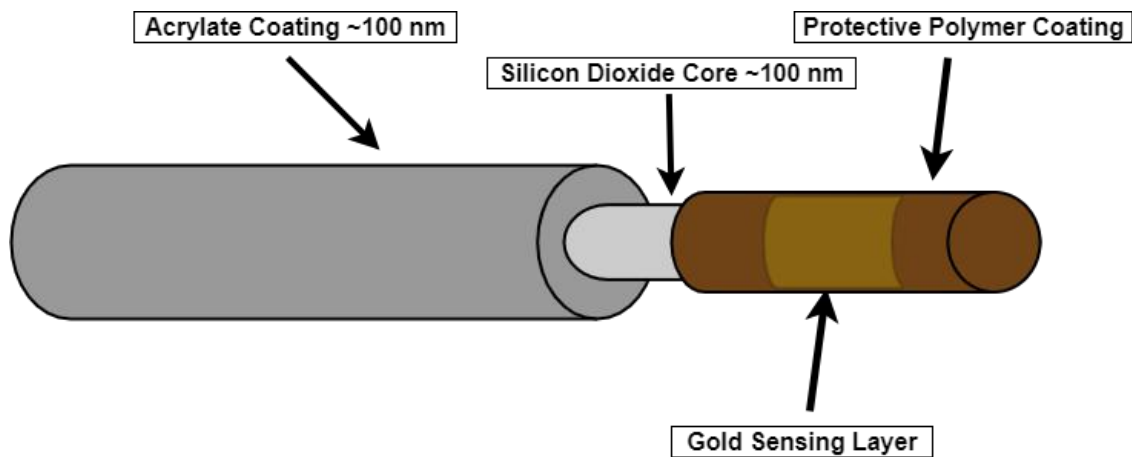




Development of a polymeric dip coating procedure for nanosplasmonic fiber optic sensors

Utilizing polymers for fiber sensor coatings in lithium-ion batteries

Master's thesis in Materials Chemistry

Simon Lindholm

MASTER'S THESIS 2020

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Department of Chemistry and Chemical Engineering
Division of Polymer Technology
CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden 2020

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Abstract

It is possible to increase the charging rate and the effective energy density of Lithium-ion batteries by using Au/SiO_2 Nanoplasmonic fiber optic sensors to accurately measure the physical and chemical state of the battery. These fiber sensors are placed inside the battery and therefore need to have high chemical resistance to withstand the harsh battery environment. The chemical resistance of the fiber sensor can be improved by applying a polymeric coating to it. One way of applying such a coating would be with a dip coating procedure.

A dip coating procedure utilizing a polyvinylidene fluoride co hexafluoropropene copolymer was produced during the course of this project. An attempt to produce a similar dip coating procedure utilizing a polypropylene grafted maleic anhydride copolymer was also made which proved unsuccessful. The PVDF-HFP dip coating procedure was used to consistently manufacture polymer coatings with a thickness below 50 nanometers that did not significantly impact the fiber sensor sensitivity. However, the improvement to the chemical resistance of the sensor with this particular dip coating procedure was questionable. After treatment with hydrofluoric acid the coated substrate showed clear signs of having been etched. The cause of this lack of improvement to the chemical resistance is thought to be a problem with the adhesion of the polymer coating to the substrate surface.

Keywords: PVDF-HFP, PPMA, NPS, FTIR, XPS, Ellipsometry, Dip coating.

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1

Introduction

The world has in the last few decades seen a sharp increase in the severity and frequency of natural disasters caused or exacerbated by climate change [1]. Phenomena such as droughts, floods and hurricanes kill thousands and displace hundreds of thousands every year [2, 3]. As global temperatures rise scientists say that these problems will worsen. The immense human misery caused by these events have led to agreements such as the Paris Climate Accords, where the signatory countries pledge to transition away from fossil fuels to more sustainable sources of energy and raw materials [4].

Solar and wind power are some of the largest and fastest growing sources of renewable energy and this trend is set to continue as efforts to combat climate change escalate [5]. However, these energy sources have a major drawback in that they are dependent on season and weather. Solar power for example is less effective during winter when there are less hours of sunshine per day. Human energy consumption does not always line up with when renewable energy is most readily available, so in times where renewable sources are unable to provide enough energy, the gap is typically filled with energy produced utilizing fossil fuels.

An alternative method of dealing with the weather dependence of these renewable energy sources is to overproduce energy when conditions are favorable and store the surplus energy in batteries for later use. One of the leading battery types for this kind of application is lithium-ion batteries. These types of batteries are widely popular due to their high energy density, high power density and long cycle-life [6]. One problem with lithium-ion batteries is that it is difficult to accurately measure their internal operating parameters such as the real-time state of charge [7]. These batteries are therefore designed in such a way as to underutilize their available capacity to avoid stresses associated with overcharging/overdischarging [8]. This also limits the speed at which the battery charges, which is one of the downsides of lithium-ion batteries as compared to other battery types [9].

The ability to accurately measure inside the battery would enable the battery to be charged and discharged further and charged faster than what is normally possible, which would increase the effective energy density of the battery [8, 9]. For this purpose, the company Insplorion AB has been developing a nanoplasmonic (NPS) fiber probe sensor for lithium-ion batteries which can be inserted inside the battery. The NPS fiber probe sensor can monitor the chemical and electrical changes locally inside the LIBs [7].

The NPS fiber sensor is vulnerable to metallic lithium and hydrofluoric acid, which could be produced during charging/discharging of the battery and thermal degradation of the electrolyte, respectively [10]. These compounds will very quickly degrade the sensor, making it too limited in service-time to be useful. Insplorion are therefore developing a polymeric dip coating procedure in which a polymer can be used

to coat the NPS fiber sensor, thus providing good chemical and physical stability.

The purpose of the project was to develop a dip coating procedure for Insplorion's fiber probe sensors. The project started with a literature study which investigated a number of polymers that would be suitable for this application. Two polymers from this list were then selected along with a few compatible solvents.

The next step was the development of the actual dip coating procedure, where polymer coatings were applied on various flat and fiber substrates using dip coating. Dip coating parameters such as temperature, solution concentration and withdrawal speed were varied in order to find the optimal dip coating procedure.

The thickness of the polymer coatings was evaluated using ellipsometry. Ellipsometry, along with several of the other analytical techniques that will be mentioned below, is only capable of measuring flat substrates. This is why most of the dip coating procedures were tested on these substrates, even though the end goal was to coat fiber sensors.

Ellipsometry is only capable of measuring the thickness of a point on the polymer coating, so it is not able to give any information about the uniformity. This was instead evaluated using X-ray photoelectron spectroscopy (XPS) and gold etch testing.

The chemical resistance to hydrofluoric acid was evaluated by submerging coated flat substrates into an HF solution and analyzing it using fourier transform infrared spectroscopy (FTIR).

Finally, the impact of the polymer coating on the fiber sensor sensitivity was evaluated with bulk refractive index sensitivity (BRIS) measurements.

The results of these measurements were compared with those from a fluoropolymer previously used by Insplorion AB for fiber probe sensor coating applications. This fluoropolymer will henceforth be referred to as FP1.

1.1 Aim

This project aims to find a suitable polymer and develop a dip coating procedure to coat the nanoplasmonic fiber sensor. The coating must be thinner than 50 nm and be resistant to hydrofluoric acid and lithium-ion electrolyte. It also has to be able to withstand the standard operating conditions of the battery without degrading and not interfere with the sensor's functionality.

1.2 Limitations

This project is limited to test 2 polymers which are compared to a polymer previously tested at Insplorion AB. It does not cover any testing inside actual lithium-ion batteries, instead the conditions inside the battery are approximated when the durability of the coating is tested. Thermal conditions have been considered during the selection of the polymers but no thermal degradation tests have been performed.

2

Theory

2.1 Nanoplasmonic Sensing

When metallic materials are subjected to an electric field the electrons in the free electron gas will begin to collectively oscillate, the quanta of this collective oscillation is called a plasmon[11]. These oscillations occur at the plasma frequency which is characterized by the Equation 2.1.

$$\omega_p = \sqrt{\frac{n_e e^2}{m \epsilon_0}} \quad (2.1)$$

Where n_e is the number density of electrons, e is the electric charge, m is the electron mass and ϵ_0 is the permittivity of free space. A polarization excitation of a particle caused by coupling to an electromagnetic wave is called a polariton. There can be many types of polaritons depending on what the photon couples to, but for the purposes of this project the only polariton of interest is the Surface Plasmon Polariton, often shortened to just Surface Plasmon (SP).

