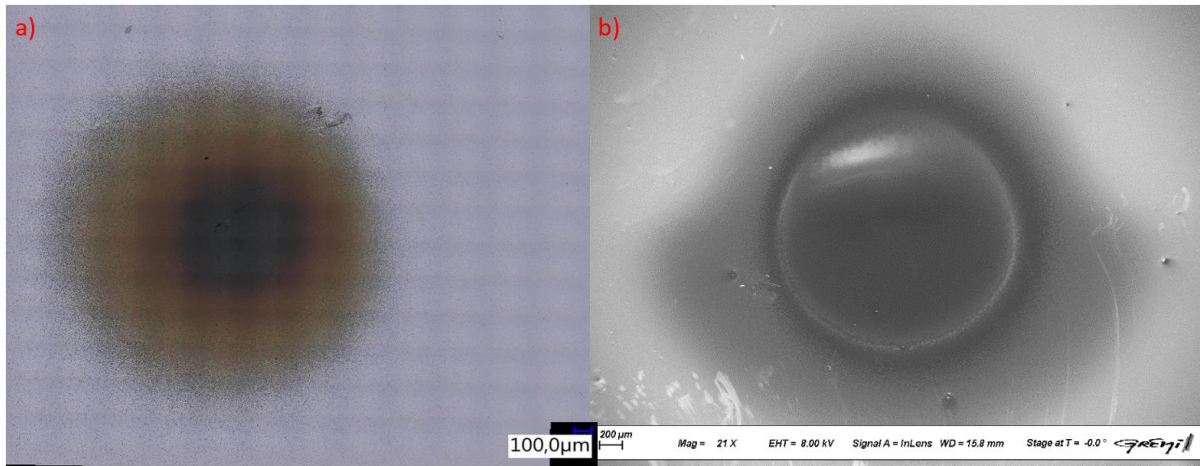


Figure 3.44 Optical assembled image in a) and SEM Picture (b) of the sample deposited in the hole when no voltage is applied across the sample.

- For an applied voltage across the sample equal to $V_{appl}=17V$

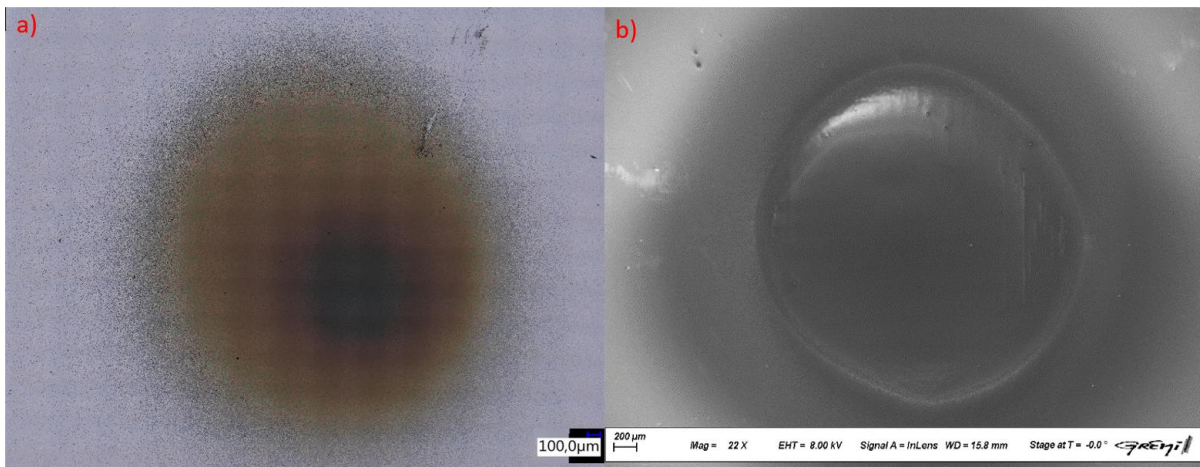


Figure 3.45 Optical assembled image in a) and SEM Picture (b) of the sample deposited in the hole when a bias of $V_{appl}=17V$ is applied across the sample.

- For an applied voltage across the sample equal to $V_{appl}=30V$

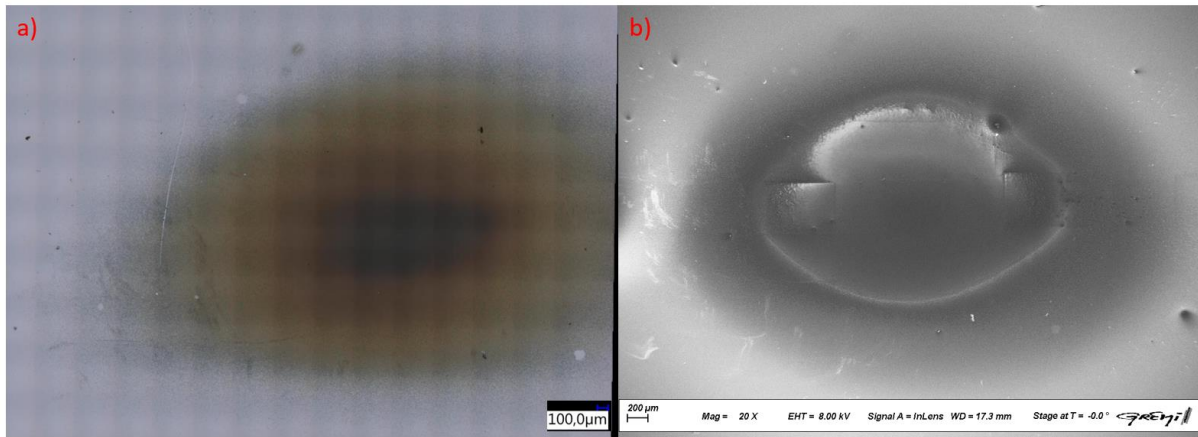


Figure 3.46 Optical assembled image in a) and SEM Picture b) of the sample deposited in the hole when a bias of $V_{appl}=30V$ is applied across the sample.

- For an applied voltage across the sample equal to $V_{appl}=40V$

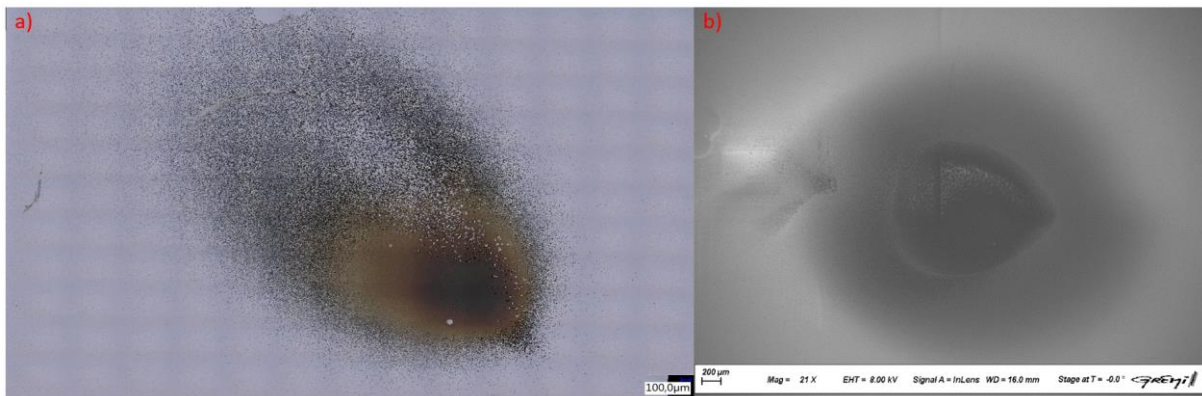


Figure 3.47 Optical assembled image in a) and SEM Picture b) of the sample deposited in the hole when a bias of $V_{appl}=40V$ is applied across the sample.

Optical and electron microscope pictures, that the applied voltage can strongly influence the shape deposit. By increasing the applied voltage, the deposition pattern becomes elongated in the same direction as the applied bias. For low voltages, the deposition retains the usual circular shape. In the case of $V_{appl}=30V$ the deposit takes the form of an elongated ellipse while in the case of $V_{appl}=40V$ it resembles the shape of a bullet. In the last example, the deposition becomes completely inhomogeneous, the edges of the deposition are no longer defined.

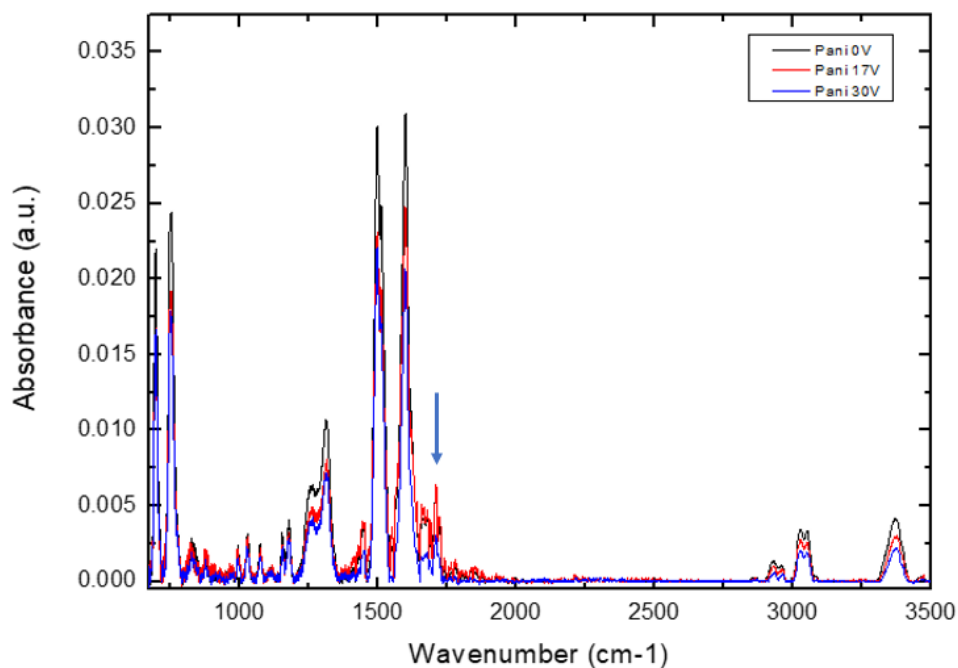


Figure 3.48 Comparison of FTIR Pani spectra of samples deposited with a transversal bias across the substrate

The comparison of the FTIR spectra of deposited samples (figure 3.48) shows that even though the morphology is strongly affected by the applied voltage the composition remains quite similar. The main difference is a decrease of the oxygen content in the film, as indicated by the band at 1670 cm^{-1} , as the applied bias increases.

The application of a bias transversally to the substrate not only influences the morphology or shape of the deposit on a sub-millimeter scale but also on a sub-micrometer scale.

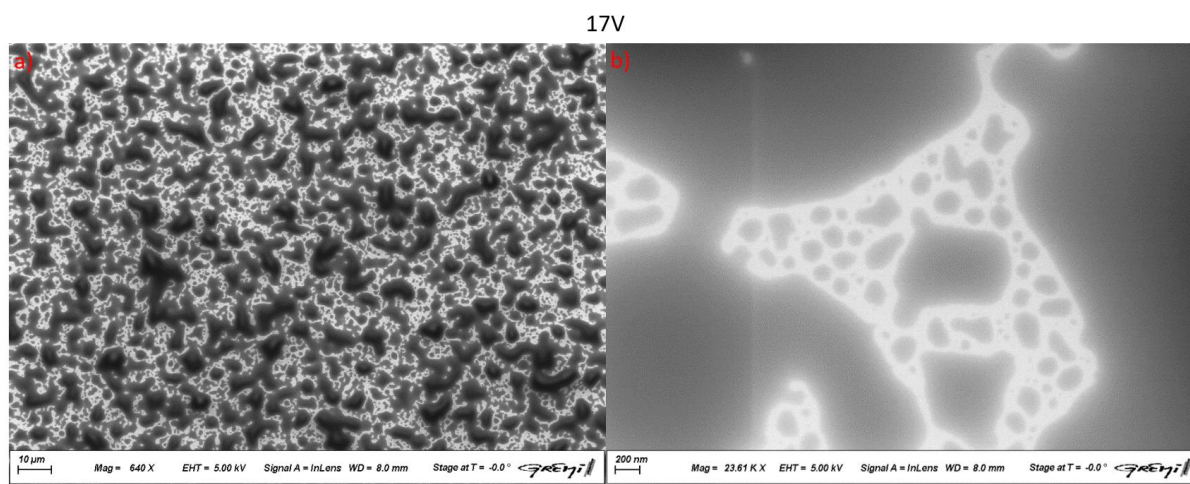


Figure 3.49 Touring pattern at μ size (a) and nm size scale (b) for the sample deposited with

$V_{appl}=17V$.

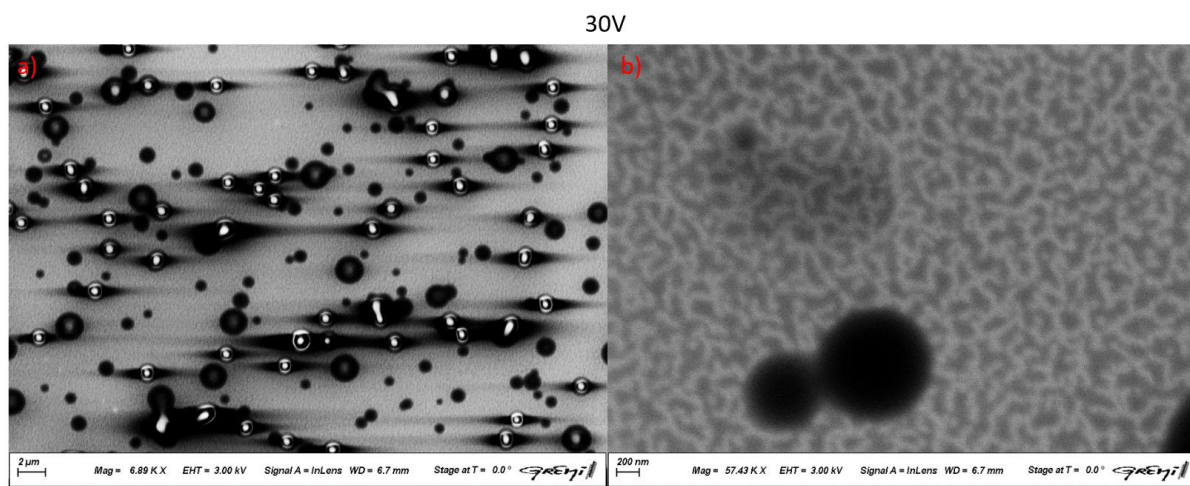


Figure 3.50 Turing pattern at μ size (a) and nm size scale (b) for the sample deposited with $V_{appl}=30V$.

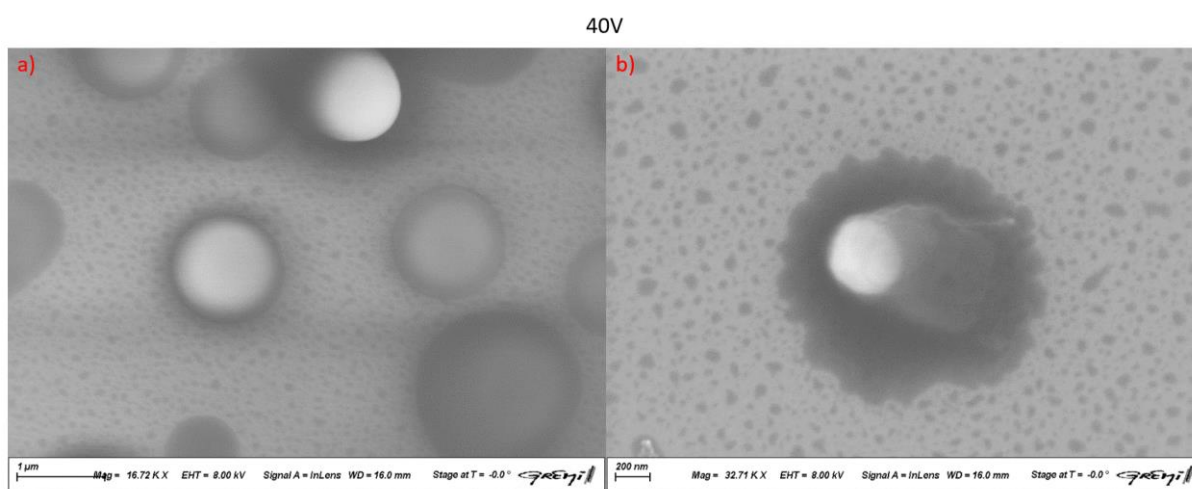


Figure 3.51 Turing pattern at μ size (a) and nm size scale (b) for the sample deposited with $V_{appl}=40V$.

Figures 3.49/3.50/3.51 show SEM pictures taken from the corona region of the blob structure. The complex pattern of this film changes accordingly to the bias voltage applied to the substrate. The shape of the pattern resembles what in literature is called a “Turing pattern”. Turing pattern is a complex 2D pattern that arises when imbalances between diffusion rates make a stable steady-state system sensitive to heterogeneous perturbations. Turing discovered that when two diffusible substances interact with each other they can create a system that can generate a spatial pattern [48]–[52].

3.9.2 Quartz microbalance experiment

To investigate (the effect of charged reactive species on) the deposition process in more detail a quartz microbalance has been employed in combination with the cup electrode. The experimental system used is shown in figure 3.52. The quartz microbalance has been inserted and placed into the cup electrode under the channel.

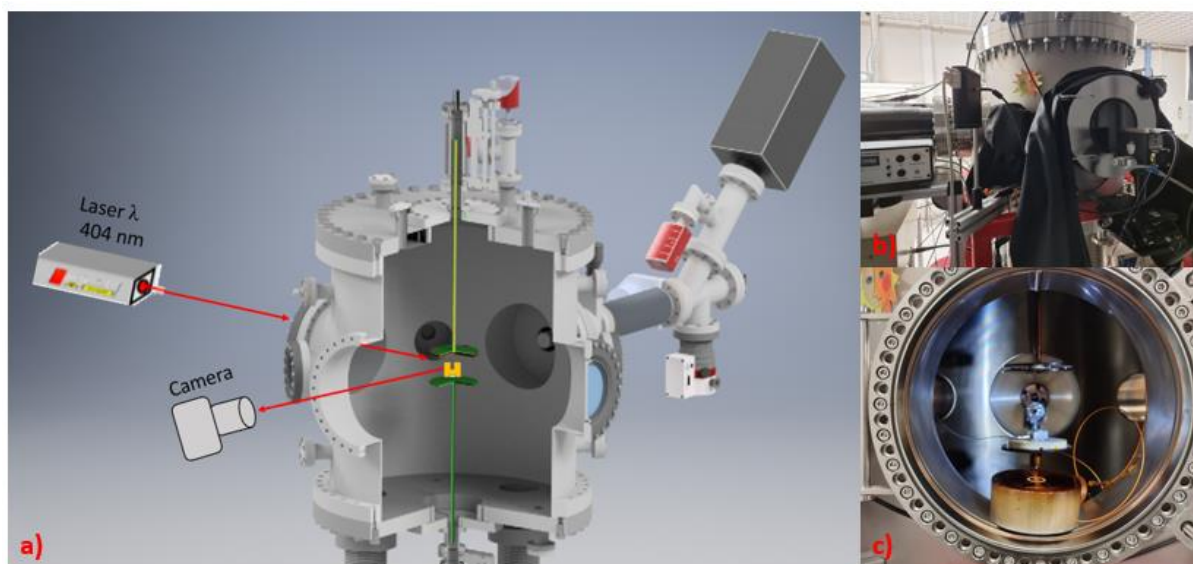


Figure 3.52 Sketch of the experimental setup a) and b). In c) is shown the cup electrode and on the backside the quartz microbalance.