SPs are electromagnetic waves coupled to the longitudinal charge density wave at the interface between a metal and a dielectric material or air [12]. For the coupling to occur, the material that supports the SP needs to have a negative real dielectric constant and a smaller imaginary dielectric constant [13]. The coupling is at its strongest at the resonant wavelength, which is utilized in Nanoplasmonic Sensing. Because of the resonant nature of the coupling this sensing technique is often called Surface Plasmon Resonance.

In fiber optic nanoplasmonic sensing, non-monochromatic light is sent through a fiber optic cable that has had a nanoplasmonic material deposited on a length of the fiber. The rest of the fiber is covered with a coating that provides total internal reflection. If the fiber is surrounded by a dielectric material, some of the light transmitted through the fiber will be absorbed or scattered by the surface plasmon [7]. The detector can then compare the incident light intensity with the intensity coming out of the light source and generate an extinction spectrum. The fiber sensor architecture with a polymer coating can be observed in Figure 2.1.

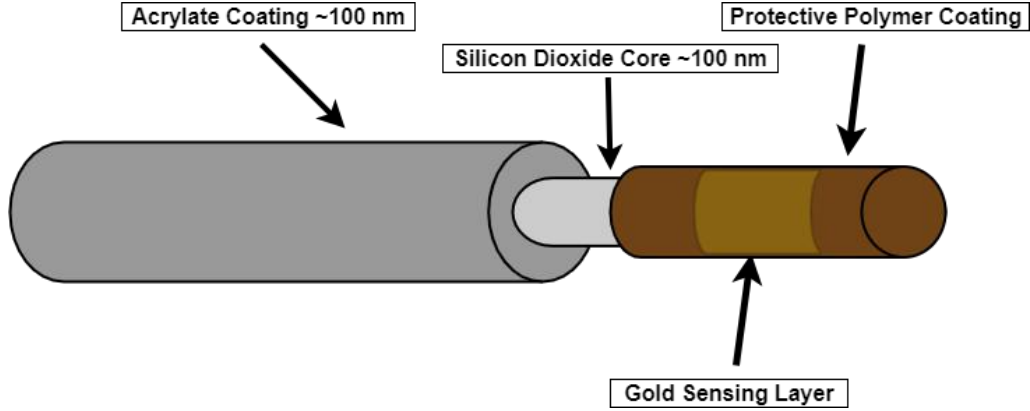


Figure 2.1: Fiber architecture, featuring an inner SiO_2 core, a *Acrylate* coating and a gold sensing layer with a polymer coating on top of it. Figure is not to scale.

The extinction in an NPS spectrum summarizes the loss in transmission of light due to absorption and scattering by the nanoplasmonic material. The extinction peak is where the loss of transmission is the highest, and this occurs at the resonant wavelength. Both the amplitude of the extinction peak and the wavelength at which it occurs is dependent on the refractive index of the dielectric material in which the sensor is placed [13]. Therefore, if a change in the refractive index of the dielectric material were to occur, both the extinction peak amplitude and position would change. The change in resonance peak position ($\Delta\lambda_{max}$) is roughly linearly dependent on the change in refractive index. Therefore, if the correlation between concentration of an analyte and refractive index is known, the shift in resonance peak position can be used to determine the concentration of the analyte in a solution. An example of an extinction spectrum can be found in Figure 2.2.

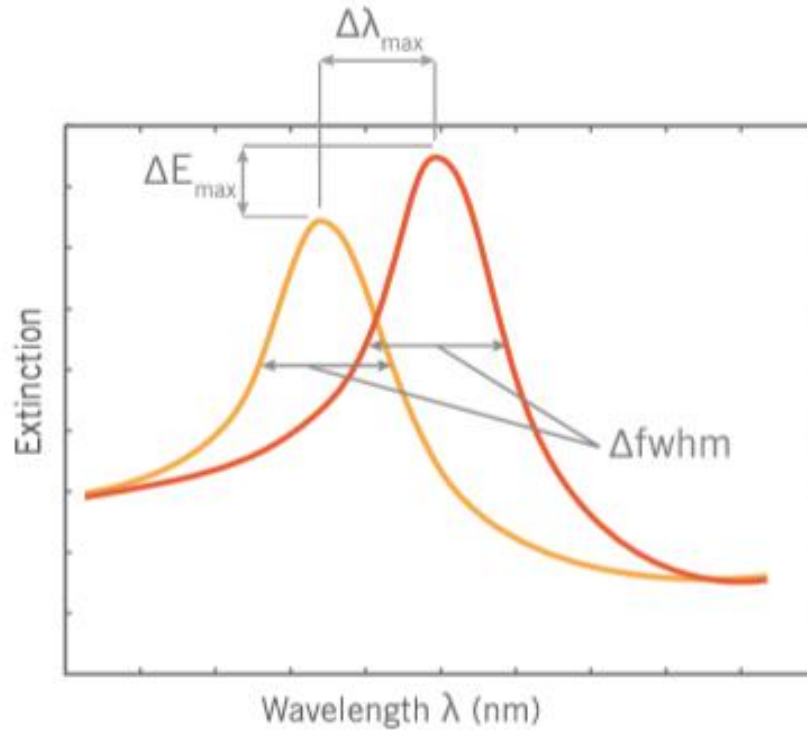


Figure 2.2: Extinction spectrum, featuring illustrations of the difference in extinction amplitude, resonance peak position and full width at half maximum. Image obtained with permission from [14].

2.2 Dip Coating

One of the simpler ways of applying a film coating onto a surface is with the dip coating method. The basic premise is that a substrate is lowered into a vessel containing a coating material in a solvent. The substrate is then withdrawn from the solution and the solvent is evaporated, leaving a coating on the substrate. The dip coating procedure can be divided into 4 major stages, immersion, dwelling, withdrawal and drying. The critical stage for the film properties is the withdrawal stage [15].

Although the process itself is quite simple, there are many forces acting upon the coating solution during dip coating which makes the prediction of the properties of the film rather complicated. The major forces impacting the film quality are the capillary force, viscous drag, and gravitational force. The interplay between these forces have their largest impact on the overall film properties during the withdrawal step of the dip coating procedure. During withdrawal, it can be useful to look at these forces as belonging to one of two categories, entraining forces, or draining forces. Draining forces are those that draw the coating solution away from the

substrate towards the solution and entraining forces are those that work to keep it on the substrate.

The most important parameter in determining the dominating forces during film formation is the withdrawal speed. The behavior of the film formation can be divided into two regimes, the capillary regime, and the viscous drag regime [16]. In the capillary regime the thickness of the final film is mainly affected by the evaporation of the solvent and the capillary forces drawing the solution from the meniscus formed where the substrate meets the solution. The capillary regime is dominant at very low withdrawal speeds, i.e. speeds below 0.1 mm/s. The thickness of the final film formed in this regime can be described by Equation 2.2 [17].

$$h_0 = \frac{k_i E}{Lu} \quad (2.2)$$

h_0 is the final film thickness, k_i is a material proportion constant which is related to the ratio between solvent and polymer, E is the evaporation rate of the solvent, L is the width of the substrate and u is the withdrawal rate from the solution. We can see that since the withdrawal speed is situated in the denominator, an increased withdrawal speed will lead to a decrease in film thickness. As the evaporation rate increases as the temperature is raised, and since it is in the numerator of the equation, an increase in temperature will yield a thicker film.

The other regime is the viscous drag regime, where the viscous drag overtakes the capillary force as the dominant force. Modeling in this regime is conducted with the Landau-Levich equation [18], which is valid for Newtonian fluids when the withdrawal speed exceeds 1 mm/s. The Landau-Levich equation is seen in Equation 2.3.

$$h_s = \frac{0.94\eta_s^{\frac{2}{3}}}{\gamma_s^{\frac{1}{6}}(\rho_s g)^{\frac{1}{2}}} u^{\frac{2}{3}} \quad (2.3)$$

h_s is the wet film thickness, 0.94 is a material constant, η_s , γ_s and ρ_s are the viscosity, surface tension and density of the solution, g is the gravitational constant and u is the withdrawal speed. One major difference between this regime and the capillary one is that an increase in withdrawal speed increases the thickness of the film. Since the evaporation rate is not featured in this equation, the temperature of the solution has little effect on the thickness of the film beyond changes in the physiochemistry of the solution. This equation does not consider the evaporation of the solvent, but a variation of this equation, as featured in Equation 2.4, does.

$$h_0 = k_i D u^{\frac{2}{3}} \quad (2.4)$$

By introducing the material proportion constant from Equation 2.2 into Equation 2.3, the evaporation can be accounted for. Because the evaporation is considered in this equation, it can predict the dry film thickness h_0 . This model also combines the physiochemical constants from Equation 2.3 into a single global constant D . There exists an intermediate regime between the withdrawal speeds 0.1 mm/s and 1 mm/s

where none of the other regimes are dominant. This regime can be described by combining the models from Equation 2.2 and 2.4 into the unified Equation 2.5.

$$h_0 = k_i \left(\frac{E}{Lu} + Du^{\frac{2}{3}} \right) \quad (2.5)$$

With both regimes considered, this model more accurately predicts the final thickness of the coated film, especially at coating speeds close to the regime threshold withdrawal rates or in between them.

2.3 Ellipsometry

The polarization of transverse waves such as electromagnetic radiation is described by their oscillations in space. The electric and magnetic field vectors oscillate perpendicular to each other and perpendicular to the direction of the electromagnetic wave. The polarization of the wave, by convention, is decided by the phase shift of the electrical field vectors [19]. If the electric field vectors are in phase, i.e. their phase difference is equal to zero, the polarization is said to be linear. If the phase difference is 90° the polarization is circular. In all other cases the polarization will be elliptical.

When light is obliquely reflected off a surface, the path that it travels can be described as traveling through a plane of incidence. The electric field of the electromagnetic wave can then be described as two field vectors, one traveling parallel to the plane of incidence and perpendicular to the direction of the light. The other one travels perpendicular to both the plane of incidence and the direction of the light. The component traveling parallel to the plane is called the p polarization component and the one traveling perpendicular to the plane is called the s polarization component.

A typical Ellipsometry equipment setup looks like the one displayed in Figure 2.3. It features a light source, that emits light through a polarizer which linearly polarizes the incoming light. It is then reflected on the sample in the sample holder. The reflected beam is then sent through an analyzer which splits the beam into its p and s components before they enter the detector. To maximize the degree of polarization after reflection, oblique incident angles Φ between $50-75^\circ$ are used.

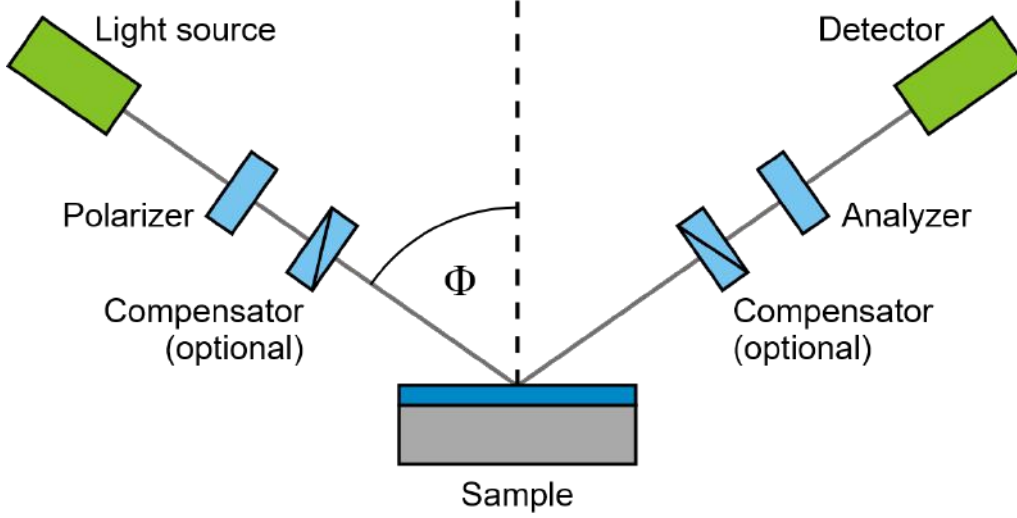


Figure 2.3: Equipment setup featuring all the necessary and optional components in an ellipsometer. Figure made by Buntgarn, at the english wikipedia project under the license CC BY-SA 3.0 [20]

The operating principle of ellipsometry is that the polarization of the light beam is changed when it is reflected off the sample. Material properties such as dielectric function, refractive index and film thickness determine the extent of the polarization that the beam undergoes when it is reflected. The polarization change is described by the reflectance ratio ρ , as can be seen in Equation 2.6 [21].

$$\rho = \frac{r_p}{r_s} = \tan(\Psi)e^{i\Delta} \quad (2.6)$$

Where r_p and r_s are the amplitudes of p and s after reflection and normalized to their initial value. $\tan(\Psi)$ is the amplitude ratio before and after reflection and Δ is the phase difference between p and s .

The optical constants and the film thickness cannot be directly obtained from the parameters Δ and Φ , to do that you need to fit the data to a model. More commonly analyzed materials such as silicon dioxide or metals like gold typically have a specific model. Materials such as polymers typically does not. It is therefore necessary to use a model which can work with some unknown parameters. If the polymer film can be assumed to be transparent, then Cauchy's model is oftentimes used if the refractive index is known [22], [23]. Cauchy's model fits the data according to Cauchy's equation, as can be seen in Equation 2.7.

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} + \dots \quad (2.7)$$

Where n is the refractive index at a specific wavelength, λ is the wavelength and

A , B and C are parameters related to the film thickness. The ellipsometer used in this project only uses the first 2 terms of the equation.

2.4 X-ray Photoelectron Spectroscopy (XPS)

X-ray Photoelectron Spectroscopy, or XPS, is an analytical technique which utilizes the photoelectric effect to analyze sample surfaces when they are subjected to X-ray bombardment in a vacuum [24]. When the electrons on the surface absorb the incident x-rays they will excite. The emitted electron will then have the kinetic energy of the incident X-ray minus that of the binding energy of the electron to its atom. The kinetic energy of the emitted electrons is dependent on the X-ray source. The analysis performed in this project was done with an aluminum X-ray source that yields incident X-rays with an energy of 1486.6 eV, but a magnesium X-ray source which yields 1253.6 eV X-rays can also be used.

The electrons emitted during X-ray photoelectric emission are typically the lower energy orbital electrons such as those in the 1s orbital. The specific orbital electrons which are emitted depend on the composition of the material and the energy of the incident X-rays. This will leave an electron hole in a lower energy orbital while higher energy orbitals are filled. A higher energy orbital electron will therefore move from its orbital to fill the lower energy one. The gap in energy between these orbitals will then be released and used to excite another electron which will also be ejected into the surrounding vacuum. This electron is called the auger electron [25]. Contrary to the photoelectron, the auger electron will have a characteristic kinetic energy which is not dependent on the energy of the incident X-ray[26].

The XPS setup is presented in Figure 2.4. It features an X-ray source, a sample, an electron energy analyzer, and an electron detector. The X-ray source, as the name suggests, supplies the X-rays which bombard the surface of the sample. The electron energy analyzer measures the kinetic energy of the emitted electrons and the detector counts the number of electrons that are emitted.

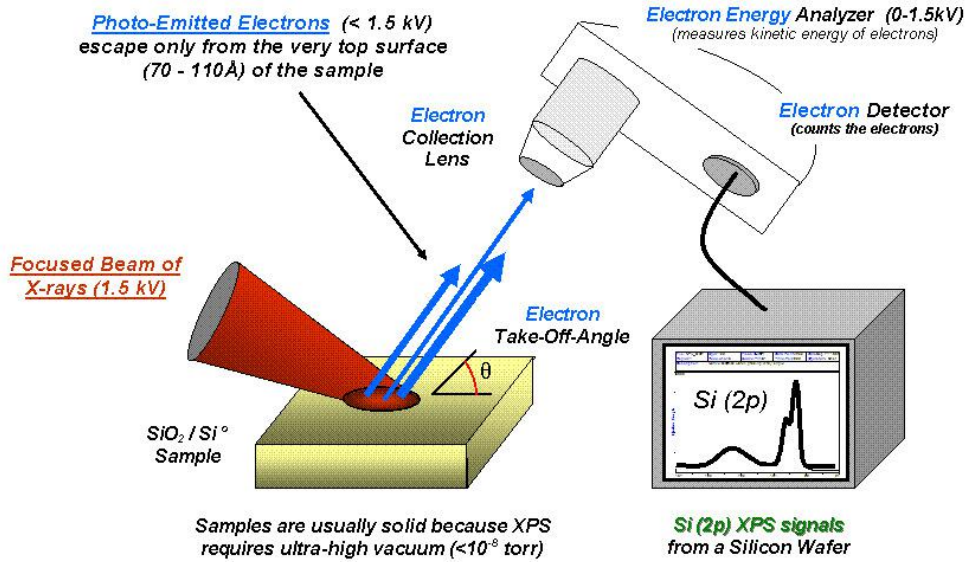


Figure 2.4: XPS equipment setup featuring all components necessary for XPS analysis. Image taken from public domain [27].