The design of the cup electrode allows the user to bias specific parts of the electrode by replacing some of the metal parts with ceramic ones. In this case, the channel has been biased with an external voltage in order to block eventually charged species formed inside the plasma and prevent them to reach the target substrate. The scheme of the electrode used is shown in figure 3.53.

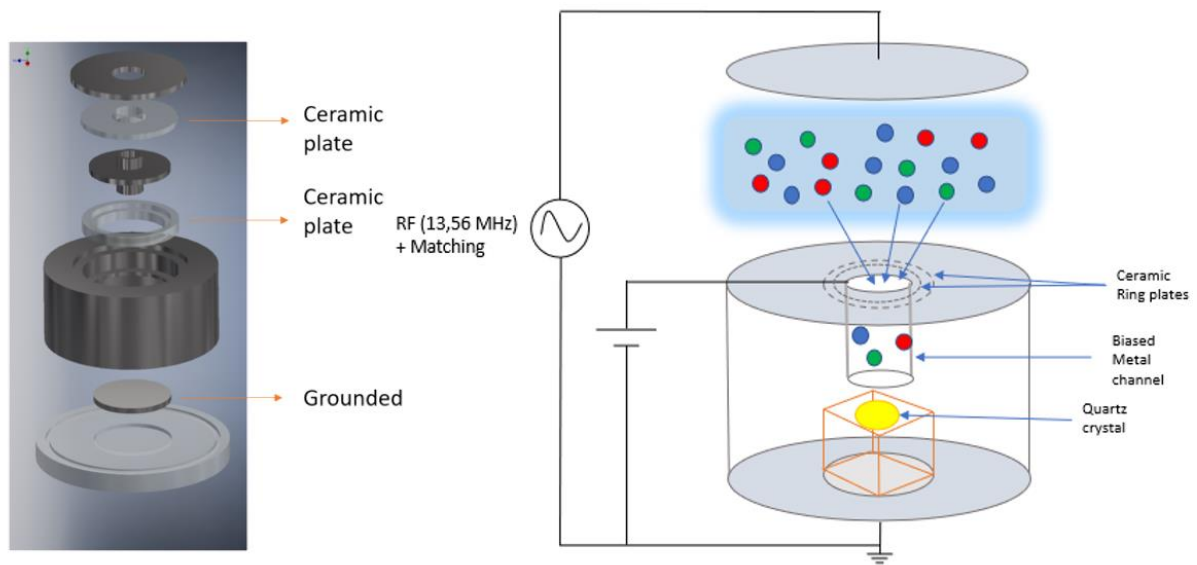


Figure 3.53 Sketch of the electrode design used for this experiment.

The target substrate is the quartz crystal placed on the metal disc at the bottom side of the electrode (figure 3.53), which is at ground voltage. A laser with a wavelength of $\lambda=404$ nm was employed to visualize the formation of particles during the experiment. Images were recorded every 30 seconds.

Figure 3.54 shows the thickness and growth rate calculated from the QCM measurements as function of time. The thickness has been calculated by assuming a material density of 1 g/cm^3 and assuming that the film grows homogeneously on the QCM (surface area 1.25 cm^2) by using the following equation [53]:

$$T_f = \frac{N_{at} d_q (F_q - F_c)}{d_f F_q^2} \quad (\text{equation 3.18})$$

The growth rate is then calculated by numerical differentiation.

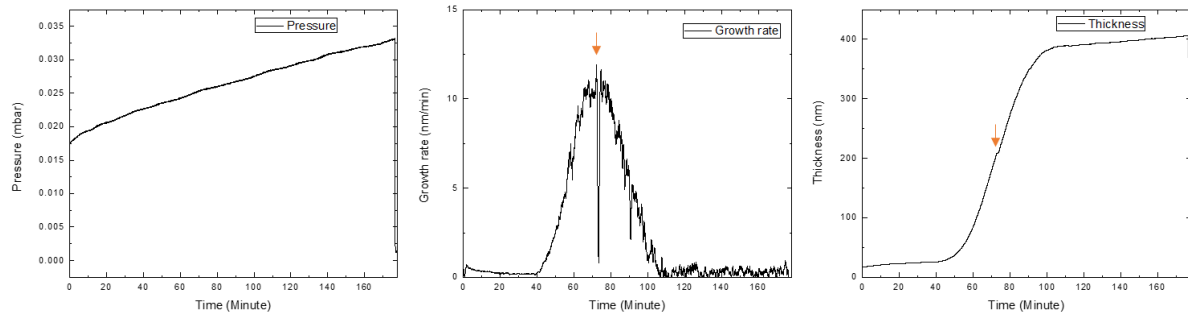


Figure 3.54 Pressure, growth rate, and thickness evolution measured during the experiment.

The results show that the growth rate is very small (close to zero) and almost constant for the

first ≈ 40 minutes of the experiment. After 40 minutes the growth rate increases drastically finally reaching a maximum value of 12 nm/min. After this peak, the growth rate decreases reaching again a value close to zero. During the experiment, a voltage of 20V has been applied for a few seconds to the channel (about 70 minutes after the discharge was ignited). As soon the channel is biased, a notable decrease, a factor of 10, of the growth rate is observed. At this point, the charged species which may contribute to the film deposition on the substrate are blocked and prevented to reach the surface of the substrate. This blocking of charged species reduces the polymerization reactions on the surface which implies a reduction of the film growth. This effect is also observed in the graph which shows the calculated thickness of the sample in function of time. At the point, where the voltage is applied to the channel (orange arrow) a small plateau is observed for the measured thickness.

The results underline again that:

- (i) External electric fields can be used to influence the deposition process suggesting that charged species play a dominant role.
- (ii) The deposition process in channel-type electrodes does not start immediately after the plasma is switched on but only after a considerable amount of time suggesting that it needs time to accumulate or produce those species that are responsible for the deposition or at least influence it.

The last point resembles the process of particle formation where it also takes a certain amount of time for the particles to form. And indeed, the laser light measurements do show the formation of nanoparticles. So even though the plasma is pulsed the formation of nanoparticles is not suppressed in the present experiment. However, it takes much more time for the particles to form than in a non-pulsed plasma.

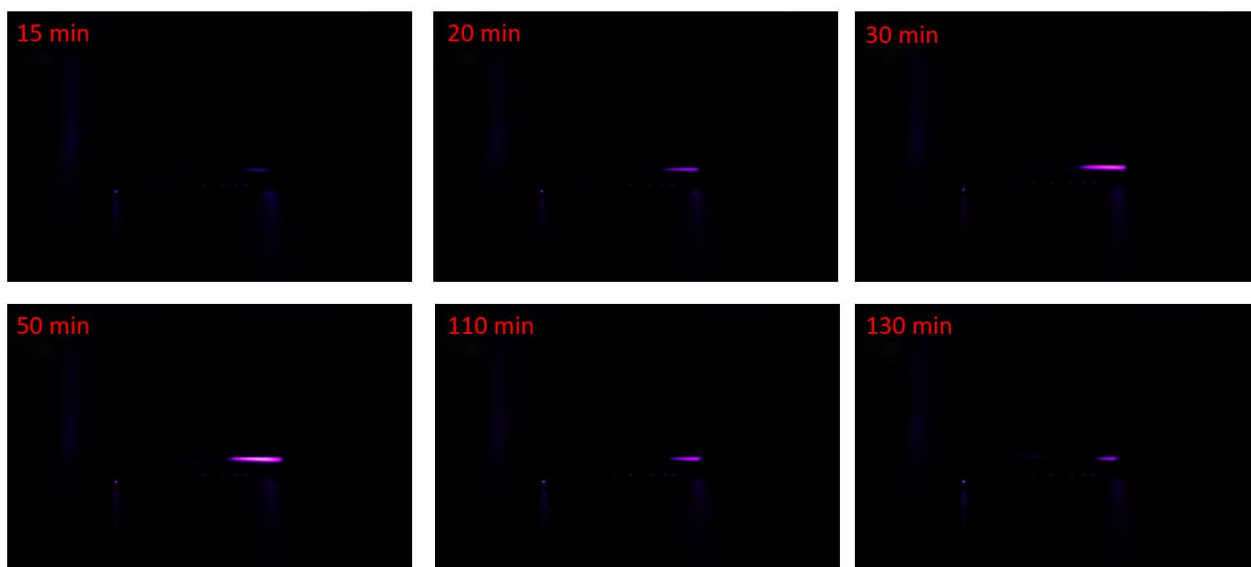


Figure 3.55 Images were recorded with the camera at different times, to detect nanoparticle formation during the deposition experiment.

The laser light scattering images (figure 3.55) show that only around 15 minutes after the ignition of the plasma, one can detect the formation of a dust particle cloud above the bottom electrode. The intensity of the scattering light increases slowly until it reaches a maximum of approximately 50 minutes after the start of the process. The intensity then starts to decrease visibly after around 70 min and then completely disappears after around 130 min from the start of the process. Even though there seems to be some kind of correlation between the formation of particles and the deposition process it has to be stressed that the deposits are not made from nanoparticles.

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Chapter 4

4.1 IODINE DOPING

4.1.1 Introduction

One of the main appealing properties of conductive polymers and in particular of polyaniline is the possibility to improve the electrical properties of films through the process of doping. The doping process has been described clearly by Nobel laureate A.G. MacDiarmid and A.J. Epstein: *“Doping is a phenomenologically-based concept. It does not imply the involvement of any specific mechanism or process. In the conducting polymer field, a chemical dopant is a substance, a relatively small quantity of which drastically changes the electronic, optical, magnetic, and/ or structural properties of the film and is accompanied by a large increase in conductivity”*[1]–[3]. The electrical properties of polyaniline can be controlled by varying the oxidation state of the main chain through protonation of the amine nitrogen chain. As described in chapter 1 polyaniline possess three different forms (according to the oxidation state) but only the “half oxidized form” named emeraldine can be usefully employed for electronic applications. Several studies have been conducted in the literature regarding the doping process of PANI which can be performed by an acid media (generally HCl or HI) which enables the formation of the salt form of the polymer which is conductive [1], [4]–[7].

The doping of polyaniline can be performed in two ways. The first one is one-step process that allows the incorporation of the dopant element directly during the growth process where the gas mixture is a mix of monomer and dopant agent.[8]–[10] The second method is post-process doping which is performed after the synthesis.[11] In this Ph.D. work, the second doping process has been preferred compared to the first one to not contaminate the main synthesis plasma chamber.

The conductivity of polyaniline films is in the order of 6.28×10^{-9} S/cm but can be improved through doping up to 10^1 S/cm. [3], [10], [12]–[14] The doping of Iodine (I_2) is widely used in literature to improve the electrical properties of conjugated polymer films. The I_2 acts as an electron acceptor (proton donor) and when it is used for the doping, the electrons of the double bonds are getting transferred to the Iodine and this leaves the polymeric chain positively charged. This electron transfer causes an imbalanced electron arrangement which makes the film conductive. [10], [15], [16]

In literature the reported conductivity of polyaniline doped with Iodine is in the order of $10^{-2}/10^{-3}$ S/cm. [5], [12], [17], [18]

4.2 Post synthesis doping process

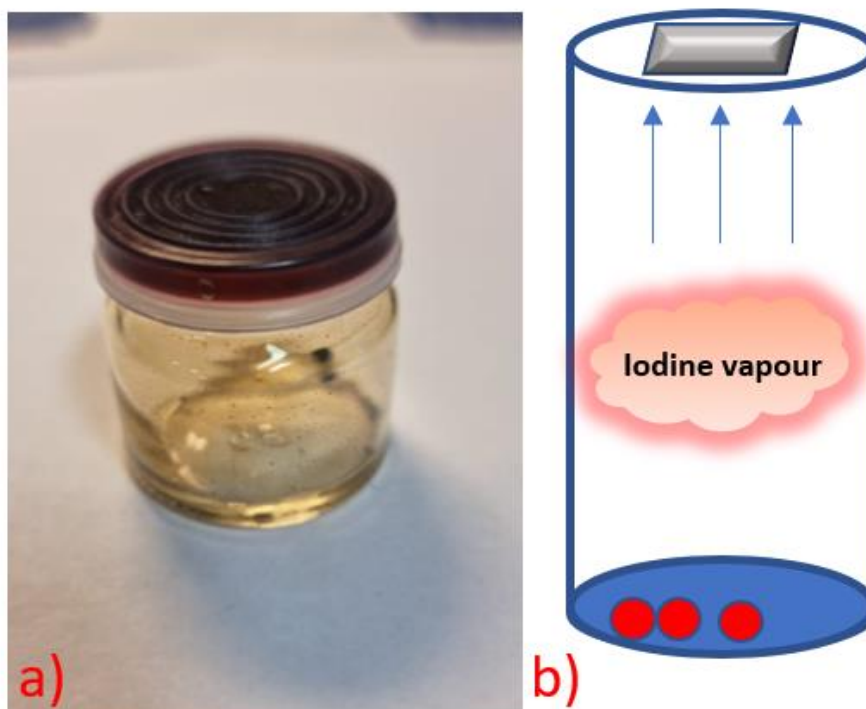


Figure 4.1 Picture and sketch of the system used for doping. The iodine spheres placed at the bottom of the glass container evaporate and create an atmosphere of iodine vapor which dopes the target sample placed on the top side of the container.

The scheme used for the ex-situ doping process is shown in figure 4.1. The thin film sample is attached to the lid of a small glass container. The iodine source consists of small spheres (Carl Roth I_2 >99.5% sublimated) which are placed in the glass container. To create a saturated atmosphere of Iodine the glass container is placed in a warm bath at a temperature of $\approx 40^\circ\text{C}$.

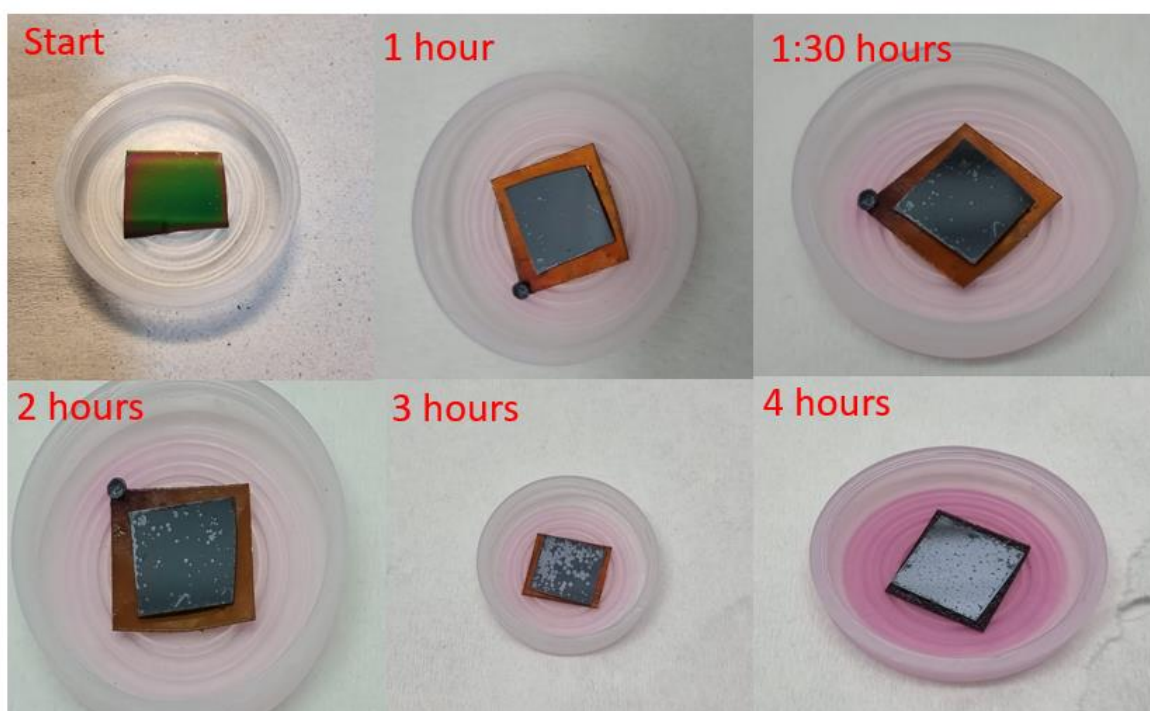


Figure 4.2 Evolution of morphology of doped films under iodine in function of exposure time.

The doping process of the sample was monitored in time. As shown in figure 4.2, the morphology of the samples changes with increasing exposure time to iodine vapor. After 1 hour of exposure, the film color completely changes due to the incorporation of iodine inside the thin films [19]. As soon as the exposure time increases further, small *bubble structures* start to appear on the surface of the thin films, The number of these *bubble structures* increases until after 4 hours (from the start of the process) the film almost completely disappears from the surface. The Iodine doping appears to cause the film to peel off from the silicon wafer. After 4 hours, the microstructures on the surface of the sample appear to consist of film clusters wrapped and folded around themselves. The doping process probably tends to create cracks and defects in the film, which start to wrap themselves, due to mechanical stress created by the iodine incorporation in the film structure.

In order to investigate this process, the doping experiment has been repeated with several samples as shown in figure 4.3 (i.e. with samples placed on top of the electrode and samples placed under the 2 cm hole). The samples were analyzed with an optical microscope and with SEM.