The data acquired from the XPS analysis is typically presented as electron count or counted electrons per second plotted against the binding energy of the electron. The binding energy can be calculated with Equation 2.8 [28].

$$E_{Binding} = E_{Photon} - (E_{Kinetic} + \Phi) \quad (2.8)$$

Where $E_{Kinetic}$ is the energy of the electron as measured by the electron energy analyzer and Φ is the work function which is a correction term which accounts for energy that the electron loses as its being absorbed by the analyzer [28]. The binding energy is characteristic for the atom it originates from. The ability to detect the elements present on the surface of a sample from their electrons characteristic binding energies is where the usefulness of the analytical technique stems from.

A distinction between bonded atoms and atoms in their elemental state has so far not been made, but there is a way to determine whether the atom is bonded or not. It is also possible to determine the type of bond and which atoms are bonded. This is possible because the electrons binding energy is changed when the atom is bonded to another atom [26].

As the kinetic energy of the emitted electron cannot be higher than the energy of the incident X-ray, the escape depth of the emitted electrons is very shallow. The escape depth depends on the X-ray angle of incidence, with flatter angles having

shallower escape depth due to the extra distance they must travel to the surface. The depth is typically up to around 10 nm [28].

As has been established, XPS can provide accurate compositional information on surface samples, with the exception being H and He atoms which it is not able to detect [28]. However, the need for a high vacuum means that the technique is very expensive. Another downside of the technique is that the analysis time is very long.

2.5 Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectroscopy is the study of the transitional energy absorption between the quantized vibrational energy levels of molecular bonds [29]. Each atomic bond in a molecule has a set of allowed movements, called vibrational modes, that it can perform. Since the energy levels for the different movements are quantized, this means that they will only be excited when energy corresponding to that energy gap is supplied.

This energy can come from both heat and electromagnetic radiation but for the purposes of infrared spectroscopy the electromagnetic radiation is what matters. The electromagnetic radiation wavelengths which correspond to the vibrational mode energy gaps are typically in the infrared spectrum. This is the reason why this field of study is called infrared spectroscopy. The wavelength in IR spectroscopy is commonly expressed in the wave number (cm^{-1}) which is the inverse of the wavelength. The wavenumbers of absorption for the vibrational modes are characteristic for specific atomic bonds. For example, the Oxygen-Carbon bond in a carbonyl group has a unique absorption peak in an IR transmission spectrum which can be used to identify the presence of such a bond in a molecule [30].

In the most basic IR spectroscopy setup, you have a light source that can emit various wavenumbers of light, a sample through which the light can be transmitted or absorbed and a detector. Light of varying frequencies in a predetermined interval is shined through the sample into the detector which measures the ratio between the transmitted light and the emitted light. This spectrum is then compared to a reference spectrum in air without a sample. Dividing the sample spectrum by reference spectrum yields the infrared transmission spectrum which will show absorption peaks at the wavenumbers corresponding to the sample's vibrational modes.

The Fourier Transform Infrared Spectroscopy (FTIR) setup, as seen in Figure 2.5, features a few extra units compared to the simpler IR setup mentioned earlier in the text. The light coming from the light source is split in the beam splitter which redirects it towards two mirrors. One of the mirrors can move on an axis either closer or further away from the beam splitter. The light is then recombined at the beam splitter before being sent through the sample and into the detector. These extra units that were just described are collectively called a Michelson Interferometer [31].

The light source in FTIR spectroscopy emits a beam containing several wavenumbers of light in the desired spectral region. The wavenumbers are then blocked and

transmitted via wave interference in the interferometer by adjusting the position of the movable mirror so that each beam coming into the sample has a different set of wavenumbers.

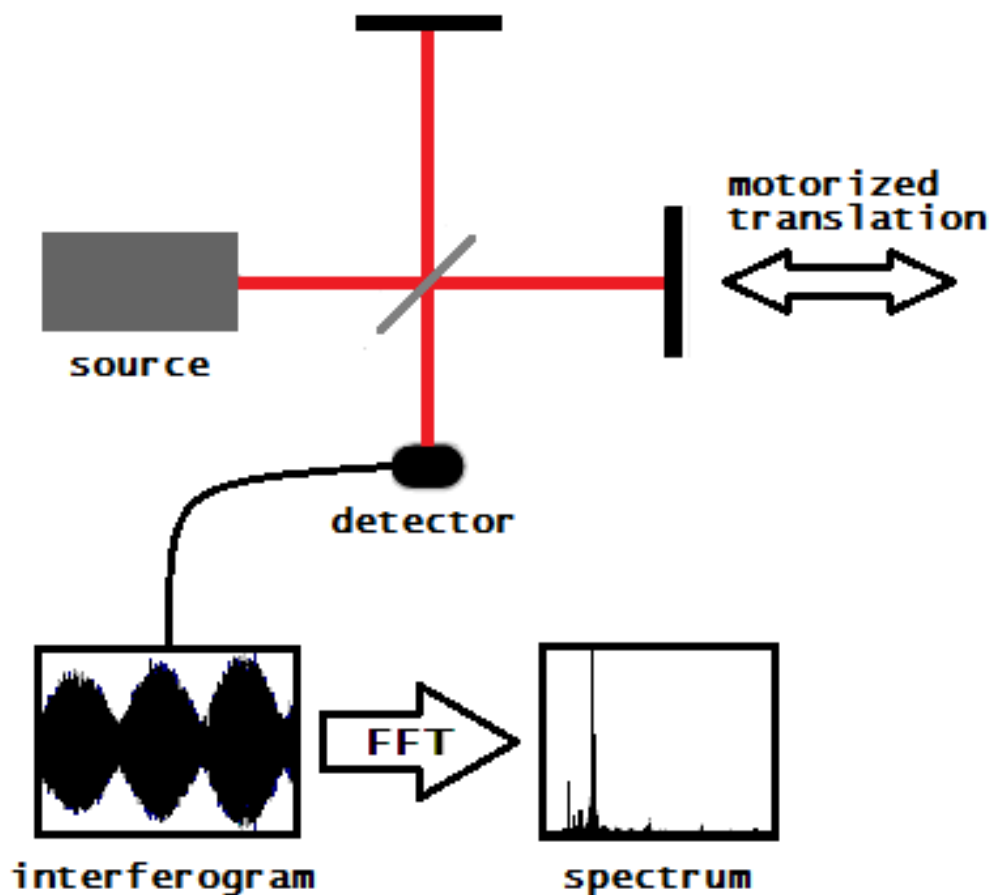


Figure 2.5: Michelson interferometer and other components of FTIR setup. Figure created by Stigmatella aurantiaca at English Wikipedia and licenced under CC BY-SA 3.0 [32].

What results from this analysis is an interferogram containing measured light and mirror positional data. Utilizing Fourier Transform you can convert the data into the typical transmission infrared spectrum. The main reason why FTIR is used above other IR spectroscopic techniques is its high throughput [33].

3

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3.1 Equipment

The following chapter covers the equipment necessary to apply and test the polymeric coating. This includes equipment for substrate cleaning, dip coating, and evaluation of the thickness, uniformity, chemical resistance and sensor sensitivity.

3.1.1 Branson 2510 Ultrasonic Cleaner

The Branson 2510 Ultrasonic Cleaner is a tool for cleaning substrates. the cleaning process it utilizes is colloquially called sonication and it works by inducing cavitation bubbles with the help of ultrasonic waves [34]. The cleaner contains a bath which can be filled with water, the substrate can then be placed into a flat beaker which is subsequently filled with a solvent like isopropyl alcohol (IPA) and placed in the water bath. The cavitation bubbles rips the contaminant particles off of the substrate. They are then solvated or dispersed in the solvent. This is an effective and gentle method of removing particles from a substrate with as little interaction with the substrate as possible.

3.1.2 UV/Ozone Cleaner

The ozone cleaner is used for the substrates second cleaning step. The working principle is that the cleaner generates ozone which breaks down the contaminant particles on the substrate surface into smaller and more volatile compounds. These particles are then irradiated by high energy ultraviolet light which removes them from the substrate via sublimation. The ozone in combination with the high energy ultraviolet radiation can also generate hydroxide radicals which can react with the surface of the substrate [35]. For example by promoting the formation of silanol groups at the silicon/air interface on a silicon substrate. This can provide benefits in adhesion between a substrate and coating by increasing the surface energy of the substrate. The substrates are placed in the sample tray with the surface that is to be cleaned facing upwards in the ozone cleaner. The tray is then reinserted back into the ozone cleaner.

3.1.3 Ossila Dip Coater

The Ossalia dip coater is the tool used for the dip coating [36]. The substrates are secured by the dip coater clamp and it has a maximum travel distance of 10 cm. The withdrawal rate is able to be varied between 0.01 mm/s and 50 mm/s, meaning that the dip coating can be performed in both the capillary and the viscous drag regime.