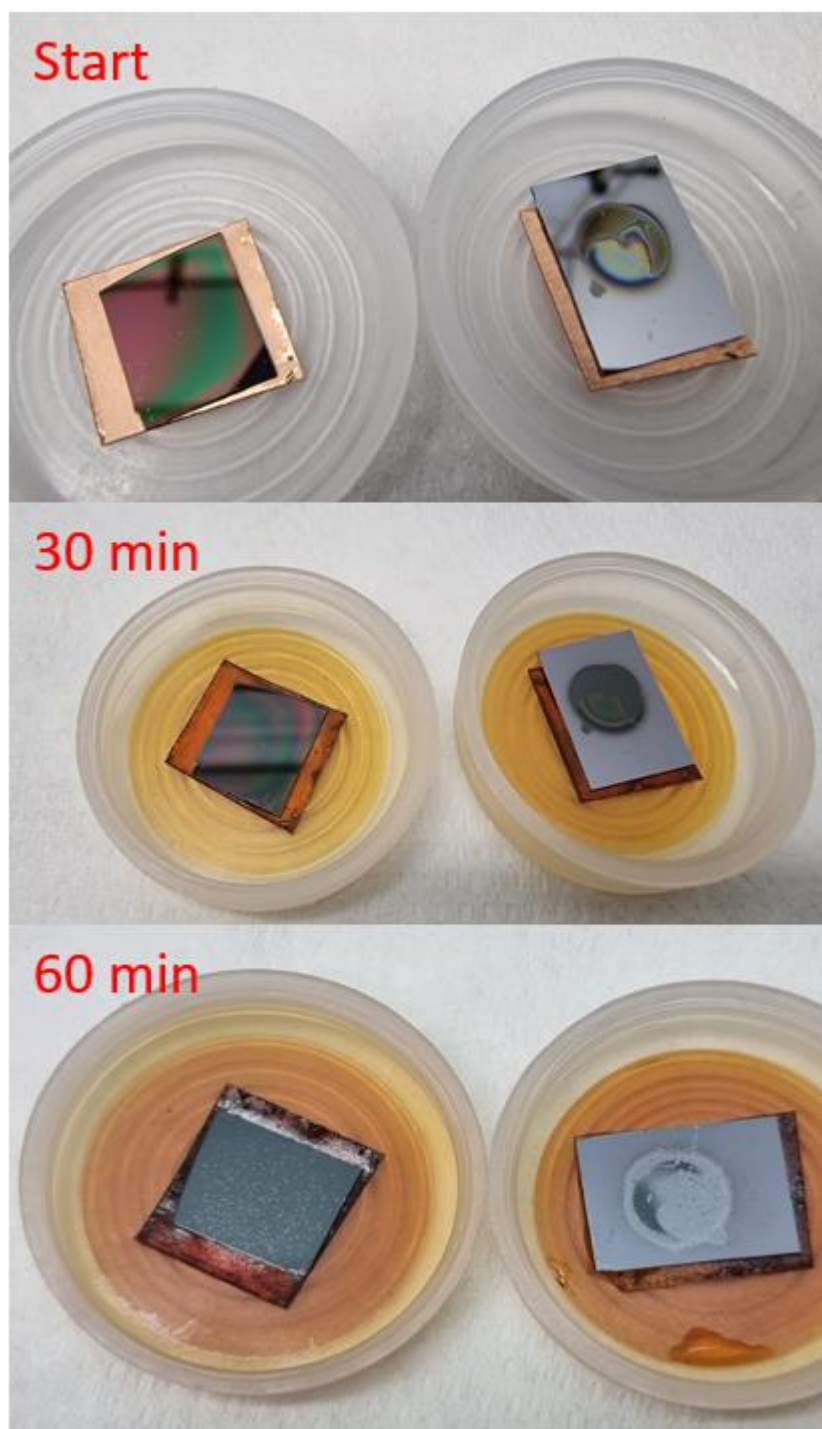


Figure 4.3 Doping process photos of samples Top and 2 cm after 60 min of exposure.

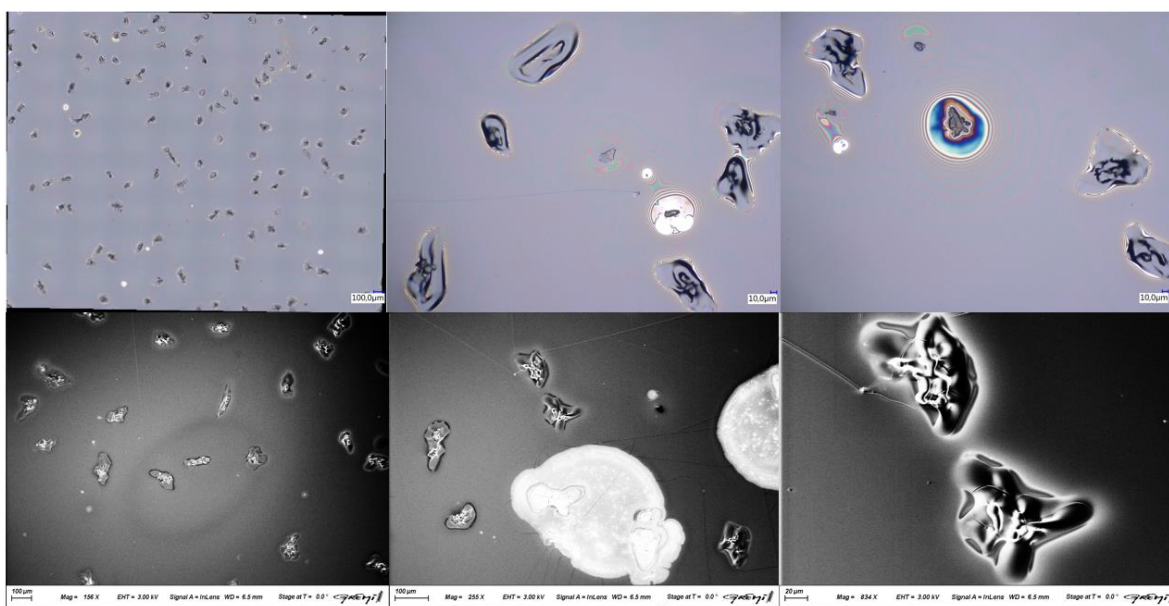


Figure 4.4 Optical and SEM images of the sample deposited on top of the electrode.

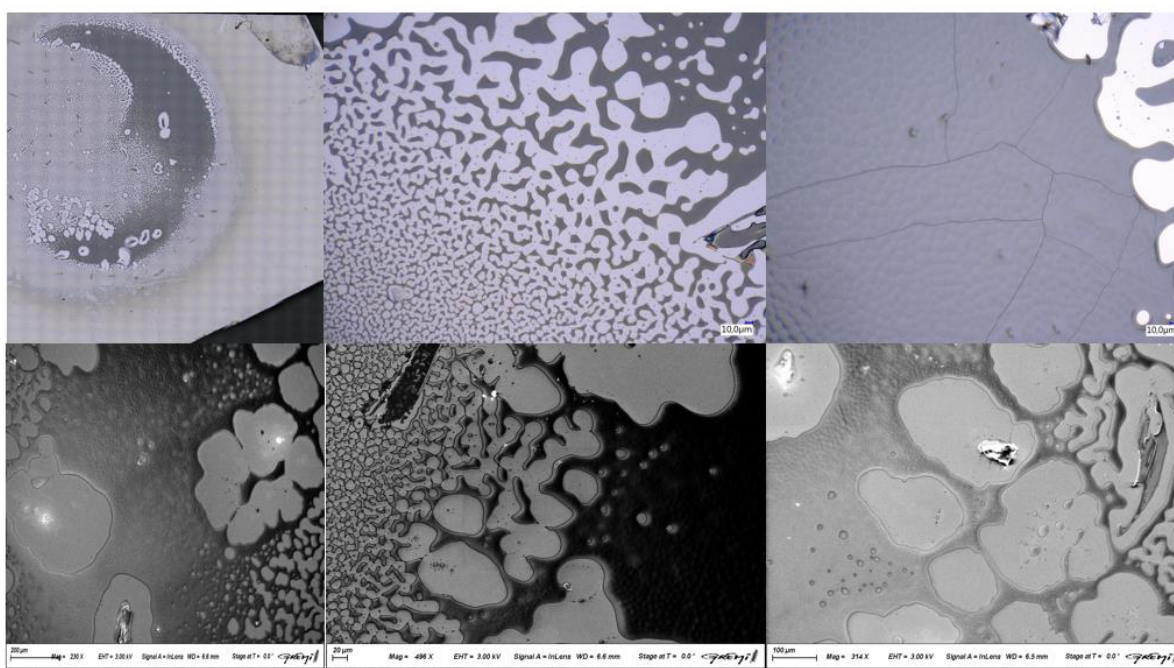


Figure 4.5 Optical and SEM images of the sample deposited in 2 cm hole size.

The images acquired with the optical microscope shows that the doping process is changing the morphology of the two types of films in a different way. The “top film” (figure 4.4) shows the formation of clusters of folded film on the surface due to iodine incorporation. Even though the majority of the film is folded into the cluster, it is possible to observe a thin layer of film below the cluster structures.

Concerning the 2 cm sample (figure 4.5), the doping process causes the formation of cracks of

the film due to stress created by iodine incorporation. Moreover, on the film surface it is possible to observe the formation of patterning or an increase of the roughness. This phenomenon is also described in literature and occurs when the structures which form the polyaniline films agglomerate together. The iodine incorporation creates stress which results in the formation of a crack at grain boundaries [19]. The formation of sharp cracks in the film is clearly visible in the “2 cm sample” both in optical and SEM images.

Similar results were obtained for samples placed in the 1 cm hole (figure 4.6). SEM images show the formation of cracks on the surface of the “blob” after the doping process.

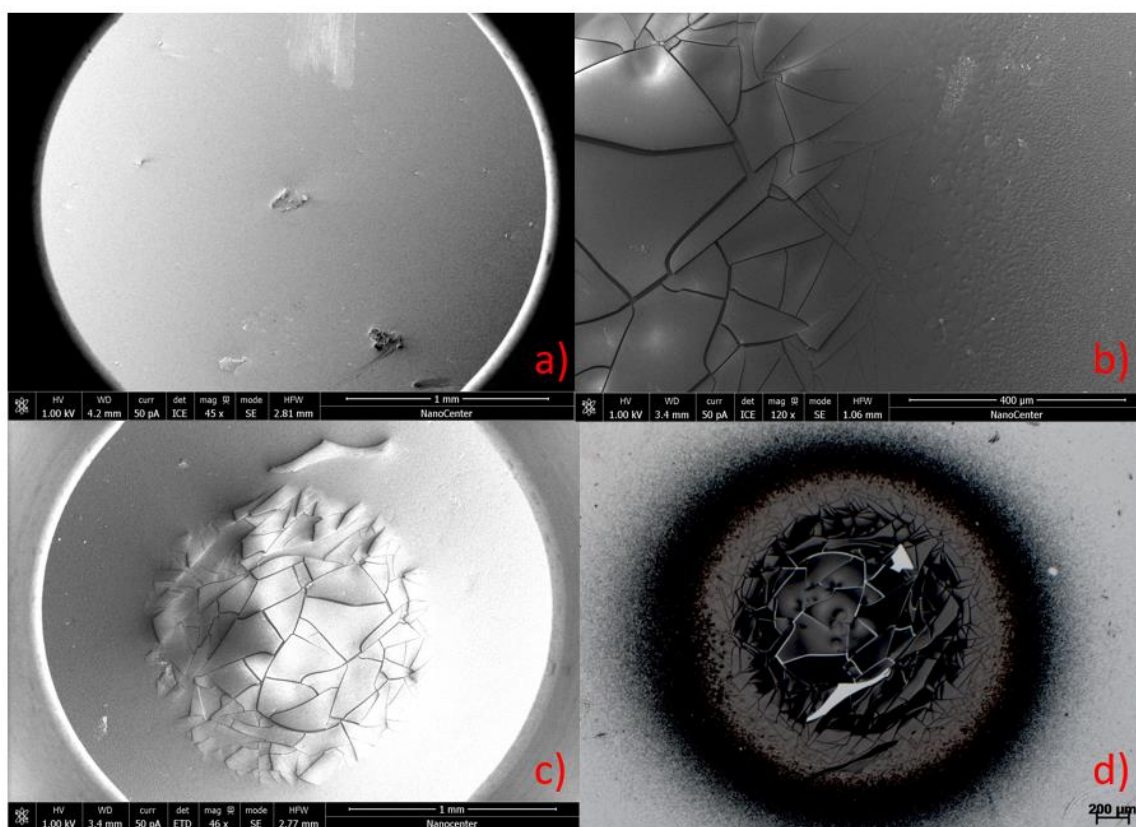


Figure 4.6 SEM and optical microscope images of sample deposited in 1 cm after the doping process.

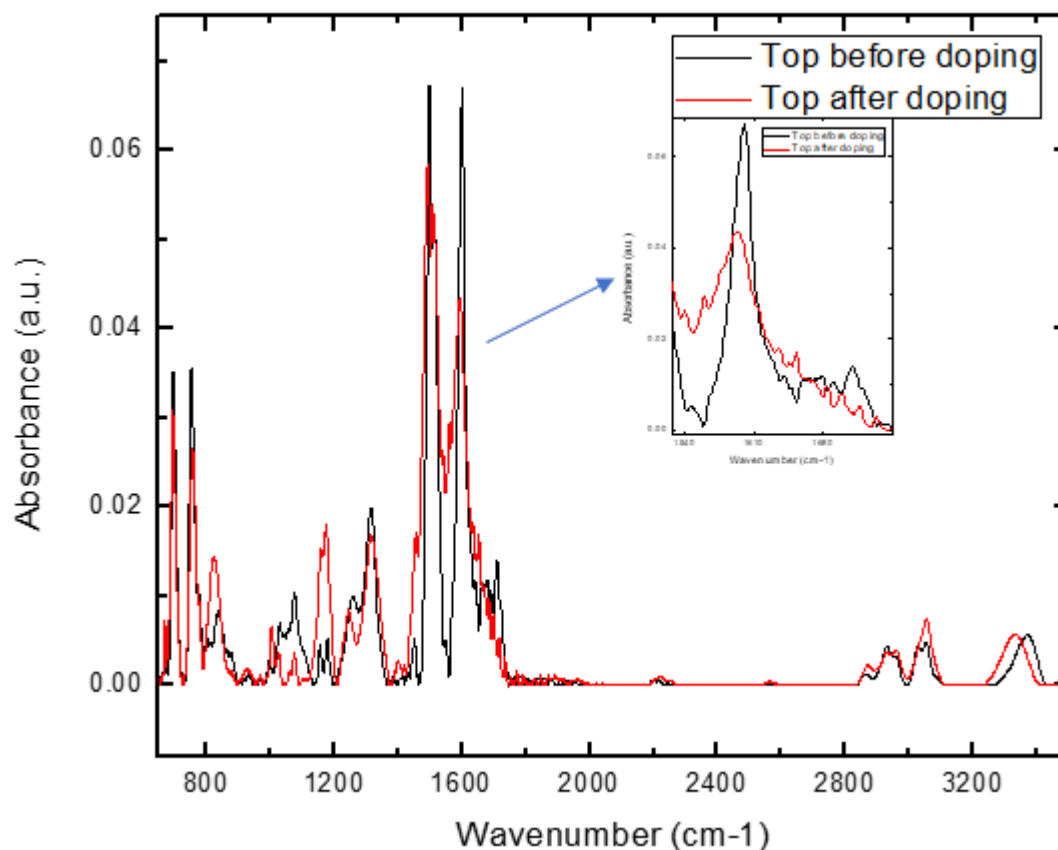


Figure 4.7 FTIR comparison of films before and after iodine doping process.

FTIR analysis was performed to control the film composition before and after the doping process. The main effect due to iodine doping is the “blue shift” of some peaks: the quinoid peak at 1600 cm^{-1} and the N-H stretching vibration at 3379 cm^{-1} . Moreover, a considerable reduction of the intensity of the Quinoid peak is observed. Those findings are in agreement with the literature, in fact, the iodine doping reaction occurs at the quinoid units in the polyaniline molecular chains [20]. An increase of the peak at 1177 cm^{-1} referring to C-C interaction is observed.

The increase of the peak at 830 cm^{-1} referred to para substituted aromatic ring may indicate that iodine incorporation could also take place on para position on the aromatic ring.

4.3 Iodine doping mechanism

During the film exposition to Iodine (I_2) different species including iodide (I^-), and polyiodides (I_3^- and I_5^-) directly participate in the charge transfer process with the N-atoms in the quinone diamide unit of the polyaniline chain (1) and form a transfer complex (2) which due to intramolecular redox reaction can form a radical named semiquinone di cationic radical (3).

This radical due to rebalancing of charges, rearrange in a more stable form which results in the conductive form (salt) of polyaniline (4) [3], [6], [20], [21].

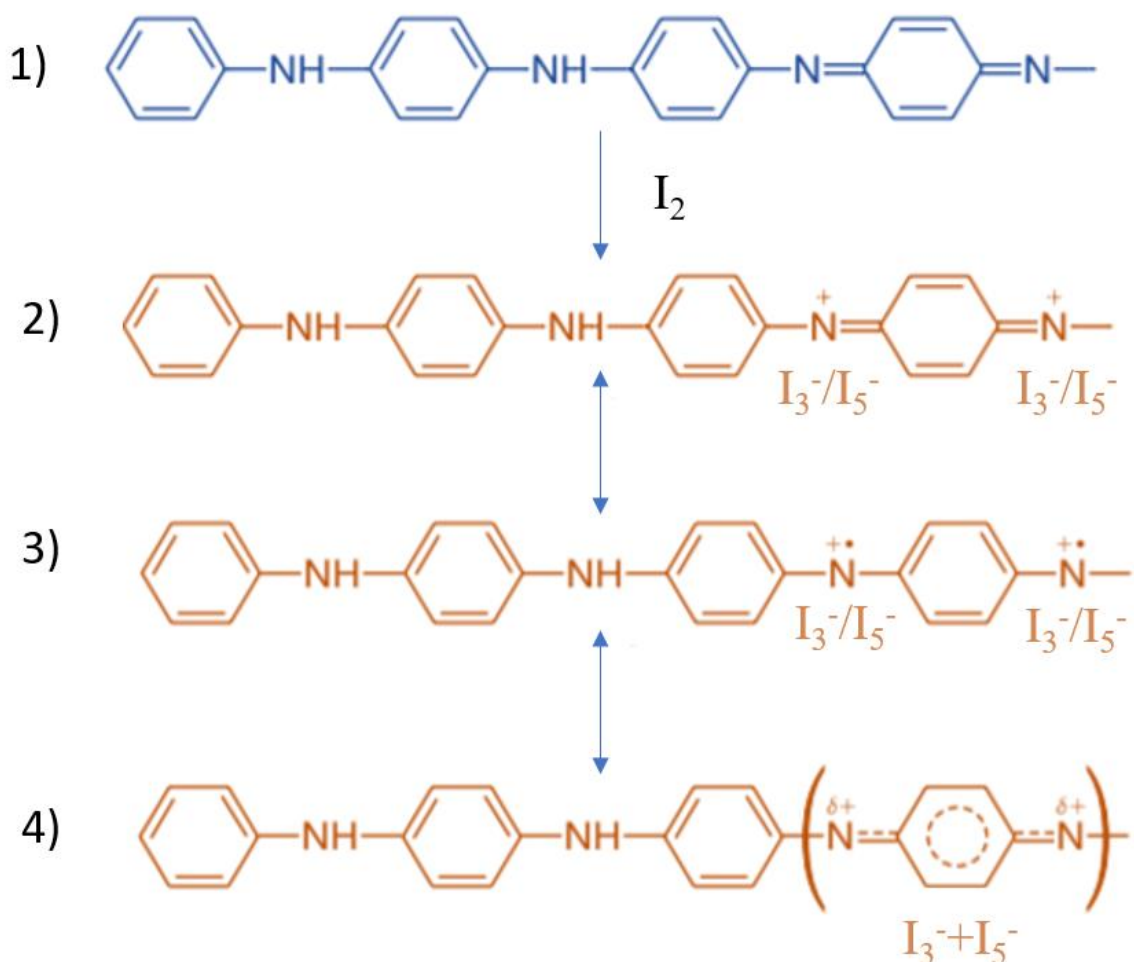


Figure 4.8 Iodine doping mechanism of the polyaniline.

4.4 Comparison of doping processes

The samples doped so far were all produced in pure aniline and zero pumping speed (“new deposition protocol”). Samples produced according to the old deposition protocol i.e. in an Ar/aniline (20:1 sccm) mixture with the pump running show a different response to the doping.

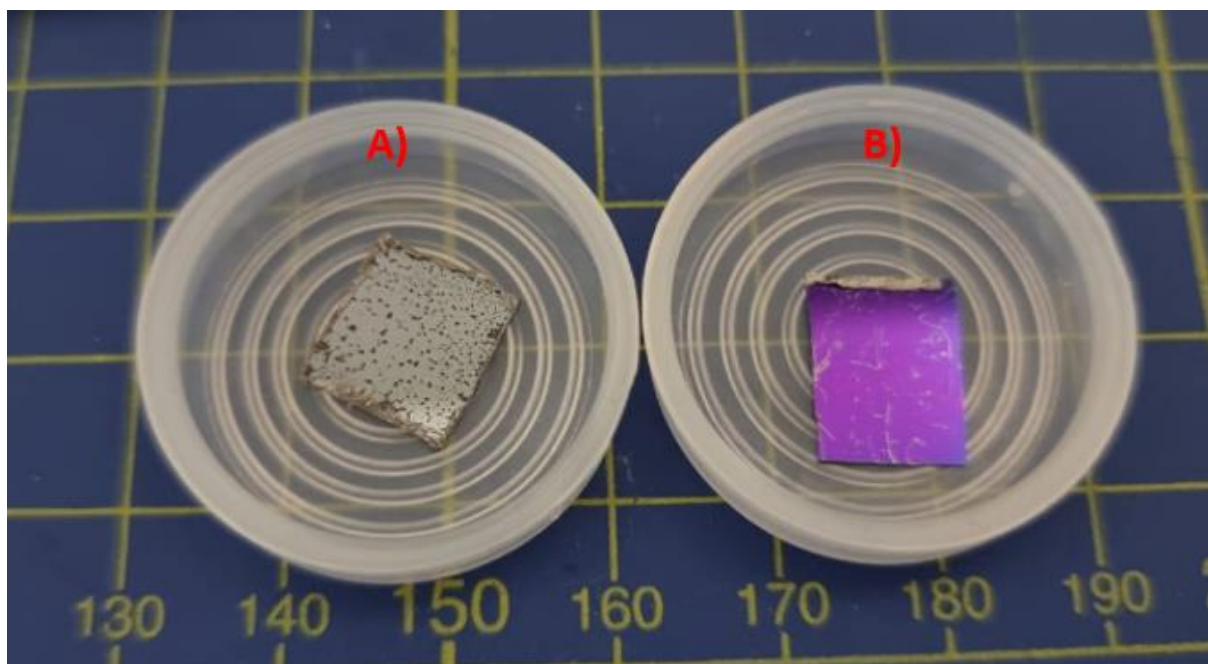


Figure 4.9 Comparison of doping process for 2 different polyaniline sample. In A sample produced in pure aniline mixture and B sample produced in Ar/aniline mixture after 24 hours of exposure.

Figure 4.9 shows two different films after they had been exposed for 24 hours to iodine vapor. Sample A was produced according to the new protocol (pure aniline, no pumping), sample B according to the old one (Ar/aniline, with pumping). (Both films were placed on top of the electrodes when they were produced.) In contrast to sample (A), sample (B) shows no visual changes after the iodine exposure. The explanation for this difference could lie in the different structure of the two films. Sample (B) being produced in an Ar/aniline mixture with higher power has a more crosslinked structure compared to the sample (A) which is produced in pure Aniline with a milder plasma.

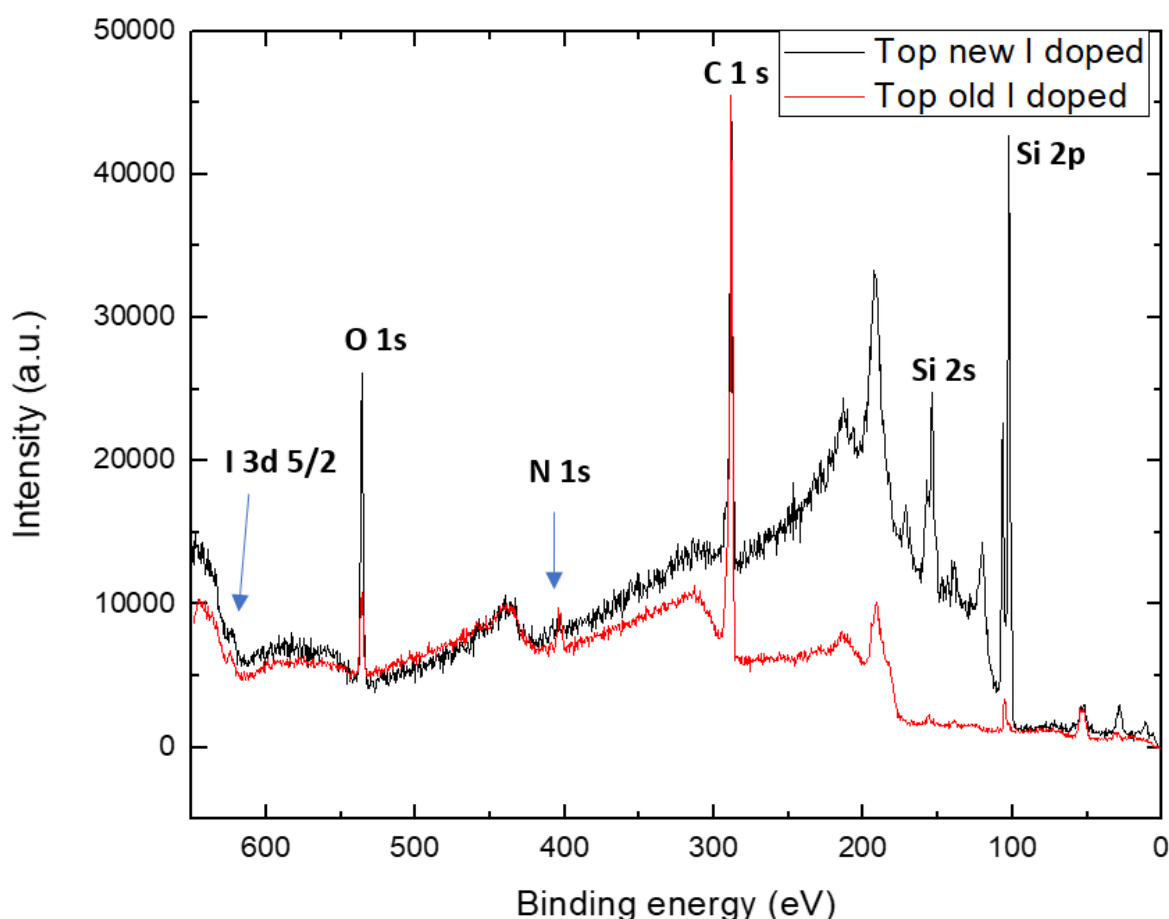


Figure 4.10 FTIR comparison of sample A) and B) described before in figure 4.9 after the iodine exposure.

Figure 4.10 shows XPS spectra of the two samples (A) (black curve) produced in pure aniline and (B) (red curve) produced in an Ar/aniline mixture after the doping. The XPS spectra have been normalized to the intensity of the C 1S peak at 284 eV. The sample in black shows the presence of a high intensity peak at 100 eV and 154 eV referring to Si 2p and Si 2s. Moreover, also the quantities of carbon C 1s at 24 eV and nitrogen N 1s at 400 eV are lower in the sample (A) compared to the sample (B). All these features confirm that the film prepared in pure aniline peels off the Si wafer and forms small clusters on the silicon surface while the film prepared in Ar/aniline is more resistant.

The Pani sample deposited in the 1 cm hole (the blob in figure 4.6) was analyzed by XPS at various locations on the surface. The different locations are named z=34-36.5-37.5-39.5-40 and the center of the blob corresponds to the position z=37.5.

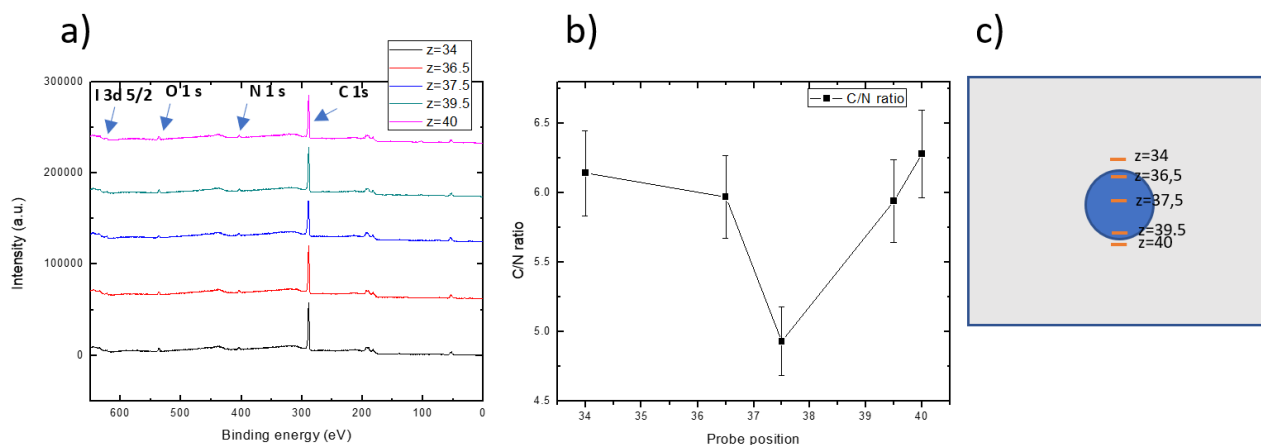


Figure 4.11 a) XPS spectra acquired on different positions on the sample, b) the C/N ratio calculated for the different positions and c) a sketch of the probed system used in this analysis.

The XPS analysis shows that the composition of the sample slightly changes. The lowest C/N ratio is found for the position $z=37.5$ which correspond to the center of the “blob”. However, the iodine content is found to be the highest at the center of the blob.

Summary

The material characterization with XPS showed the presence of iodine in the doped films and the FTIR analysis results are in agreement with what was reported in literature regarding the effect of the incorporation of iodine in polyaniline films: a shift of the quinoid peak at 1600 cm^{-1} and the N-H stretching peak at 3379 cm^{-1} . Moreover, the change in the ratio of benzenoid to quinoid indicates that the iodine doping influences mostly the quinoid structure. This effect is commonly reported in literature as the doping mostly happen in the proximity of the quinoid structure of the polyaniline chain by forming the salt form of Pani.

The results show that the Pani films prepared with pure aniline have a better structure, which should be closer to the emerald polyaniline structure. However, they are more susceptible to degradation and cracking when exposed to iodine. Further studies are required to solve this problem in order to increase the iodine doping level in the polymerized films. In conclusion, the doping studies showed interesting results and will be used as basis in further studies in order to optimize the process and solve the problems of stability.

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Chapter 5

5.1 Summary and outlook

The previous chapters clearly proved that the plasma-based deposition of thin films is a rather complex process that involves many different species and time scales. The process of thin film deposition is illustrated in figure 5.1. Due to the electron impact dissociation of the monomer, a great variety of different species is created in the plasma volume. These species may initiate further chemical reactions in the plasma volume leading to the formation of larger molecules, they may diffuse to the surface and react there, or they may be destroyed by subsequent collisions with electrons before they can reach the surface, or they may simply be pumped out of the plasma chamber.

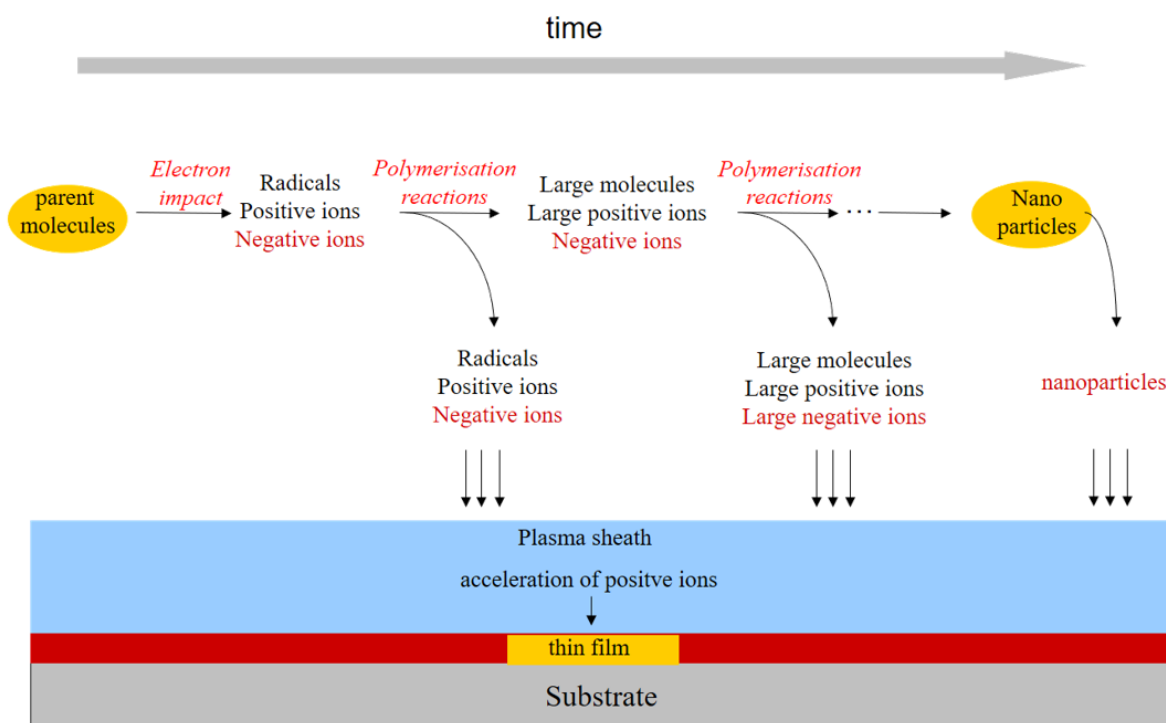


Figure 5.1 Sketch of possible gas and surface interaction that can occur in a reactive plasma.

This simplified scheme not only illustrates the potential complexity of plasma-assisted polymerization processes but also suggests possible ways to control such processes, especially with respect to the deposition of thin films. In simplified terms, there are two main ways to control the plasma process and thus deposition of thin films.

- The first possibility is to influence the plasma-chemical reactions taking place in the plasma volume which can be achieved by the choice of the external discharge parameter like power, pumping speed, duty cycle, gas flow rate, or pressure.

- The second possibility is to control the species flux arriving on the substrate by using filtering techniques.

Both possibilities have been used in this work and can of course be applied to any type of monomer. In particular, the channel electrodes with their underlying idea of filtering certain species before they reach the substrate open up new possibilities for controlling the species flux in various plasma reactor designs working with different kinds of monomers.

The goal of the remainder of this chapter is to discuss some applications as well as some techniques that have not been used extensively in this thesis but have the potential to be used in future studies.

5.2 The double pulse technique

The use of pulsed discharges is of crucial importance for the deposition of thin films from organic monomers. A first indication of the importance of pulsed discharges comes from the Yasuda parameter. By using a pulsed discharge, the average power delivered to the discharge is lowered. This results in a smaller Yasuda parameter, which helps to preserve the structure of the original monomer and avoid excessive crosslinking of the deposited thin film. In principle, the Yasuda parameter can easily be reduced by choosing long enough plasma off times i.e. a sufficiently small duty cycle. However, the absolute values of plasma-off time and plasma-on time must be properly adjusted with respect to the rise time of the various species and their lifetime in the discharge to achieve the desired effect i.e. to make the plasma milder. (It is easy to see that a plasma with a plasma-on time of 1 week and a plasma-off time of 2 weeks is not really a pulsed plasma in this sense). In addition, long plasma-off times resulting in a strong drop in the electron density sometimes make it difficult to re-ignite the plasma in the next cycle, making it thus difficult to maintain a stable plasma.

Another aspect concerns the confinement of the negative ion component. By choosing the proper pulse parameters (pulse frequency, duty cycle), the transport of the negative ions and thus their density can be controlled. This is of particular importance for polymerization reactions in the plasma volume involving negative ions, reactions that can be essential for the formation of nanoparticles.

To obtain better control over the diffusion of negative ions and the Yasuda parameter, a new technique was used: “the double pulse technique”. Here two frequencies are used to pulse the discharge, the main frequency f_m and the sub-frequency f_s with $f_m > f_s$. This is achieved by using two pulse generators. The first generator is used (as usual) to trigger (with the frequency

fm) the output of the oscillator that drives the main amplifier. The second pulse generator is used to trigger the output of the first pulse generator with the frequency f_s . The resulting rf signal with which the plasma is finally operated is schematically shown in figure 5.2.

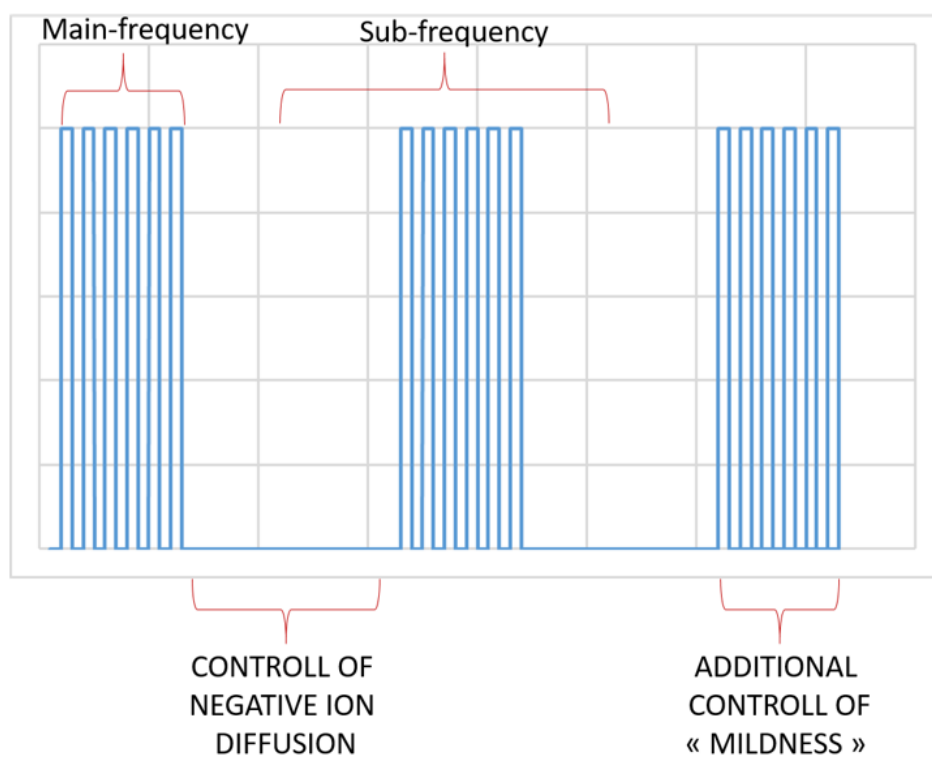


Figure 5.2 Scheme of the double pulse RF signal.