3.1.4 Frontier MIR FTIR

The FTIR measurements were conducted with the instrument Frontier MIR Spectrometer which is manufactured by Perkins-Elmer [37]. This spectrometer is capable

of detecting light with wavenumbers varying between 350 and 8300 cm^{-1} .

3.1.5 M-2000 Ellipsometer

The ellipsometry measurements were conducted at Chalmers University of Technology using the instrument M-2000 Ellipsometer which is manufactured by J.A. Woollam[38]. It is capable of measuring at multiple angles of incidence per measurement and at wavelengths up to 1690 nm. The ellipsometer is operated using the software V.A.S.E. which is used to set the experimental parameters and model data.

3.1.6 XPS PHI5000 Versaprobe III

The instrument used to perform the XPS measurements was the PHI5000 Versaprobe III at the CMAL department at Chalmers University of Technology. The instrument uses a monochromated Al X-ray as an X-ray source with an energy of 1486.6 eV and has a lower detection limit of 1 atomic percent in the sample.

3.2 Substrates

A variety of different substrates were used during the course of this project. Insplorion are mainly concerned with optical fibers, since that is the substrate used for their battery sensors. However, several of the analytical techniques used to evaluate the polymer coating are not compatible with that geometry. These techniques include Ellipsometry, FTIR and XPS. They all require flat substrates, therefore most of the coating experiments in this project were performed on flat substrates that have a thickness of 1 mm and side lengths varying between 5 and 15 mm.

Three types of flat substrates were used, bare silicon (Si), silicon dioxide SiO_2 on Si and thin layer gold (Au) deposited on either silicon dioxide or silicon. The different substrates were used to check the adhesive behaviour of substrate with the polymer coating. The gold layer needed a nanometer thin adhesive layer of either chromium or titanium between it and the SiO_2 [39].

The optical fiber consists of a silica glass rod and an acrylate coating. The acrylate coating was removed from the fiber and a Au NPS structure was deposited on 1-2cm of the fiber. The polymer coating was then applied to protect the Au NPS structure.

3.3 Preparation of polymer solutions

During the course of the project, a multitude of polymer solutions were produced and used to apply coatings to the various substrates. The PPMA and PVDF-HFP solutions were produced from scratch whereas the FP1 solutions were based on previous work done at Insplorion and was included in this project as a reference.

3.3.1 Polyvinylidene fluoride - hexafluoropropylene solutions

The PVDF-HFP polymer solutions were the ones most thoroughly examined during this project. Solutions with concentrations between 1, 2, 3, 5 and 7 wt% were made and used for coating experiments.

The solutions were made with either acetone or DMSO as solvents. Since acetone

and DMSO are miscible, some mixed solvent solutions were also made and used for coating experiments.

The different PVDF-HFP solutions had very similar preparation methods, the only difference was variations in heating during the solvation period. The first step for preparing the solution was to calculate the weight of polymer and the volume of solvent that needed to be added into the solution. The polymer was then added to a vial placed on a scale, until the calculated amount had been added. The calculated amount of solvent was then added in a fume hood using a measuring glass and a pipette. The solution was then placed on a hotplate which was set to stir at a rate of between 300-500 rpm depending on the size of the stir bar.

The acetone solutions were not heated during solvation and were dissolved after roughly 1-2 hours. The mixed solvent solutions were solvated while heated to 40 °C and it took 3-4 hours for the polymer to dissolve in those solutions. The DMSO solutions were heated to 60 °C during solvation on the hotplate and dissolved about as quickly as the acetone solutions.

3.3.2 Polypropylene grafted maleic anhydride solutions

The PPMA solutions were harder to dissolve compared to the PVDF-HFP solutions. Only single-solvent solutions were made with this polymer and the concentrations tested were 1, 2 and 3 *wt%*. They were all solvated at temperatures of around 70-80 degrees and it took around 3-4 hours. If these solutions are left without stirring for prolonged periods of time, the polymer precipitates and they will need to be stirred under heating for about an hour before they can be used during coating experiments again.

3.3.3 Fluoropolymer 1 solutions

The FP1 solution was prepared differently than the solutions with the other polymers in that the polymer was already dissolved in a 7 *v%* premade solution. This was then diluted with the solvent to the desired concentration. The FP1 was only meant to be a reference to compare with the PVDF-HFP and PPMA so only one solution with a concentration of 3 *v%* was prepared. After mixing the polymer solution with the solvent the desired solution was solvated during stirring for half an hour.

3.4 Application of polymer coating using dip coating

The polymer solutions were as mentioned in Section 3.3.1, 3.3.2 and 3.3.3 produced in wide variety. This section will describe the general dip coating procedure used for these experiments, with a brief paragraph in the end describing the different heat treatments for the different types of polymer/solvent combinations that were used during the course of the project. How variations of the dip coating parameters such as solvent, concentration, temperature, withdrawal speed and substrate type impacted the coating properties will be detailed in a later chapter.

The first step in dip coating after the solution is prepared is to clean the substrate.

For the flat substrates, cleaning was done first with 10 minutes of sonication and then with 10 minutes of ozone/UV cleaning. The fibers were only cleaned in UV/ozone for 10 minute because they could not fit into the beaker as it was not wide enough.

Before initiating cleaning, the polymer solution was placed on the hot plate for stirring at 500 rpm and at whatever coating temperature was used. After the substrates had been cleaned, the solution was taken from the hot plate and placed on the dip coater platform. The substrate was then secured in the dip coater clamp and the dip coating submersion speed, hold time and withdrawal speed were set. The submersion depth was set so that the solution level was as far up the substrate as possible without touching the clamp. When the dip coating was done, the substrate was placed either in an oven or in a small vial in a heating block through a lid which had a hole drilled through it, thus creating a makeshift oven which could be used inside a fume hood.

The PVDF-HFP coatings made with acetone as a solvent were dried at 100 °C for 10 minutes. The coating made with DMSO or DMSO/Acetone were instead dried at 130 °C, due to DMSO having a higher boiling point than Acetone. The PPMA coatings solutions in which toluene was used as a solvent were dried at 120 °C for 15 minutes after coating. The FP1 coatings were prepared with two steps, a drying step and a curing step. The drying step was conducted at 80 °C for 15 minutes after which it was transferred to the other oven which was set to 180 °C, where it was cured for 30 minutes.

3.5 Literature study: Selection of polymer and solvent

The initial part of this project consisted of a literature study. The primary purpose of this study was to select the two polymers that were to be used for the dip coating experiments. Solvents which are compatible with these polymers were also selected during this time. The experimentation with the polymer solutions is a very slow iterative process, so there would only be time to properly evaluate one or two polymers. It was therefore of great importance that the properties of the selected polymers were thoroughly investigated as to ensure the greatest chance of being able to provide a coating adhering to the standards that Insplorion had set.

A handful of polymer properties that were deemed critical for the functionality of the polymer as a coating were investigated as a part of the literature study. Arguably the most important one was the chemical resistance, and specifically the resistance to hydrofluoric acid, since this can form in lithium-ion batteries during degradation if water bypasses the battery seal [10].

One of the other important properties was the service temperature range, which was mainly decided by the glass transition temperature. This was because the melting temperatures of the polymers were typically a lot higher than the maximum service temperature of a lithium-ion battery, whereas some of the polymers that were investigated had a glass temperature that was in the range of, or below, the lower service temperature. This becomes a problem because some polymers tend

to become very brittle below the glass temperature. One of the battery cell types Inspilorion are testing their sensors in are pouch cell batteries. A feature of these battery cell types is that they swell by up to 10% during charging, this can cause compressive stresses inside the battery and therefore on the fiber [40]. If the polymer coating is too brittle, this can cause it to crack or fracture, thereby compromising the protection it provides. The compressive strength and elastic modulus of the polymers was also investigated for this reason.

Another important property was the permeability. A high permeability means that smaller molecules such as hydrogen fluoride might be able to penetrate the protective coating and damage the gold layer, meaning that a polymer with a low permeability is preferable. The optical properties of the polymer were also a point of concern. The opacity and the refractive index specifically were the properties investigated. There was no real preference for the refractive index but since it affects the sensor behavior it was included in the study. The opacity was of great importance since it was necessary for the coating to be transparent or at least translucent for it not to impede the light interactions on the surface of the gold nanolayer.

The last family of properties that were investigated were the electrical properties such as dielectric strength, resistivity and conductivity. These were not that important but there was nevertheless a preference for materials with a higher dielectric strength, higher resistivity and lower conductivity. This is because of the fact that there is a chance of charge buildup in the coating during battery usage, which can impede the function of the sensor, so a high resistivity and high dielectric strength will help prevent or mitigate this charge buildup.