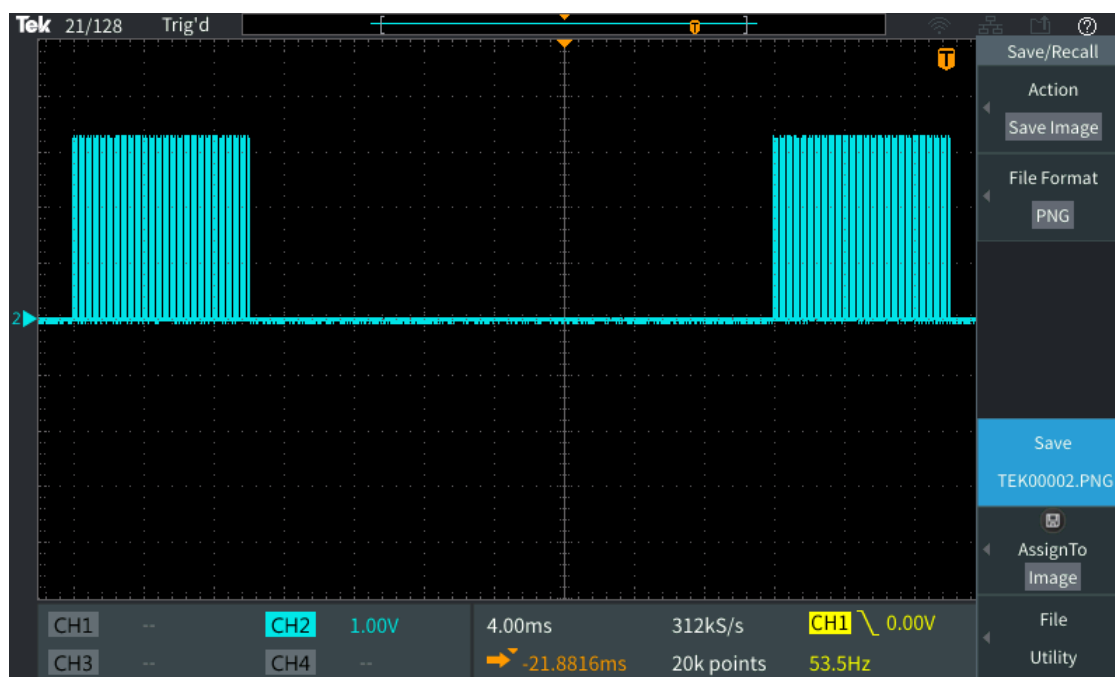


Figure 5.3 Image from oscilloscope of the double pulse signal.

To test the double pulse technique a deposition experiment with the following pulse parameters was performed.

-Main pulse: 50 μ s on/ 500 μ s total cycle -> Duty Cycle 0.1

- second pulse: 10 ms on/40 ms total cycle -> Duty Cycle 0.25

As it is shown in table 1 (see the average power column) the application of a double pulse results in a very mild plasma:

Experiment protocol	Gas mixture	Power	Duty Cycle	Average Power	Pressure
Single pulse	Aniline sccm	1 4W	0.25 (10 ms/40 ms)	1 W	0.18 mbar
Double pulse	Aniline sccm	1 4W	0.25 (10 ms/40 ms) /0.1 (50 μ s/500 μ s)	0.1 W	0.18 mbar

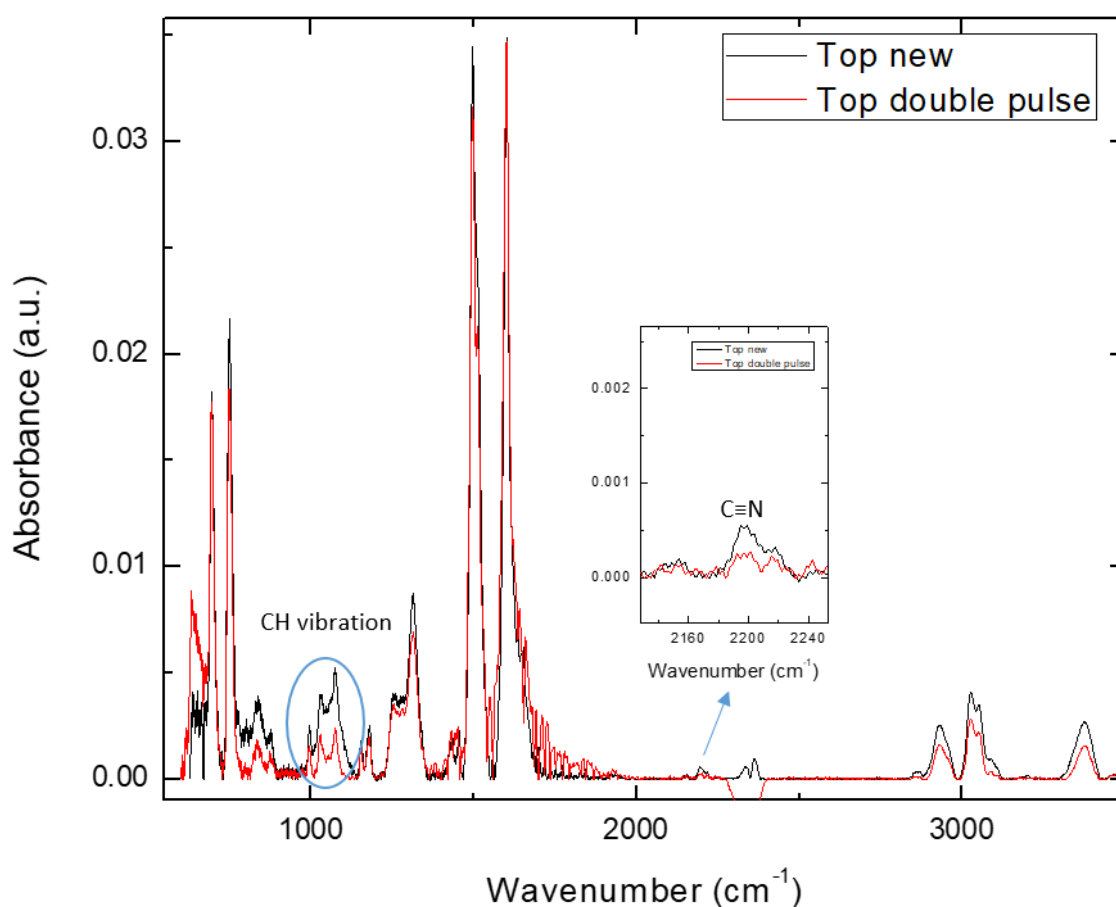


Figure 5.4 FTIR spectra comparison of sample produced with the new protocol (black) and with the double pulse technique (red).

Figure 5.4 shows the FTIR spectra of two films deposited with a single and a double pulse technique respectively (both samples were placed on top of the structured electrode). Both spectra are normalized to the quinoid peak at 1600 cm^{-1} . A comparison of both spectra only shows minor differences between them. The most notable difference concerns the band at $\approx 1100\text{ cm}^{-1}$ resulting from CH vibrations [1]. Another difference is the peak at 2217 cm^{-1} resulting from the presence of $\text{C}\equiv\text{N}$ groups. This peak is also slightly smaller for the sample produced with the double pulse method indicating that the fragmentation of the original monomer is smaller. This new innovative method can be easily employed for other kinds of monomers and processes in order to control polymerization processes in reactive plasmas. The full potential of this method should be explored in future studies.

5.3 Control of thin film deposition in acetylene plasmas

Although the channel type electrodes were mainly used in this work in plasmas operated with aniline or aniline/argon mixtures they can be employed for each type of monomer. This was tested in this work for the case was acetylene. Acetylene is a relatively simple monomer compared to aniline. Since the structure is quite simple, the number of primary reactions involving the dissociation of the monomer is much smaller than in the case of the more complex aniline monomer.

The parameters chosen for the deposition were chosen according to the aniline deposition protocol: work with no pumping system, use of a pure acetylene gas (without noble gas), low power and low Duty Cycle in order to have a mild plasma deposition that would allow to retain the original monomer structure.

The parameters chosen for the deposition are shown in table 2:

Experiment	Gas mixture	Power	Time	Duty Cycle	Pressure	Pumping system
1	5 sccm Acetylene	4W	60 min	0.25 (10 ms/40 ms)	0.18 mbar	Off
2	1 sccm Acetylene	4W	60	0.25 (10 ms/40 ms)	0.18 mbar	Off

3	0.5 sccm Acetylene	4W	60	0.25 (10 ms/40 ms)	0.18 mbar	Off
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5.3.1 Control of deposition in acetylene mixture

The results from the different deposition processes shown in table 2, are discussed in the following paragraph:

The deposition of acetylene using an input flow of 5 sccm resulted in the production of a uniform and homogeneous film on top of the electrode but in the 2 cm hole the deposition was characterized by the presence of dust particles as shown in figure 5.5

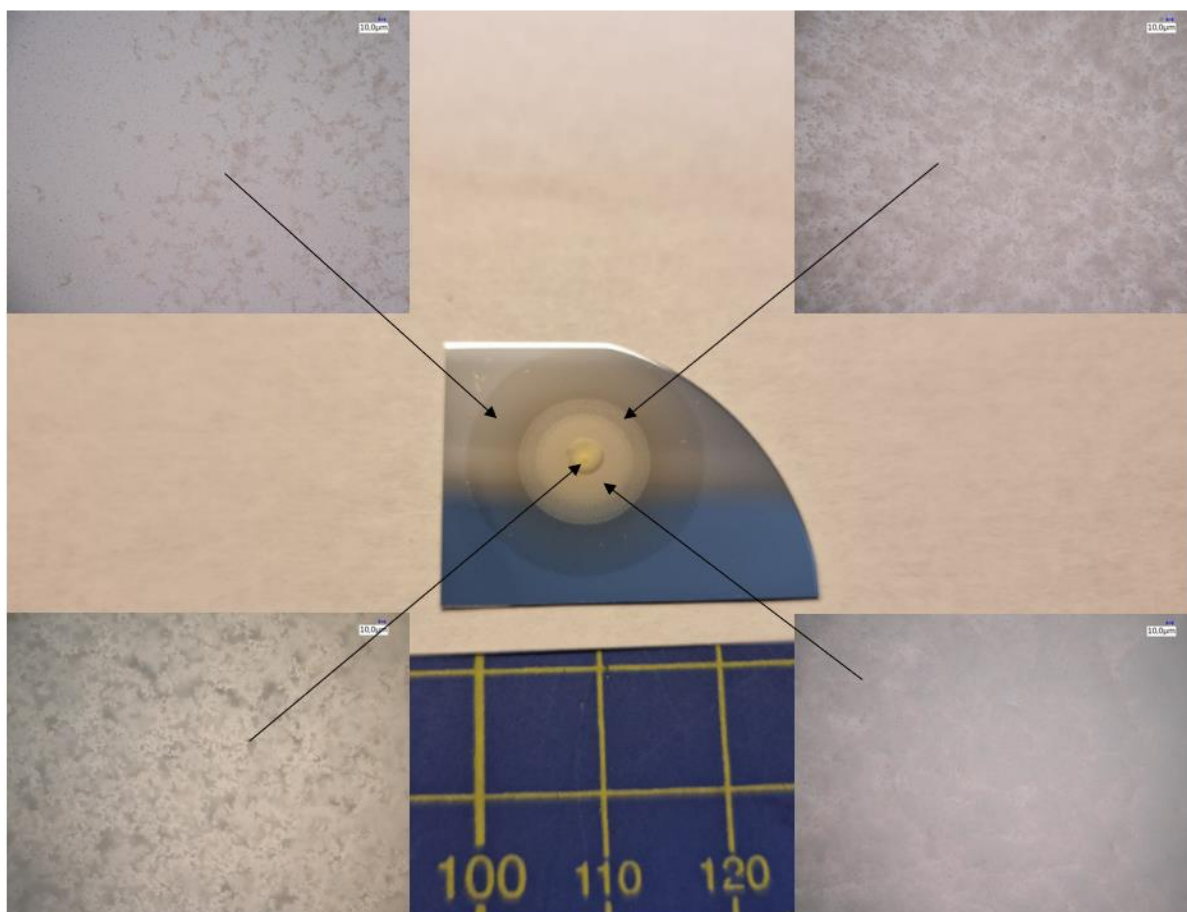


Figure 5.5 Analysis of the sample produced with a gas mixture of 5 sccm Acetylene in the 2 cm hole. The images have been acquired with an optical microscope.

The deposit shows 4 different rings in which the density of deposited dust particles increases when moving from the outer size to the center. The lateral size of the deposition is around 2 cm which is the size of the hole on which the substrate is placed below.

The deposition of acetylene with 1 sccm input flow resulted in the production of a film on top of the electrode. However, in this case, the film on top was showing also the presence of a layer of dust particles on top of it as shown in figure 5.6 A. The sample deposited in the 2 cm hole resulted in the production of a thick and homogeneous layer made entirely by dust particles.

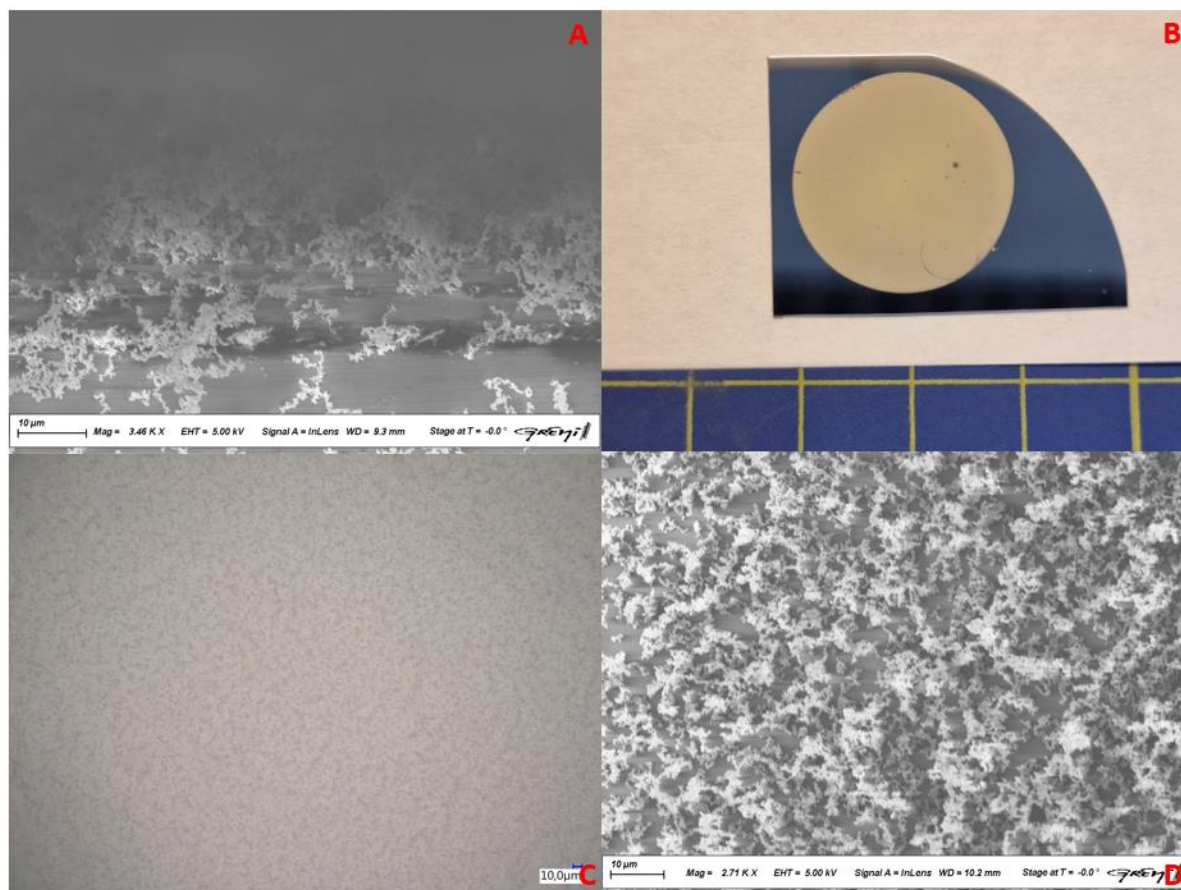


Figure 5.6 In A SEM image of the sample placed on top of the electrode, it is possible to observe dust chains on top of the film. In B, C, D images from the optical microscope of the sample deposited in the 2 cm hole size. A uniform layer of dust is visible.

The deposition of acetylene with 0.5 sccm shows results similar to the case of 1 sccm. The layer of dust particles deposited in the 2 cm hole is in this case much thicker compared to the one obtained with 1 sccm. However, it is less homogeneous.

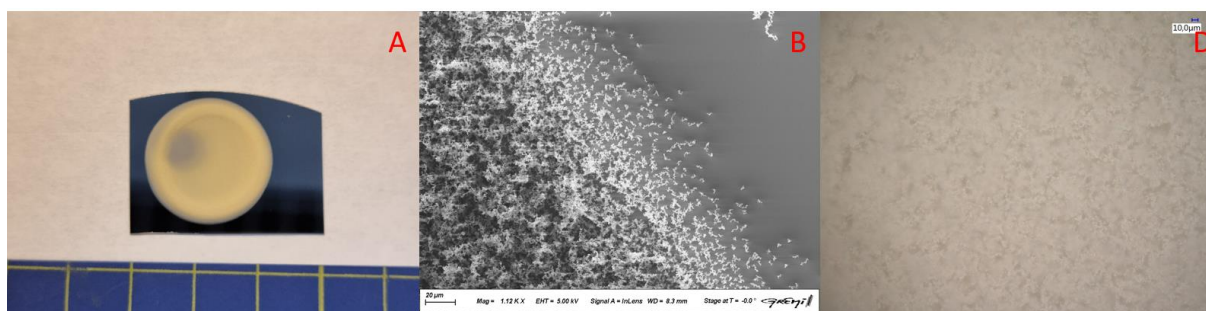


Figure 5.7 Images acquired with camera (A), SEM (B) and optical microscope (C) of the thick dust film deposited with an acetylene input flow 0.5 sccm.