The final part of the literature study consisted of attempts to try and find similar instances where the polymers that were investigated during the study had been used to make thin coatings in the range of tens of nanometers utilizing dip or spray coating. Spray coating was included since it was a method considered during the early stages of the project, but ultimately dropped in favor of a more narrow focus solely on dip coating. The specific polymers investigated and their properties will be presented and discussed in Section 4.1.

3.6 Bulk Refractive Index Sensitivity Measurements

In order to evaluate how the presence of the polymer coatings affected the NPS fiber sensor its sensitivity was evaluated from the Bulk Refractive Index Sensitivity (BRIS). This is only possible on fibers, not on flat substrates. The measurement setup for the BRIS measurements is presented in Figure 3.1.

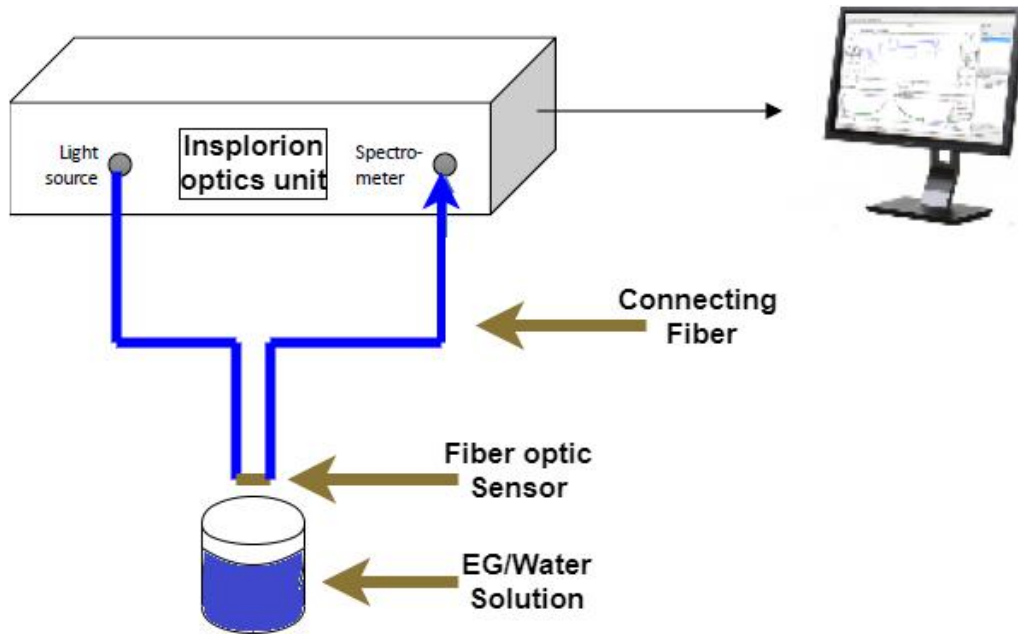


Figure 3.1: The BRIS measurement setup featuring Insplorion's optics unit.

The transmission measurement setup of the optical fiber sensor is shown in Figure 3.1. Both ends of the NPS fiber sensor were spliced with pigtails and connected to the Insplorion optics unit. Before splicing the fiber, the ends had to be stripped of coating, both on the coated fiber and the ends of the pigtails. All fiber ends were then cut to achieve a straight edge using a cleaver unit. The fiber endings were then spliced with a splicer.

The sensitivity was then measured using the Insplorer software developed by Insplorion. First a reference spectrum in air was obtained. The desired wavelengths between 500 and 800 nanometers were then selected and the measurement was initiated. The polymer coated NPS fiber section of the fiber was then submerged in a number of water/Ethylene Glycol (EG) solutions with varying concentrations and therefore refractive index (RI). The solutions used were pure water, 5%-, 10%-, 20%- and 45% EG. The solutions were used in ascending order of EG concentration starting from the pure water. After the fiber had been tested in the 45% solution the other solutions were retested, this time in descending order of EG concentration starting from the 20% EG solution.

3.7 Gold etch testing

The gold etching test is a way of investigating the uniformity of the applied polymer coating. The gold etchant fluid consists of potassium iodide and iodine and is capable of etching gold at a rate of 28 ångström per second [41]. If a nonuniform polymer coating exists or if the polymer has enough free volume that etchant can diffuse

through it, the gold underneath will be etched.

The gold etch experiments were performed with the help of the dip coater. Both fibers and flat substrates could be and were tested. The substrates were secured via the clamp and the manual mode on the dip coater was used to submerge them in the gold etchant, which was poured in a ceramic beaker. During the first 5-10 minutes, the substrates were raised and inspected to see if the etching had begun quite frequently. When the etching started, the time was noted down and the frequency of the inspections was lowered somewhat. The state of the etching was noted down upon each subsequent inspection and the etching was continued until the substrate was completely etched or if the sample had been in the etchant for about an hour. The integrity of the coating was evaluated by ocular inspection since the etching of the gold on the substrate was visible without optical instruments.

3.8 FTIR measurements

The FTIR measurements were conducted as a way of evaluating the chemical resistance of the polymer coating to hydrofluoric acid treatment. For each coating procedure, two flat silicon dioxide substrates were coated and one of them was treated with 2% HF for 10 minutes. They were then analyzed using ATR-FTIR spectroscopy and their spectras were superimposed and compared. This method sought to see to what extent the carbon and fluoride peaks of the PVDF-HFP would be reduced in intensity and if the silicon peaks would become more prominent as a result of the protective coating layer being destroyed and it therefore being easier for the IR radiation to penetrate. The FTIR measurements were performed by Anders Mårtensson at Chalmers University of Technology and I could not be present due to restrictions caused by the covid-19 outbreak.

3.9 Ellipsometry measurements

The ellipsometry measurements were conducted in a cleanroom environment at Chalmers University of Technology. The samples were placed on the sample tray and the incident angles 65° , 70° and 75° were selected. The models for the different layers and their thickness were then selected, with the exception of the polymer coating layer, as this is the only layer with an unknown thickness. The other layers have specific models for their material, but the polymer coating is modeled with Cauchy's model, which is illustrated in Equation 2.7. An estimation of the coating thickness was then input into the program and the analysis was run. The model was then fitted to the spectrum obtained from the analysis. The accuracy of the model was evaluated with the Mean Square Error (MSE), which acts as a measure of the uniformity of the coating. The thickness is presumed to be accurate if the MSE is below 1.

3.10 XPS Measurements

The XPS measurements were conducted as a way of evaluating the uniformity of the polymer coating. The measurements were performed by Dr. Eric Tam at Chalmers University of Technology. I was not present during the measurements due to coronavirus restrictions. XPS analysis is too slow to be performed in a sweeping manner,

3. Methods and Materials

so nine spots were selected on the 10mm x 10mm substrates, and the spectrums obtained for the samples each correspond to one of those points. The XPS instrument in question had a probing depth of 3 nm.

4

Results and discussion

The results given in this project are brought forth and discussed in the following chapter. The results show how polymer choice, solvent choice and the different dip coating parameters impact coating characteristics such as thickness, uniformity, chemical resistance and sensor sensitivity. It also covers the results of the research that went in to selecting polymers and accompanying solvents appropriate for the task of formulating a polymer dip coating procedure.

4.1 Literature study

The following section details the different polymers that were considered for the polymer coating as well as a justification for why they were, or were not, chosen. The section also looks at possible solvent candidates for the chosen polymers and the final solvents chosen to use for the dip coating experiments.

4.1.1 Polymer selection

There is a very wide range of different polymers and copolymers to choose from when it comes to an application such as the one in this project. Therefore, there was a need to narrow it down to a manageable number of polymers that could then be explored further. The plan was to investigate polymers belonging to one of two categories, they were either polymers that are generally known for having good chemical resilience or they were polymers that have been used in optical fiber applications, either as cladding, fiber core or coating. Unfortunately, none of the polymers in the second category were sufficiently resistant to hydrofluoric acid. These included the polymers polydimethylsiloxane (PDMS), polyimide (PI), polystyrene (PS) and polyether ether ketone (PEEK). The polymers of the former category include polypropylene (PP), polyvinylidene-fluoride (PVDF), high-density polyethylene (PEHD), low-density polyethylene (PELD) and polyvinyl chloride (PVC). The strategy was then to select two of the polymers of the former category and consult a supplier or expert on a specific copolymer that was suitable for the particular polymer coating application in this project. The properties of the previously mentioned polymers were collected from the polymer database CES Edupack and are presented in Table 4.1.

Table 4.1: Physical, chemical, optical and electrical properties of a range of polymers

	PP	PVDF	PEHD	PELD	PVC
E_c^1	1.6-1.78	1.21-1.27	0.621-0.896	0.172-0.283	2.18-3.41
σ_c^2	42.9-45.1	45.5-49	18.6-24.8	10.8-17.4	50-67
T_g^3	(-14)-(-6)	(-27)-(-40)	(-125)-(-90)	(-125)-(-90)	102-118
Upper T^4	81.2-99.1	140-150	90-110	81-95	85-100
Lower T^5	(-17)-(-3)	(-37) - (-17)	(-82)-(-72)	(-68)-(-58)	(-51) - (-31)
n^6	1.48-1.5	1.42	1.53-1.55	1.57	1.53
Transparency	Transparent	Translucent	Translucent	Translucent	Opaque
HF resistance ⁷	Satisfactory	Satisfactory	Satisfactory	Satisfactory	Probably Satisfactory
Dielectric Str. ⁸	17.6-18.4	10.2-11	17.7-19.7	17.7-39.4	23.6-24.6
ρ^9	10^{23}	10^{20} - 10^{21}	10^{24} - 10^{25}	10^{24} - 10^{25}	10^{21} - 10^{22}
σ^{10}	10^{-21}	10^{-19} - 10^{-18}	10^{-24} - 10^{-23}	10^{-24} - 10^{-23}	10^{-20} - 10^{-19}
Permeability ¹¹	58.3-99.7	0.42-2.77	49.8-69.4	113-193	3.49-6.96

¹ Compressive elastic modulus (*GPa*)² Compressive elastic strength (*MPa*)³ Glass transition temperature ($^{\circ}C$)⁴ Upper service temperature range ($^{\circ}C$)⁵ Lower temperature range ($^{\circ}C$)⁶ Refractive Index⁷ Resistance to HF (40 %)⁸ Dielectric strength (*MV/m*)⁹ Resistivity ($\mu\Omega/cm$)¹⁰ Conductivity (%*IACS*)¹¹ Permeability to O₂ ($cm^3mm/(m^2dayatm)$)

The goal of this part of the literature study was to narrow the selected polymer candidates down to just two polymer types. As mentioned before, chemical resistance and resistance to HF were some of the most important properties of the polymer coating, since its purpose was as a protective coating. As these polymers had been chosen specifically for their good chemical resistance they all had a satisfactory resistance to HF, with the exception of PVC which was rated "probably satisfactory".

The next property that was considered during elimination was transparency. In order for the polymer to not interfere with the sensing properties of the fiber, it was imperative that it should be transparent or at least translucent. The opaque polymers PVC was therefore excluded.

The permeability of the polymer is another important property. In order to prevent penetration of the polymer coating by molecules of compounds harmful to the gold sensing layer, it is important that the permeability of the polymer is low. Of the remaining polymers, PVDF comes out on top in this regard by a large margin.

PVDF has a O_2 permeability of 0,417-2,77 $\frac{\text{cm}^3 \text{ mm}}{\text{m}^2 \text{ day atm}}$, the other polymers are more than an order of magnitude worse, with PELD being the worst.

The mechanical properties regarding compressive stress is also a factor in deciding which polymers to use. The properties of PP and PVDF are pretty similar in this regard. PVDF has a slightly higher compressive strength and PP has a higher compressive elastic modulus. The polyethylene polymer types are a lot worse with LDPE having especially low compressive elastic modulus and strength.

The mechanical properties of polymers vary with temperature. It is common for polymers to become brittle below their glass transition temperature. The normal operating temperatures of lithium ion batteries range between -20 - 60 °C [42]. It was therefore preferable that the lower operating temperature of the polymer was below the lower battery temperature range. For the PVDF and PE polymers this was not a problem, but the Tg of PP is higher than this temperature. According to the information provided in the specialchem material selection platform omnexus, the brittle/ductile transition temperature of homo- and copolymers of PP varies between -20 and -10 °C [43]. This transition would ideally be lower than the lower operating temperature of the LiB but it is not a deal breaker as it is very close.

It is important that the electrical properties of the polymer coating, and the polymer by extension, discourage charge buildup on the coating when it is in use inside an operating battery. The polymer should therefore have low conductivity, and high dielectric strength and resistivity. The polyethylenes are the best in this respect, closely followed by polypropylene. PVDF is quite a bit worse.

The polymer that fares the best in this investigation seems to be the PVDF and it is therefore chosen as the 1st polymer to use for dip coating experiments. The second polymer should then be chosen between PEHD, PELD and PP. PELD and PEHD share most of their strengths but PELD is significantly worse than PEHD when it comes to compressive mechanical properties and permeability. PELD can therefore be disregarded as a candidate as well. The final choice for the second polymer therefore lies between PEHD and PP. They both have strengths and weaknesses compared to each other. The PP is preferable when it comes to transparency and compressive properties while PEHD is better when it comes to service temperature and electrical properties. When Insplorion was asked to weigh in on this choice, they indicated a preference for PP. The polymers PVDF and PP were therefore selected for the project.

After the polymer types had been selected it was time to investigate what specific homopolymer or copolymer to select from them. One of the main issues of concern when choosing the specific polymer in this case was the adhesion between polymer coating and substrate. As previously mentioned, the substrates involved in this project are Si , SiO_2 and Au . A lot of the testing was done on Si substrates, this was done because extra layers added another potential source of error during polymer coating thickness measurements with ellipsometry. They were also the substrates that were the easiest to prepare for obvious reasons. These substrates are nonpolar. The fiber sensors that the polymer coating is supposed to protect are made of

gold and silicon dioxide. SiO_2 contain silanol groups at the substrate surface that make the characteristics of the surface hydrophilic. According to an article written by David E. King, gold surfaces become hydrophilic when they are subjected to UV/Ozone treatment [44]. Since this treatment is performed during substrate cleaning the gold was considered to be hydrophilic for the purposes of the dip coating experiments. The polymer and accompanying solvent should therefore be polar in order to ensure good adhesion between the polymer and the sensor surface.

PVDF is a rather polar polymer with a dipole moment of 2.1 Debye [45]. A representative of the chemical supplier company Solvay was asked for a recommendation for a specific PVDF polymer grade. They suggested the polyvinylidene fluoride - hexafluoropropylene (PVDF-HFP) copolymer due to its compatibility with solution processing. The PVDF-HFP copolymer was therefore selected as the first polymer to investigate during dip coating trials.

PP is a nonpolar polymer and as a result of this adhesion with the gold and silicon dioxide surfaces might not be adequate. A way of resolving this issue would be to use a copolymer with polar groups grafted to the PP main chain. Such a polymer was suggested by professor Christian Müller of Chalmers University of Technology. This polymer was polypropylene-graft-maleic anhydride (PPMA). As the name suggests, this polypropylene copolymer had grafted maleic anhydride side groups on the polypropylene main chain. The second polymer selected was therefore PPMA.

4.1.2 Solvent selection

This section details the solvent selection process and the parameters that were investigated in order to make this choice. The final solvent choice is then outlined.

The first step in the solvent selection was to consult the literature to find which solvents were compatible with the two polymers. After a number of compatible solvents were found, the dipole moment, boiling point and safety concerns were investigated. A higher dipole moment and less harmful solvent was desired. The solvents compatible with PVDF and by extension PVDF-HFP are listed in Table 4.2 along with their dipole moment, boiling point and an evaluation of their hazardousness to work with. The hazard of working with the solvent was evaluated using the chemical management program KLARA.

Table 4.2: Solvents compatible with PVDF-HFP

Solvent	Dipole moment [Debye]	Boiling point [°C]	Hazard Rating
<i>Acetone</i>	2.88	56.05	High Risk
<i>DMSO</i>	3.96	189	Low Risk
<i>NMP</i>	4.09	202	Very High Risk
<i>DMF</i>	3.82	153	Very High Risk

As can be seen in Table 4.2, Acetone stands out as the solvent with by far the lowest Dipole moment and boiling point. The others have rather similar dipole moments

and boiling points. At this stage of the project it was not clear how the boiling point of the solvent would impact the polymer coating. It was also unclear exactly how hydrophilic the substrate surface of the gold/silicon dioxide substrate would be. It was therefore decided that two solvents would be investigated. One with a lower dipole moment and boiling point and one with a higher dipole moment and boiling point. In the former category Acetone was the only choice, so that was selected as the first solvent. All the other solvents fit into the latter category, DMSO was chosen from them based on its lower hazard rating.

The solvents compatible with the PPMA polymer are listed in Table 4.3. As the table shows, they all have a "very high risk" hazard rating. their dipole moments vary between 1.24 and 0.36 with 1,2,4-Trichlorobenzene being the highest and Toluene being the lowest. When it was time to start with the PPMA coating experiments it was very late into the project and there was not enough time to wait for new solvents to be delivered. The solvents on hand at the time were Toluene and Tetraline, ideally tetraline would have been chosen due to its higher dipole moment. However, the propensity of the tetraline to form explosive peroxides when exposed to air was deemed an unnecessary risk when the difference in dipole moments was so low. Toluene was therefore chosen instead.