The experiments show that depending on the input flow the result of the deposition process on the samples placed in the holes is mainly a layer of dust particles. The lower the input flow, the thicker is the deposited dust layer. Moreover, the lateral size of the deposition in all cases is equal to 2 cm which is the diameter of the hole below which the substrates are placed. This is opposite to what was observed for the polyaniline deposition. In the aniline case, the lateral size of the deposit was much smaller than the diameter of the hole. This might imply that the species which contribute to the film deposition in the hole are subjected to a different focusing effect, exercised by the hole that acts as a focus lens.

A pumping speed of zero was shown to be a key factor for dust particle production. Experiments with the same parameters but this time with a running pumping system showed: at the end of the process the deposition was visible only for the sample placed on top of the electrode while no signs of deposition were visible on the sample placed in the holes.

The effect of the duty cycle is playing a key role in the production of the dust layers. In the previous experiments, the pulse parameters were: 10ms on/40 ms tot cycle. The same experiments were repeated but this time with a different duty cycle: 5ms on/40 ms tot cycle. The deposition time was doubled in this case in order to have the same amount of plasma on time. By reducing the DC it was possible to avoid the deposition of dust particles on samples placed under the holes. In fact, there was no sign of deposition at all on these samples. Only the sample placed on top of the electrode showed a homogeneous and uniform thin film.

The results obtained with the structured electrode in an acetylene plasma confirm what was stated previously: *“The composition and magnitude of the species fluxes arriving at the substrate and thus the result of the deposition process depends on the discharge parameter (power, pressure, flow rates, duty cycle, electrode distance, etc.)”* and certainly on the chosen monomer. However, independent from the exact mechanisms involved in the deposition process and independent from the monomer chosen, the experimental results show that the

“structured electrode” can be used to tune the material composition of deposited films. They are an innovative tool that can be used - with different monomers - to better control the process of plasma-based thin film deposition. The results of this work will serve as the basis for further studies aimed at realizing the full potential of this method.

5.4 Enrobing of nanostructured materials

It was already mentioned that the plasma-based deposition of thin films is a useful technique to deposit polymer films on a large variety of different surfaces. One specific advantage of plasma-based deposition techniques concerns the conformal coating of structured surfaces. One important example is the enrobing of carbon-based nanomaterials as e.g. carbon nanowalls.

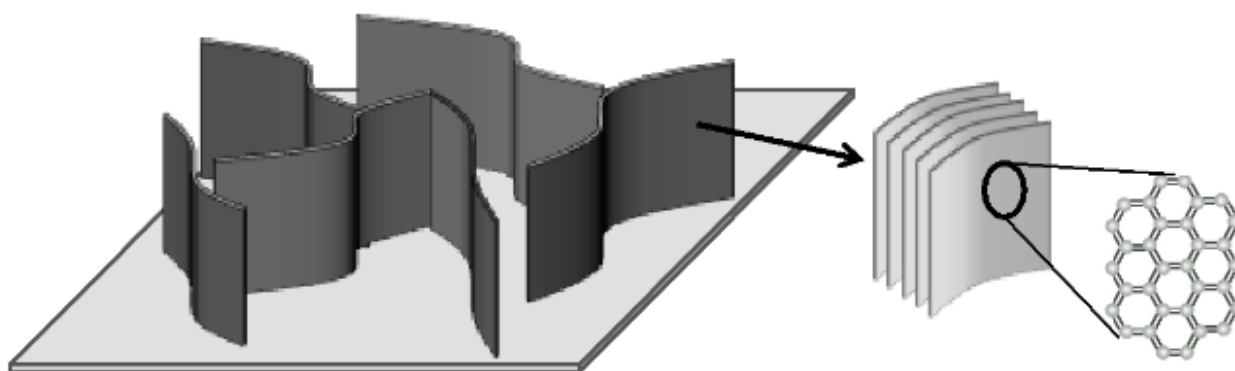


Figure 5.8 Scheme of representation of the Carbon nanowalls structure (Graphene Nanowalls)[2].

The Carbon nanowalls (CNWs) used in this work are synthesized through plasma deposition in a capacitively coupled RF plasma and consists of small graphene structures vertically orientated and deposited on a Silicon/aluminum/nickel substrate (see Ph.D. A. Jagodar). The deposition process of plasma polyaniline allows to cover and enrobe the CNWs structure, preserving the morphology of the nanostructured carbon layer.

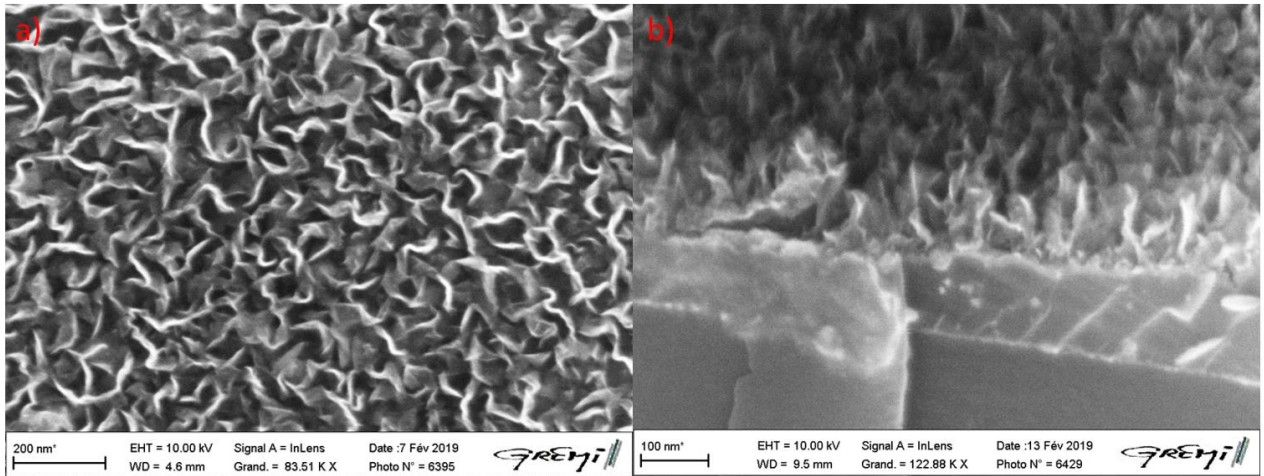


Figure 5.9 SEM images of top view (a) and cross-view (b) of Carbon nanowalls deposited through plasma deposition.

Figure 5.9 shows the SEM images of CNWs from top view a) and cross-view b). The CNWs show a length of around 200 nm and a height of around 100 nm. The carbon nanowalls were then covered with a thin film using an Ar/aniline mixture. The polymer thin film enrobing the CNWs structure is shown in figure 5.10.

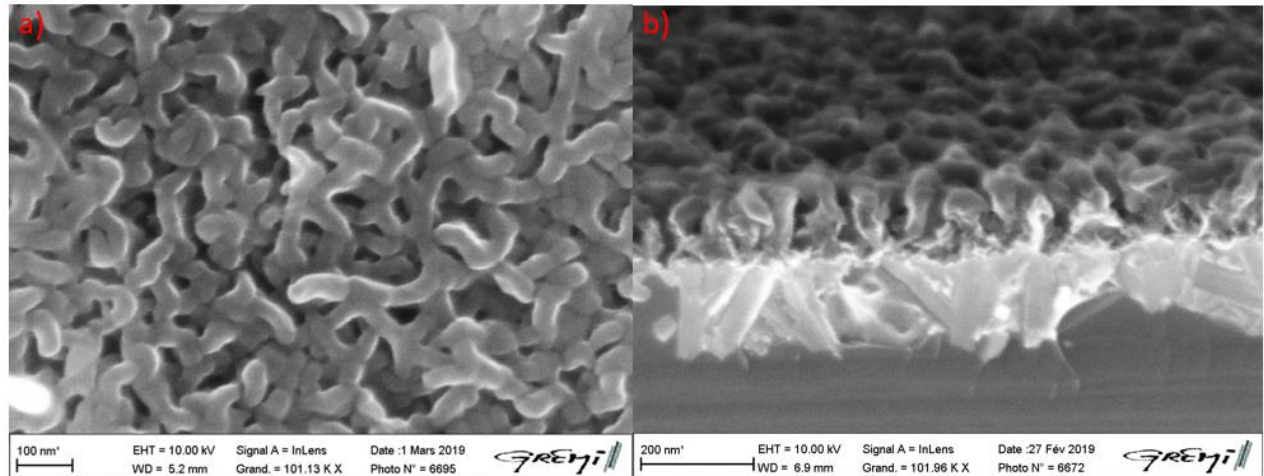


Figure 5.10 SEM images of top view (a) and cross-view (b) of Carbon nanowalls enrobed with thin Pani film deposited through plasma polymerization.

These images demonstrate the usefulness of plasma-based deposition techniques: they allow the deposition of thin films that follow the contours of the underlying structure, preserving in this way the surface morphology.

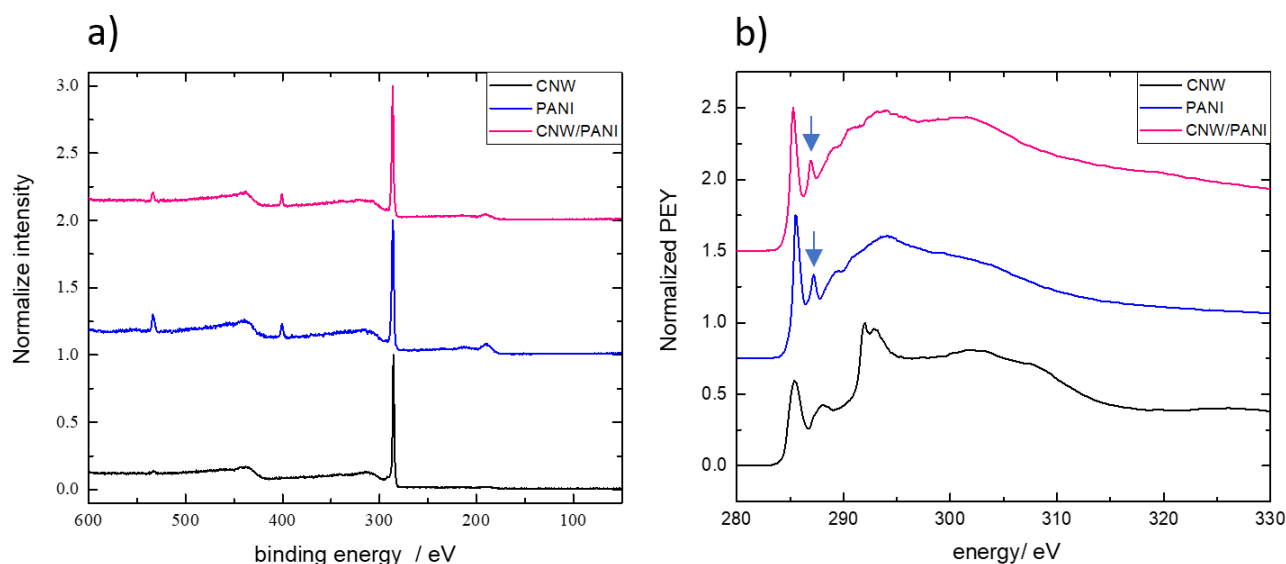


Figure 5.11 Comparison of XPS (a) and NEXAFS C K edge (b) spectra of CNW only (black), Pani only (blue), and CNW/Pani.

Figure 5.11 shows the XPS spectrum (a) and the NEXAFS spectrum (b) of CNW's only (black), Pani only (blue), and CNW covered with Pani (red).

The spectra in red (referring to Pani films on top of CNWs) show the same features as the spectra in blue (referring to Pani films deposited on Si-wafers). This confirms that the covering of the CNW's has been done successfully. (The NEXAFS spectrum of Pani (blue) and Pani on CNWs (shows an additional sharp peak at 286.7 eV referring to Carbon bonded to Nitrogen (blue arrow)).

The results confirm the great potential of plasma based deposition techniques for the conformal coating of nanostructured materials which are relevant for different applications such as supercapacitors or biosensors.

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Resume de la these

La polymérisation par plasma peut être définie de manière générale comme une technique permettant la production de "matériaux polymères" par l'application de plasmas [1]–[3]. Le premier développement de cette technique a commencé par des études concernant la formation de composés organiques dans des systèmes sous vide sous l'effet de décharges électriques. Les revêtements qui en résultaient étaient considérés au début comme des sous-produits indésirables et il a fallu plusieurs décennies, jusqu'aux années 1960 avec Goodman, pour reconnaître ce procédé comme une méthode utile pour synthétiser des matériaux polymères. Il a fallu plus de 20 ans pour que la communauté scientifique reconnaisse que la polymérisation par plasma n'est pas simplement un "autre" procédé de polymérisation, mais une technique complémentaire utile qui permet d'obtenir des caractéristiques nouvelles, intéressantes et uniques que les procédés de polymérisation conventionnels ne pouvaient pas atteindre, comme une stabilité plus élevée, l'insolubilité et l'adhésion à tout type de substrat.

Au centre de tout processus plasma se trouve, bien entendu, le plasma ou, comme il serait préférable de le dire dans ce contexte, la décharge gazeuse. Un plasma peut être défini grossièrement comme un gaz quasi-neutre partiellement ou totalement ionisé, c'est-à-dire un gaz qui contient des ions et des électrons positifs (et parfois négatifs) en plus d'atomes ou de molécules neutres, et qui est globalement neutre à des échelles inférieures à la longueur de Debye.

Les polymères conducteurs [35]–[39] sont une classe de polymères conjugués qui ont attiré l'attention de la communauté scientifique au cours des 50 dernières années en raison de leurs propriétés attrayantes (à la limite entre l'état de conducteur et de semi-conducteur) qui les rendent appropriés pour une large gamme d'applications allant de la réalisation d'électrodes, de DEL organiques [40]–[42] le stockage d'énergie (supercondensateurs et batteries) [43]–[47] de transistors [48]–[50] des applications photovoltaïques [51], [52] des revêtements anticorrosion [53] et aussi des capteurs [54]–[57].

Parmi la grande famille des polymères conducteurs, la polyaniline se distingue par sa haute conductivité électrique, ses propriétés oxydantes, sa stabilité thermique et environnementale et sa facilité de mise en œuvre [58], [59]. La polyaniline a été le premier polymère conducteur à être découvert (en 1840 par Fritzsche) [60]. mais ce n'est que récemment, au cours des 20 dernières années, qu'elle a suscité l'intérêt de la communauté scientifique suite à l'attribution du prix Nobel de chimie à Heeger, MacDiarmid, et Shirakawa [61]–[63] qui, avec

leurs études sur les polymères intrinsèquement conducteurs, ont ouvert un nouveau domaine d'applications technologiques.

La polyaniline ou PANI peut exister sous une variété de formes qui peuvent être différentes en termes de propriétés chimiques et physiques. Selon la méthode de synthèse, la base de polyaniline peut être produite sous trois formes principales : la forme entièrement réduite (leucoemeraldine), la forme partiellement réduite (émeraldine) et la forme entièrement oxydée (pernigraniline) [64].

La structure chimique principale de la polyaniline est présentée dans la figure 1.1

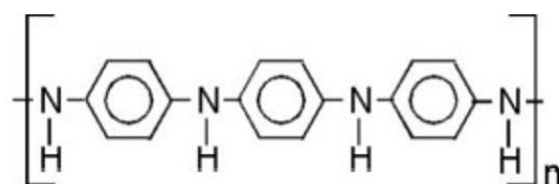


Figure 1.1 Structure généralisée de la base polyaniline.

En particulier, l'utilisation d'une méthode de synthèse complexe telle que la polymérisation par plasma rend ce processus encore plus difficile à comprendre.

Dans le cadre de ce doctorat, ce défi complexe a été relevé et est devenu l'objectif de ce travail. La clarification des différents mécanismes impliqués dans la polymérisation par plasma devrait fournir de nouveaux moyens de contrôler le processus et permettre la production de films qui peuvent être adaptés à l'application souhaitée en termes de structure et de propriétés.

Les étapes/points clés qui seront abordés dans ce travail sont les suivants :

- la synthèse de la polyaniline de plasma par PECVD
- le contrôle du processus de dépôt par l'utilisation de nouvelles techniques (électrodes structurées artisanales)
- la caractérisation des films minces produits
- le dopage des film

Chambre expérimentale

La chambre expérimentale dans laquelle le processus de plasma est réalisé consiste en un réacteur construit sur mesure qui fonctionne avec un système de plasma RF à couplage capacitif ($f=13,56$ MHz).

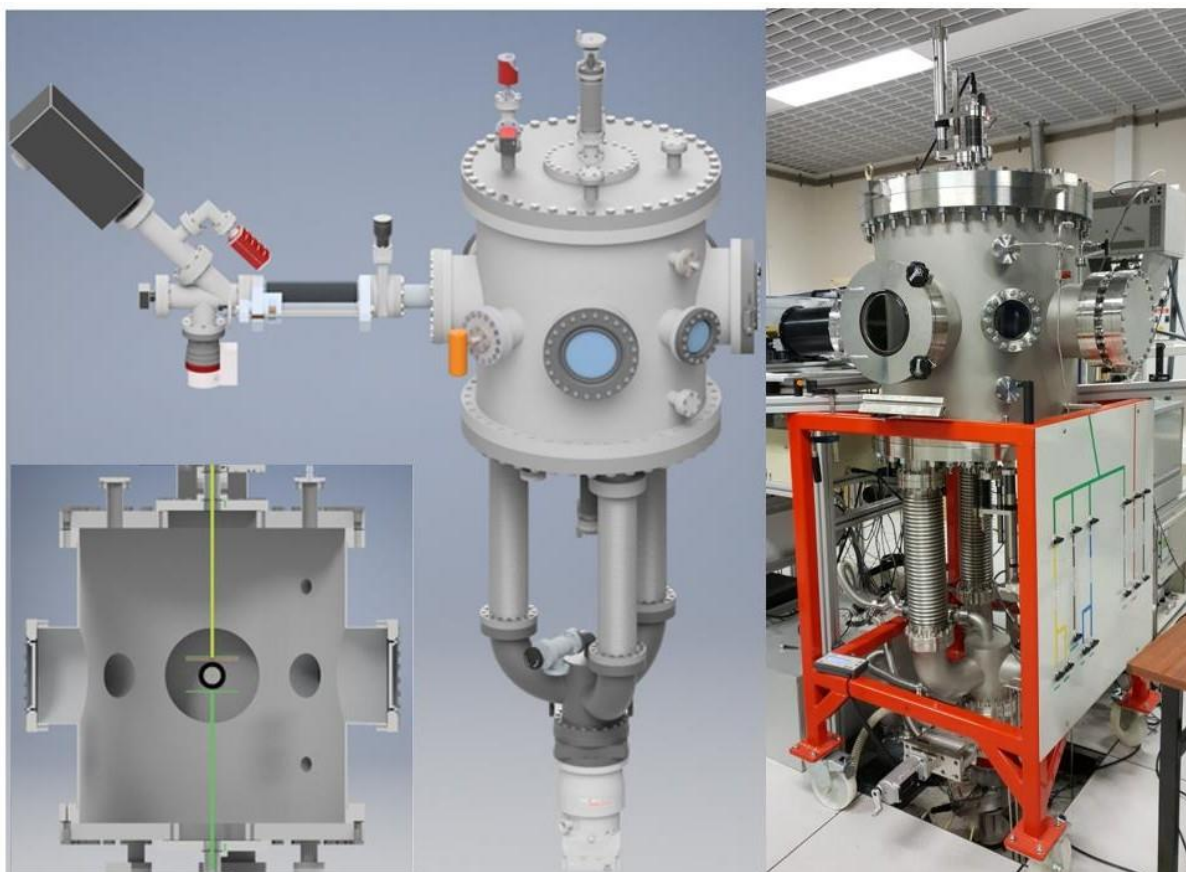


Figure 1.2 Schéma du montage expérimental utilisé dans ce doctorat pour le dépôt de film mince par polymérisation plasma.

Polymérisation par plasma

La polymérisation par plasma, comme nous l'avons déjà dit au chapitre 1, est une technique qui permet la synthèse de différents produits tels que des films minces ou des nanoparticules.

Le processus commence par la dissociation par impact électronique des molécules mères (dans notre cas, le monomère d'aniline), ce qui entraîne la production d'une grande variété de fragments différents tels que des neutres, des radicaux et des ions positifs et négatifs. [1]–[5]. Toutes ces espèces formées à l'intérieur du plasma peuvent réagir entre elles dans des

processus de polymérisation ultérieurs, qui peuvent se produire à la fois dans le volume du plasma et sur les surfaces exposées au plasma. Ces réactions conduisent à la formation des principaux produits de la polymérisation par plasma : film mince et nanoparticules.

Les détails de chaque processus plasma dépendent fortement des paramètres expérimentaux, qui sont choisis avant l'expérience. Un exemple important est l'impulsion du plasma qui peut être utilisée, si les paramètres de l'impulsion sont correctement choisis, pour éviter et bloquer partiellement la formation de nanoparticules dans le volume du plasma. L'une des principales différences entre un plasma fonctionnant en continu et un plasma pulsé concerne le rôle des ions négatifs qui sont censés jouer un rôle important dans la formation des nanoparticules. Dans un plasma fonctionnant en continu, les ions négatifs restent confinés dans le volume du plasma en raison du potentiel positif du plasma (positif par rapport aux parois entourant les plasmas). Dans la phase d'extinction d'un plasma pulsé, cependant, les ions négatifs peuvent s'échapper de la décharge [1], [6]. (si le temps d'arrêt du plasma est suffisamment long), interrompant ainsi les réactions de polymérisation qui sont potentiellement entraînées par les ions négatifs.

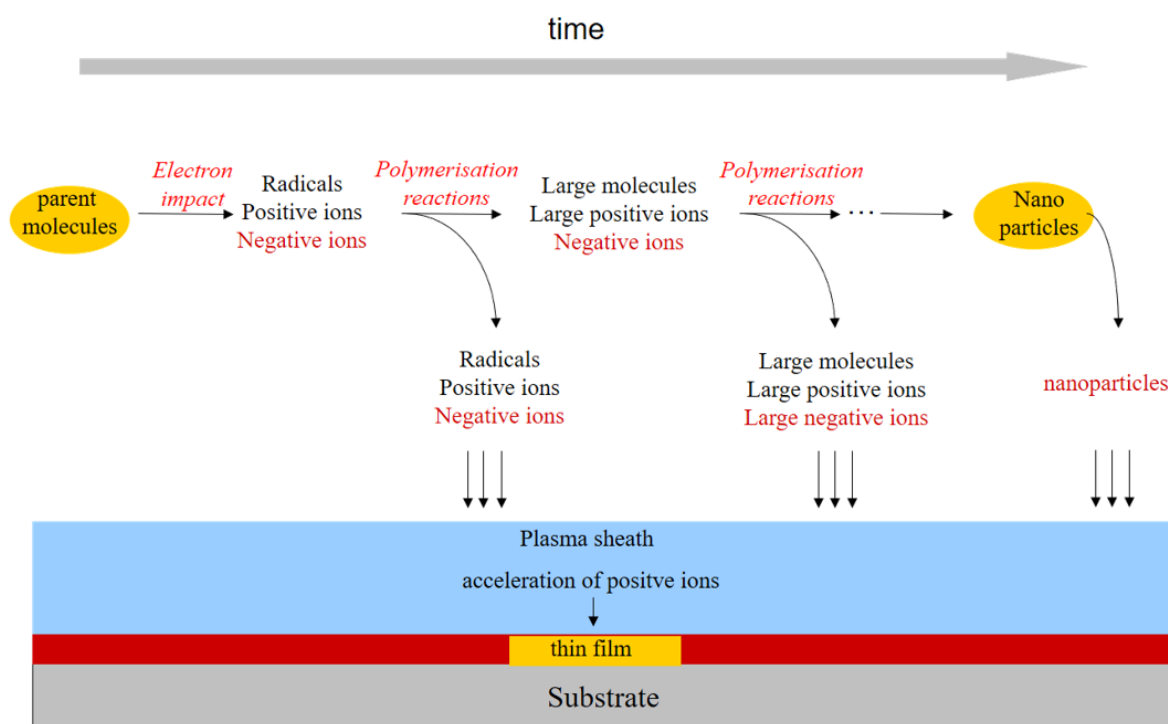


Figure 1.3 Croquis des interactions possibles entre les gaz et les surfaces qui peuvent se produire dans un plasma réactif.

En raison du nombre potentiellement élevé d'espèces et de réactions différentes impliquées dans le processus plasma, il est facile de comprendre que la polymérisation par plasma est un processus très complexe. Une meilleure compréhension du rôle que jouent les différents types d'espèces (radicaux neutres, ions positifs et négatifs) dans le processus de polymérisation est donc essentielle pour contrôler les produits obtenus, qu'il s'agisse de nanoparticules ou de films minces.

La principale contribution de ce travail de doctorat concerne la production de films minces polymères provenant de mélanges de gaz argon/aniline mais aussi d'aniline pure et d'étudier comment il est possible de modifier les propriétés des films minces de manière contrôlée.

Le dépôt est effectué dans un mélange de Ar et d'Aniline avec un rapport de 20:1 (20 sccm Ar/1 sccm Aniline). La pression est stabilisée à 0,18 mbar avant chaque processus pour augmenter la reproductibilité. La puissance moyenne d'entrée appliquée varie entre 2 et 10 W et la pulsation appliquée est $f=25\text{Hz}$ avec un rapport cyclique $DC=0.5$ (20 ms on time/40 ms tot cycle). Le processus de temps de déposition a été choisi en fonction de l'épaisseur désirée du film.

Les films déposés apparaissent d'un point de vue macroscopique assez uniformes et

homogènes. Selon l'épaisseur et les propriétés du film déposé, la couleur du film peut changer.

Analyse FTIR et NEXAFS de films minces de polyaniline polymérisés par plasma

Pour évaluer la composition des films, des spectroscopies FTIR et NEXAFS ex-situ ont été réalisées sur des échantillons déposés sur des plaquettes de silicium intrinsèque. L'épaisseur des films est d'environ 200 nm.

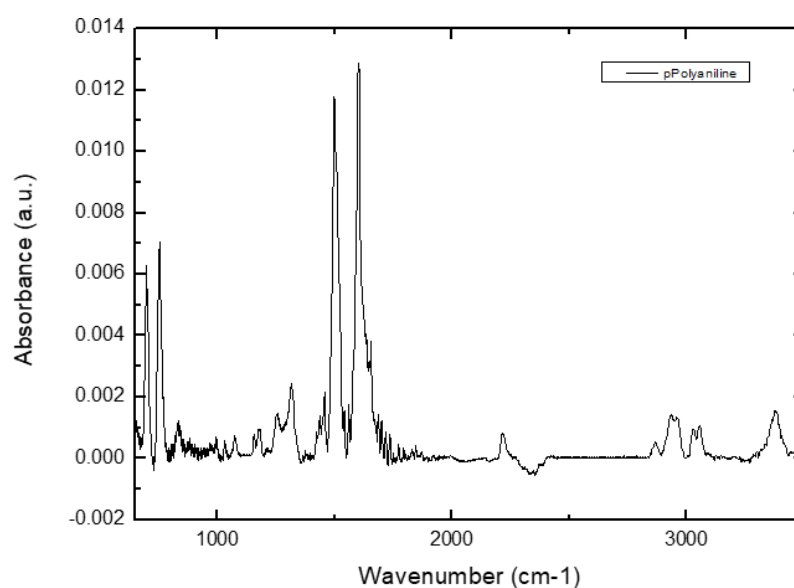


Figure 1.4 Spectres FTIR ex-situ de polyaniline polymérisée par plasma.

Le spectre infrarouge des films déposés est assez complexe (voir figure 1.4) et les principales caractéristiques sont présentées dans le tableau suivant

Vibration du lien	Nombre d'onde (cm⁻¹)
Vibration et déformation des N-H	3325/3379
étirement C-H insaturé	3020/3060
Vibration aliphatique C-H saturée	2920/2960 (ou 2800-3080)
C≡N étirement	2212-2215
étirement C=O de la cétone	1684-1673
Alkènes (non aromatiques) C=C étirement	1600 & 1670
Vibration et déformation des N-H	1633
Allongement C=C des cycles quinoïdes	1589-1600
étirement C=C des cycles benzénoïdes	1496-1500
étirement C=C des cycles benzénoïdes	1403
étirement C-N (QBQ)	1370-1376
Interactions C=C	1316
étirement C-N du cycle aromatique (amine aromatique)	1306-1317

Interactions C-C	1173
Absorption de type électronique de N=Q=N	1165
étirement C-C de la chaîne alkyle	1100
Anneau benzénique monosubstitué	730-770 & 690-710
Cycle aromatique disubstitué en ortho	735-770
Cycle aromatique méta disubstitué	690-710 & 750-810 & 880
Cycle aromatique disubstitué en para	800-840

Dans les spectres présentés dans la figure 1.4, les principaux pics proéminents donnant lieu aux caractéristiques d'absorption IR les plus fortes sont le pic à 1600 cm^{-1} lié à l'étirement C=C de l'anneau quinoïde et le pic à environ 1500 cm^{-1} lié à l'étirement C=C de l'anneau benzénoïde. La présence de ces deux structures indique une structure proche de celle de l'émeraude ou de la leucoéméraldine (chaînes polymériques mi-réduites et mi-oxydées) [11]–[13]. D'autres caractéristiques importantes à considérer sont les pics à 3379 cm^{-1} liés à la vibration N-H, à 3020 cm^{-1} liés à la contribution de l'étirement C-H aromatique, et à 2930 cm^{-1} attribués à l'étirement C-H aliphatique. Un cas particulier est le pic à environ 2220 cm^{-1} qui est attribué à la structure $\text{C}\equiv\text{N}$ (groupes nitrile) qui n'est pas visible dans le spectre de la polyaniline synthétisée avec des méthodes conventionnelles telles que la synthèse chimique ou électrochimique, mais qui est généralement présent dans la polyaniline polymérisée par plasma. Le cas analogue est le pic à 1451 cm^{-1} qui est attribué à la déformation C-H.

La spectroscopie NEXAFS est une technique complémentaire à l'IRTF et fournit des informations précieuses sur la composition et le type de liaisons du matériau. Les principales caractéristiques du bord C-K (figure a1.5) et du bord N-K (figure b1.5) sont présentées dans les tableaux suivants :

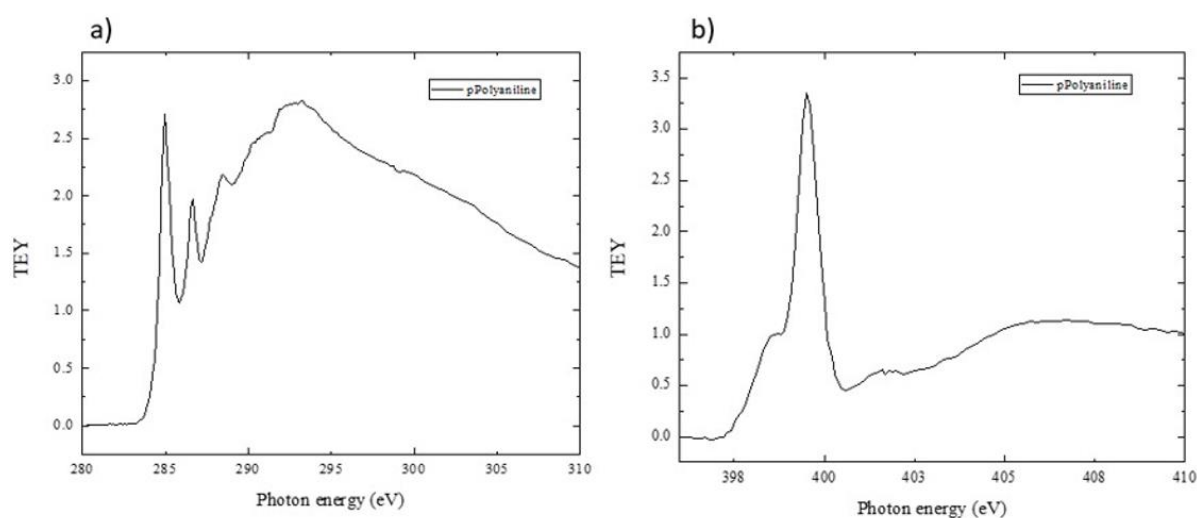


Figure 1.5 Spectres NEXAFS du bord C-K (a) et du bord N-K (b) de la polyaniline polymérisée par plasma.

C K Edge	
Obligation	Énergie des photons (eV)
Résonance π^* de C=C (aromatique)	284.9 - 285.5
π^* résonance de C $\equiv$ N / C=N	286.7
Résonance σ^* de C-H	287.4
Résonance π^* de C=O	288.8
Résonance σ^* de C-N	290
résonance σ^* de C-C	291.7
résonance σ^* de C-C	293.2
Résonance σ^* de C-O	294.3
résonance σ^* de C-C	295.8
σ^* résonance de C-O / C-C	298
σ^* résonance de C=C	303.2
Résonance σ^* de C=C/C=O	310.3
N K Edge	
Obligation	Énergie des photons (eV)
Résonance π^* de N=C	398.8
La résonance π^* de N $\equiv$ C	399.7
Résonance σ^* de N-H	402.6
Résonance σ^* de N-C	405.4
Résonance σ^* de N-C	408
Résonance σ^* de N=C	411.1
résonance σ^* du N $\equiv$ C	423.3

Les spectres NEXAFS confirment la présence des groupes caractéristiques présents dans le spectre FTIR.

Comme dans le cas du spectre FTIR, dans le spectre NEXAFS, le principal pic proéminent situé à 285 eV est attribué à la résonance π^* de C=C dans les cycles aromatiques. D'autres contributions importantes habituellement trouvées dans la polyaniline sont C-C, C-N, C=N et C-H dans le cas des spectres de bord C-K et le N-H (imine), N-H₂

(ammine) et $\text{C}\equiv\text{N}$ (nitrile) dans le cas des spectres de bord N-K.

Procédé de dépôt assisté par une méthode de filtrage

Pour étudier et contrôler le flux d'espèces vers le substrat, une électrode "à canal" personnalisée, conçue pour utiliser une électrode de masse, a été réalisée. La figure 1.6 montre un croquis de l'"électrode à canaux" qui est utilisée pour contrôler, dans une certaine mesure, le flux d'espèces atteignant le substrat. L'électrode est constituée d'une plaque métallique, caractérisée par son épaisseur l et par des trous/canaux, percés dans la plaque métallique, caractérisés par leur diamètre d .

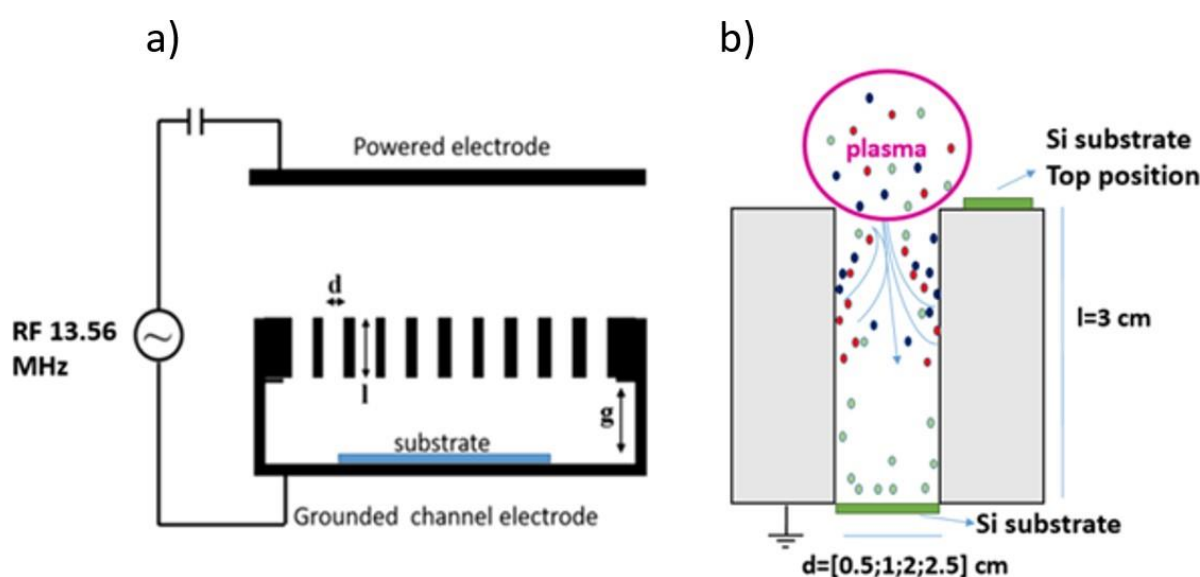


Figure 1.6 a) Schéma général de l'électrode à canal et b) agrandissement d'un seul canal. Les substrats sont positionnés directement sous les trous (distance entre l'échantillon et l'électrode $g = 0 \text{ cm}$). Dans l'expérience présentée ici, la plaque métallique d'une épaisseur de $l = 3 \text{ cm}$ ne comporte que 4 trous/canaux d'un diamètre de 0,5, 1, 2 et 2,5 cm. Pour évaluer l'effet des trous, une plaquette de référence est placée sur le dessus de la plaque métallique pendant les expériences.

Résumé

Ce chapitre expérimental a pour but de contrôler le flux de différentes espèces vers la surface et de contribuer ainsi aux propriétés des films minces déposés par plasma. Ceci est réalisé en utilisant une conception particulière d'"électrode à canal" qui est facile à mettre en œuvre dans

tout réacteur donné à des fins scientifiques ou industrielles. Comme étude de cas, le dépôt à partir d'un plasma d'aniline/argon a été étudié. La caractérisation du matériau au moyen des spectres FTIR et NEXAFS montre que cette conception d'électrode permet effectivement d'accorder la chimie du matériau déposé du caractère hautement aromatique au caractère aliphatique. Un résultat similaire est observé en recouvrant l'électrode d'une grille en acier inoxydable, qui sert à réduire préférentiellement le flux d'ions positifs arrivant sur le substrat. Ceci démontre le rôle important des ions positifs dans le processus de dépôt dans notre configuration et notre chimie particulière, affectant non seulement la vitesse de dépôt mais aussi la composition des films déposés.

Il convient toutefois de mentionner que la composition et l'ampleur des flux de neutres et d'ions pour une chimie donnée dépendent fortement des paramètres de décharge. En particulier, les radicaux neutres avec un coefficient d'adhérence plus faible pourraient être sujets à des pertes dues au pompage (un canal de perte qui dépend de la vitesse de pompage et du volume réel de la chambre de traitement du plasma) et à des pertes dues à la fragmentation par impact des électrons (un canal de perte qui dépend de la température des électrons, de la densité des électrons et du temps de séjour). Par conséquent, le rôle des radicaux neutres et, inversement, le rôle des ions positifs dans le processus de dépôt peut dépendre fortement des paramètres et peut donc varier dans différentes expériences.

Nouveau contrôle amélioré du dépôt de polyaniline par plasma

L'étape suivante est une approche mixte qui concerne à la fois le contrôle de la formation des espèces réactives formées à l'intérieur du plasma en agissant sur les paramètres expérimentaux (puissance, pression, mélange gazeux et pulsation) et également le contrôle du flux d'espèces arrivant sur le substrat en employant différents systèmes d'électrodes conçus par notre groupe de recherche. Le premier effet est un changement dans la composition du film comme le montre la figure 1.7.

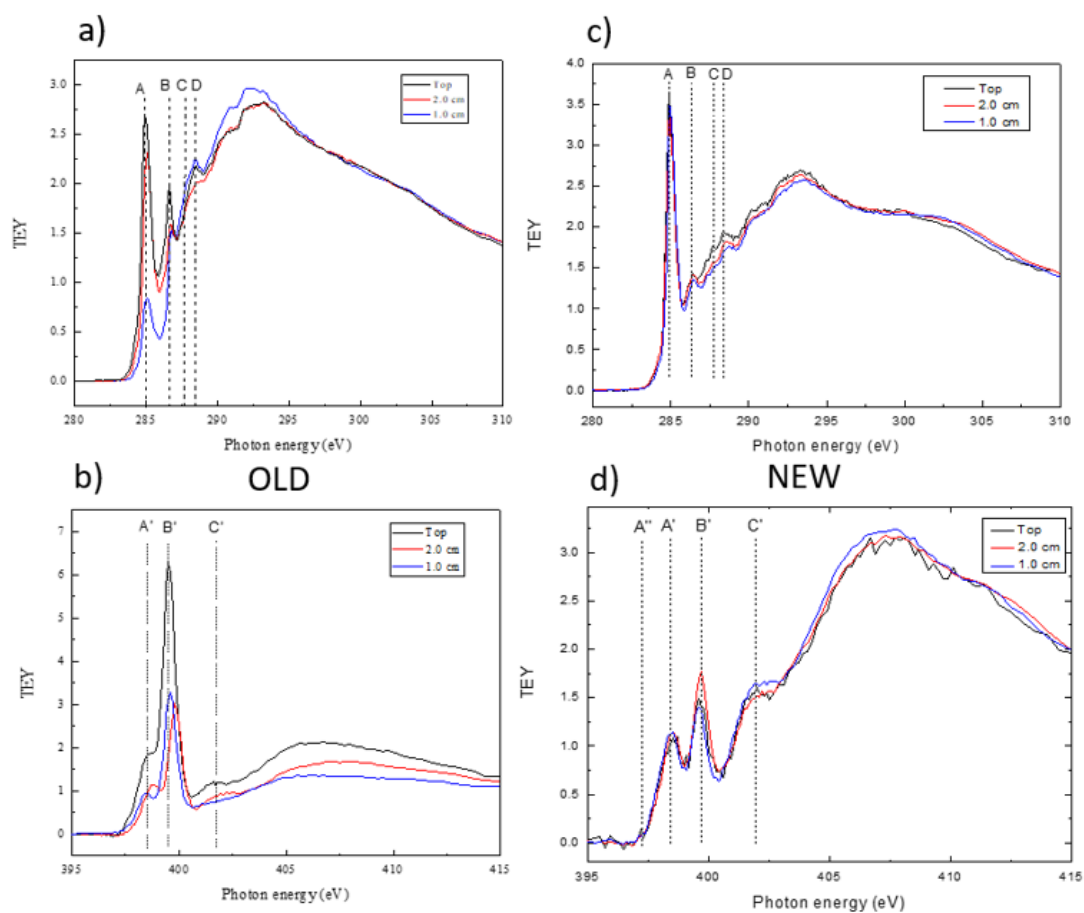


Figure 1.7 NEXAFS : comparaison du bord C K et du bord N K des échantillons déposés à travers l'électrode structurée avec l'ancien (a et b) et le nouveau protocole de dépôt (c et d).

Le deuxième effet de ce nouveau dépôt concerne la morphologie/structure de surface des films déposés dans les trous des électrodes structurées (voir figure 1.8).

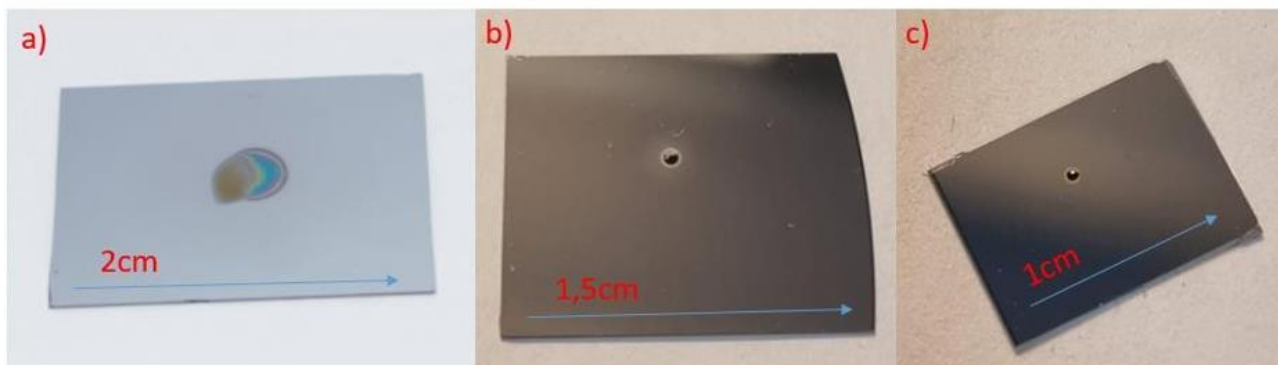


Figure 1.8 d'échantillons déposés dans les différents trous : a) dans les trous de 2 cm, b) dans les trous de 1 cm et c) dans les trous de 0,5 cm.

Résumé

Le changement du protocole de dépôt avec le choix des nouveaux paramètres expérimentaux (puissance, cycle de travail, vitesse de pompage, et en particulier le mélange gazeux) a conduit à un nouveau type de dépôt qui diffère fortement des anciennes expériences de dépôt réalisées dans des plasmas Ar/aniline avec leurs conditions de plasma plus dures. Selon les spectres FTIR et NEXAFS, la qualité des films déposés a été fortement améliorée avec une grande réduction du pic de nitrile à 2225 cm^{-1} . De plus, d'après le rapport des pics dans les spectres FTIR, la structure de la polyaniline des films déposés est beaucoup plus proche de la structure émeraude alors que la structure de la polyaniline des anciennes expériences était plus proche de la structure leuco-émeraude.

Dopage des films minces de polyaniline

L'une des principales propriétés attrayantes des polymères conducteurs et en particulier de la polyaniline est la possibilité d'améliorer les propriétés électriques des films par le biais du processus de dopage.

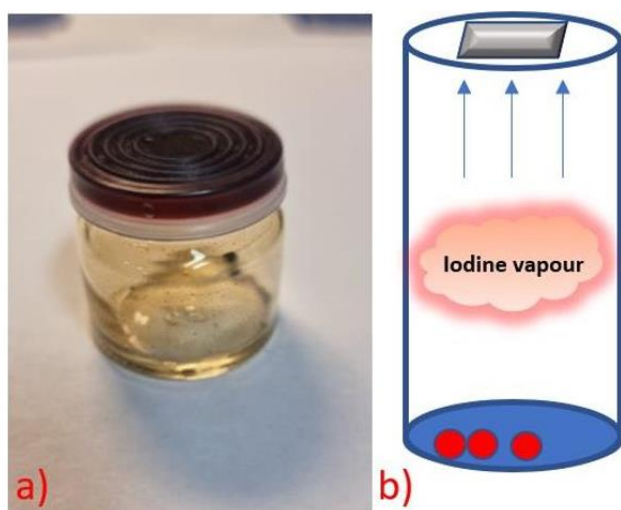


Figure 1.9 Image et croquis du système utilisé pour le dopage. Les sphères d'iode placées au fond du récipient en verre s'évaporent et créent une atmosphère de vapeur d'iode qui dope l'échantillon cible placé sur la face supérieure du récipient.

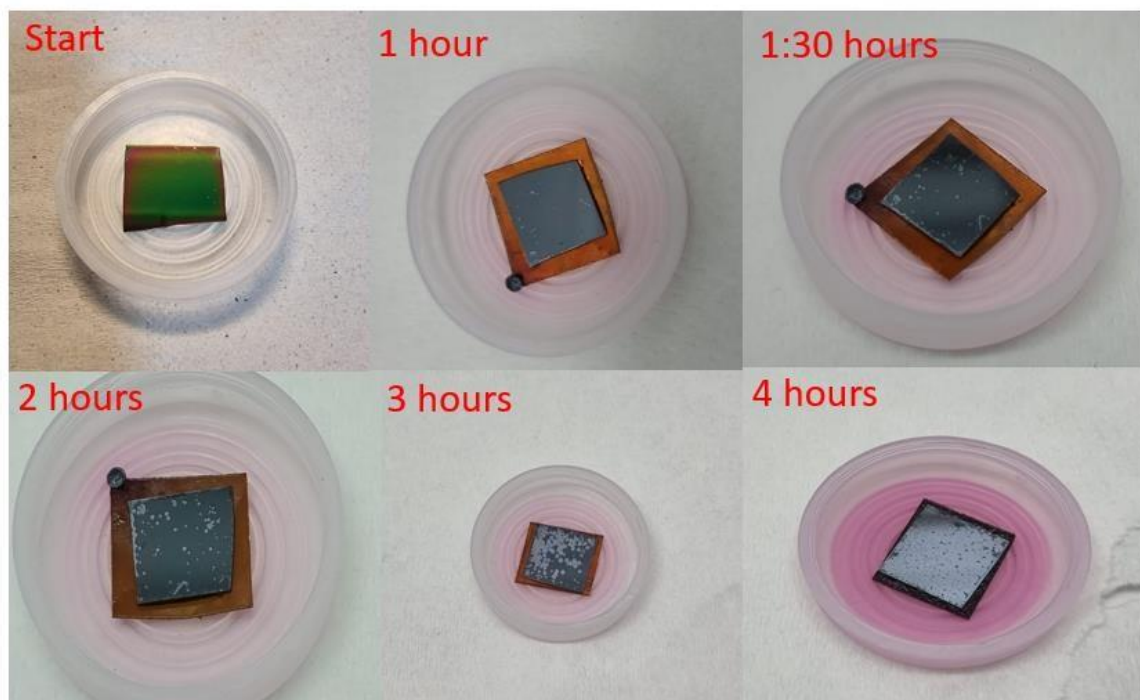


Figure 1.10 Images de l'évolution de la morphologie de l'échantillon dopé dans le temps

Le processus de dopage de l'échantillon a été suivi dans le temps. Comme le montre la figure 1.10, la morphologie de l'échantillon change au fur et à mesure que le temps d'exposition de l'échantillon à la vapeur d'iode augmente. Après 1 heure d'exposition, la couleur du film change complètement en raison de l'incorporation de l'iode à l'intérieur des films minces. Dès que le temps d'exposition augmente, des petites *structures de bulles* commencent à apparaître à la surface des films minces. Le nombre de *structures de bulles* augmente jusqu'à ce que, 4 heures après le début du processus, le film disparaisse presque complètement de la surface. Le processus de dopage à l'iode semble créer un processus d'écrasement du film sur la surface, en particulier, les microstructures sur la surface de l'échantillon à la fin du processus (4 heures) semblent faites de grappes de films enroulés et pliés sur elles-mêmes. Le processus de dopage tend probablement à créer des fissures et des défauts sur le film de surface, qui commencent à s'enrouler sur eux-mêmes, en raison de la contrainte mécanique créée par l'incorporation d'iode dans la structure du film.

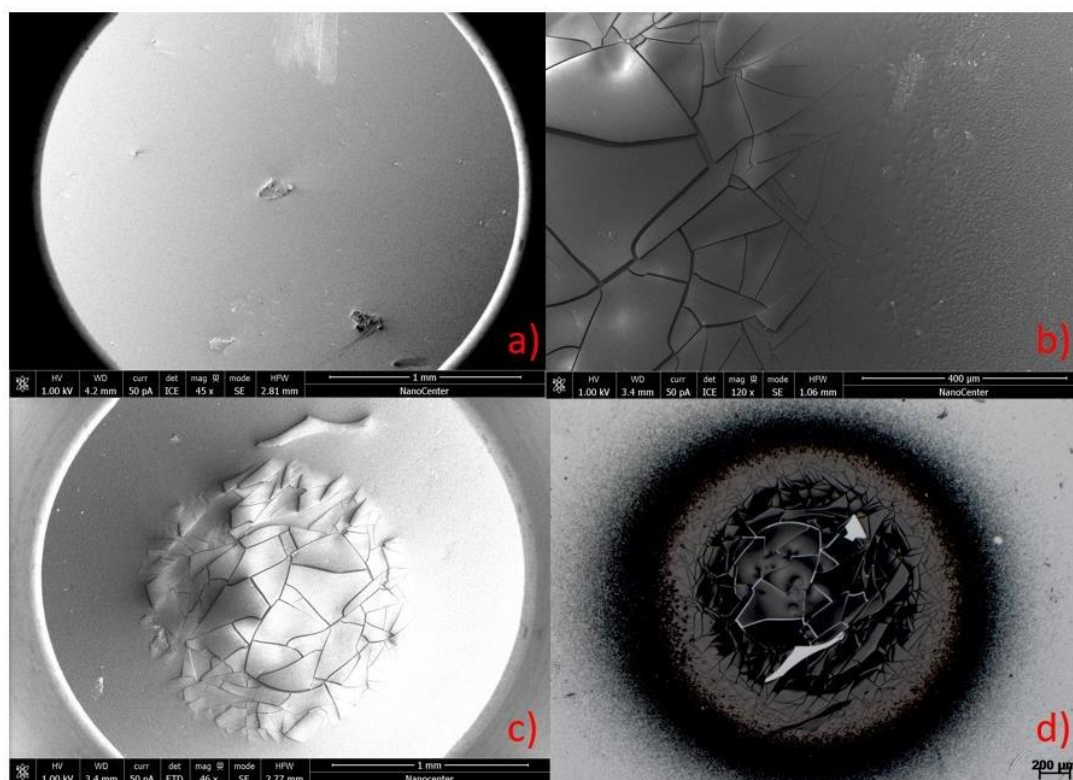


Figure 1.11 SEM (a-b-c) et images au microscope optique (d) de la surface d'un échantillon dopé de 1 cm après exposition à l'iode.

Dans la figure 1.11, il est possible d'observer la formation de fissures du film lorsqu'elles sont dues à la contrainte créée par l'incorporation d'iode. En outre, la surface du film présente la formation de motifs ou une augmentation de la rugosité. Ce phénomène est également souvent décrit dans la littérature et se produit lorsque les structures qui forment les films de polyaniline s'agglomèrent ensemble en raison de l'incorporation d'iode, créant une contrainte qui entraîne la formation d'une fissure aux joints de grains.

Dario Sciacqua

Enrobage de carbone avancé par des polymères

Résumé :

Cette contribution traite des processus de polymérisation dans une décharge RF à couplage capacitif fonctionnant dans différents mélanges (Ar/aniline, aniline pure, acétylène) pour la production de films polymères minces. Le rôle des différentes espèces impliquées dans le processus, par exemple les ions positifs, les ions négatifs, les neutres pour le dépôt de films minces dans ces mélanges gazeux en fonction de différents paramètres expérimentaux (puissance, pression, rapport cyclique, débit, taux de pompage) est l'objectif principal de ce travail. Plusieurs méthodes expérimentales, y compris différentes électrodes maison (électrode structurée, électrode à coupelle), ont été employées pour séparer et distinguer partiellement les contributions des différentes espèces au cours du processus ainsi que la possibilité de les empêcher (filtrer) d'atteindre le substrat. Le filtrage des espèces produites dans le plasma peut offrir une nouvelle perspective pour le contrôle des processus de dépôt par plasma. La dernière partie du travail concernait le processus de dopage des films déposés et l'étude de leur stabilité. L'analyse du plasma a été réalisée à l'aide de plusieurs techniques comprenant l'interférométrie à micro-ondes, la spectrométrie de masse et le FT-IR in situ. Les matériaux déposés ont été étudiés par FT-IR, NEXAFS, XPS, ellipsométrie et microscopie optique.

Mots clés : Plasma, Polymères, Polyaniline, ...

Polymer enrobing of advanced carbon

Summary :

This contribution deals with polymerization processes in a capacitively coupled RF discharge operated in different mixtures (Ar/aniline, pure aniline, acetylene) for the production of thin polymer films. The role of the different species involved in the process e.g. positive ions, negative ions, neutrals for the deposition of thin films in these gas mixtures as a function of different experimental parameter (power, pressure, Duty Cycle, flow, pumping rate) is the main focus of this work. Several experimental methods including different home made electrodes (structured electrode, cup electrode) have been employed to separate and partially distinguish the contributions of different species during the process as well as the possibility to prevent (filter) them to reach the substrate. The filtering of species produced in the plasma may give a new perspective for the and control of plasma deposition processes. The last part of the work involved the process of doping of the deposited films and the study of their stability. Plasma analysis have been done by means of several techniques involving microwave interferometry, mass spectrometry and in situ FT-IR. The deposited materials have been investigated by FT-IR, NEXAFS, XPS, Ellipsometry and optical microscopy.

Keywords : Plasma, Polymers, Polyaniline ...



GREMI 14 Rue d'Issoudun, 45067 Orléans,
France