Table 4.3: Solvents compatible with PPMA.

Solvent	Dipole moment [Debye]	Boiling point [°C]	Hazard Rating
<i>1,2,4 Trichlorobenzene</i>	1.24	213.5	Very High Risk
<i>Tetraline</i>	0.4-05	206-208	Very High Risk
<i>Xylene</i>	0-0.64	138.5	Very high Risk
<i>Toluene</i>	0.36	111	Very high Risk

4.2 Polymer solutions and dip coating parameters

The following section details the results of the iterative experimentation with the dip coating procedure for the PPMA and PVDF-HFP polymers for the flat substrates. The reason this section is restricted to the flat substrates is because the methods of analyzing the coating it contains are only possible with flat substrates. These methods being ellipsometric measurements and observations made with the naked eye.

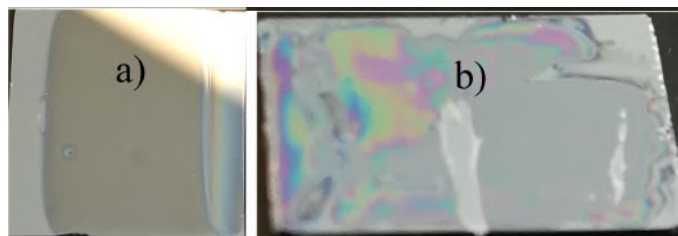
4.2.1 Solvent

The PVDF-HFP polymer was the only polymer that was tested with more than one solvent. It was also the only one tested in solvent mixtures. The solvents used for the PVDF-HFP dip coating experiments were DMSO and acetone. These solvents are miscible with each other, so some dip coating experiments were performed with mixed solvent solutions.

Table 4.4: PVDF-HFP dip coating procedures comparing single solvent polymer coatings with mixed solvent on silicon substrates. Ac short for Acetone

	Polymer	Conc.	Ac/DMSO	Withdrawal [mm/min]	T [°C]
<i>1a</i>	PVDF-HFP	3 wt%	100/0	60	20
<i>1b</i>	PVDF-HFP	3 wt%	50/50	60	40

Figure 4.1 illustrates two polymer coatings produced by the procedures detailed in Table 4.4.

**Figure 4.1:** Resulting polymer coatings from single solvent solution and mixed solvent solution. **a)** is the coating produced by single solvent procedure *1a* and **b)** is the coating produced from mixed solvent solution *1b*.

The single solvent solution with acetone as a solvent produced a far more uniform coating than the Acetone/DMSO solvent mixture solution did. This was the case for a number of different solvent mixture ratios as well as well as for DMSO single solvent coatings. A notable feature of the dip coating utilizing DMSO as a solvent was that the solvent dried very slowly which seemed to have a negative impact on the uniformity. The high boiling point might have been the problem in that case. It is also possible that there is a problem with wetting due to DMSO being too polar, as it has a higher dipole moment than acetone.

Coating procedure 1a also displays a feature of the acetone single solvent solutions that was always present in its polymer coatings. The coating consists of two parts, a thicker part at the bottom of a substrate where gravity pools the solution during withdrawal and which dries slower due to it having a thicker solution layer. The second part is a larger more uniform region above the thicker region.

Even though the lower part of the polymer coating appeared non-uniform, it was established through gold etch testing that it was not an entry-point where etchants could penetrate the coating to a greater extent than the more uniform upper region. The explanation for this likely lies in the fact that the thickness of this region is higher than that of the of the more uniform upper region of the coating. This was more or less confirmed through ellipsometry measurements of the lower region of the

coating. Due to that region being less uniform a thickness value with an acceptable mean square error was not found. But it was close enough and the difference in thickness was substantial enough that it could be assumed with confidence. If this thicker part of the polymer coating ended up covering the NPS part of the optical fiber that might cause variability in the sensitivity of the sensors. However, this was easily avoided by having a small length of the fiber facing downwards during dip coating just below the gold covered part which had not had any gold deposited on it. The lower nonuniform coating would then be applied to the normal silicon dioxide surface at the bottom while the uniform upper coating would be covering the gold surface responsible for the NPS.

4.2.2 Concentration

The concentration of the polymer solution was a key factor for the coating properties. Dip coating procedures using PVDF-HFP and PPMA were tried in various concentrations and the findings are shown and discussed in the following subsection. Table 4.5 details the coating procedure for PVDF-HFP solutions of varying concentrations.

Table 4.5: Dip coating procedure for PVDF-HFP with varying concentrations.

	Polymer	Conc.	Solvent	Substrate	Withdrawal[mm/min]
<i>1c</i>	PVDF-HFP	1 wt%	Acetone	SiO ₂	60
<i>1d</i>	PVDF-HFP	2 wt%	Acetone	SiO ₂	150
<i>1e</i>	PVDF-HFP	3 wt%	Acetone	SiO ₂	60
<i>1f</i>	PVDF-HFP	5 wt%	Acetone	SiO ₂	60

The resulting polymer coatings from the procedures detailed in Table 4.5 are detailed in Figure 4.2.

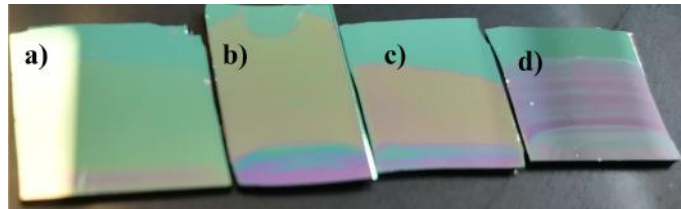


Figure 4.2: Polymer coatings produced using procedures where the concentration is varied between 1 and 5 wt%. **a)** corresponds to the 1 wt% solution procedure, **b)** the 2 wt% solution procedure, **c)** the 3 wt% solution procedure and **d)** the 5 wt% solution procedure.

A key difference that can be observed in Figure 4.2 between the coatings, is the change in colour of the uniform region of the coating, i.e. the upper region. This

region darkens as the concentration of the solution it is covered with increases, which is to say when the thickness of the polymer coating is increased. The polymer coating produced from the 5 wt% PVDF-HFP solution *1f* has visible purple stripes in what is supposed to be the uniform region with thinner more transparent regions in between the stripes. This is a common occurrence when the withdrawal speed is too high, the concentration is too high or when the solution temperature during coating is too high. The non-uniformity of the *1f* coating means that the thickness cannot accurately be measured with ellipsometry.

These specific polymer coatings were chosen because they clearly illustrate the difference in colour of the polymer coating at differing polymer solution concentrations. However, the coatings produced by *1c*, *1e* and *1f* have not had their thickness measured in an ellipsometer. The same procedures but used to coat Si substrates have been measured using ellipsometry and the resulting thicknesses are presented in Table 4.6.

Table 4.6: Coating thickness of the polymer coatings produced from dip coating procedures *1e-f*

	Coating thickness [nm]
<i>1c</i>	11
<i>1d</i>	36-42
<i>1e</i>	51-59
<i>1f</i>	411

As can be observed in Table 4.6, the thickness of the polymer coatings obtained by procedures *1c-1f* increase more or less linearly with the concentration. However, there seems to be an exponential increase in the thickness between the coatings produced by the 3% and 5% solutions. This increase is likely due to the 5% solution coating being above the critical overlap concentration, which is the concentration above which the polymer coils in the solution start to overlap [46]. This influences the relationship between the zero-shear viscosity and the concentration. This manifests in an increased power law index above the concentration in the linear mathematic relationship between the logarithm of the zero-shear viscosity and concentration [47]. Meaning that the slope of the logarithmic viscosity/concentration diagram is increased after the critical solution concentration is reached.

An estimation of the critical overlap concentration could have been found by obtaining an additional data point above the critical overlap concentration, fitting a linear curve to the logarithm of those two data points and intersecting that curve with a similar one for the data points below the critical solution concentration. The concentration of the intersection would then be the critical overlap concentration. This was not done partly due to a lack of time, but also because the coating thickness of a coating obtained above or at this concentration would have been thicker than 50 nanometers. Therefore it would not have been applicable in a viable dip coating procedure.

The paragraph above assumes that the coating thickness varies with concentration in the same way as the viscosity does, which does not necessarily have to be the case. However, the difference in thickness between 3 wt% and 5 wt% solution seem to suggest that a similar relation as that between viscosity and concentration exists between coating thickness and concentration. More data points would be required to verify whether this is the case.

The coating procedures with the PPMA were unfortunately not as successful as those conducted with PVDF-HFP solutions. A total of three concentrations were evaluated: 1, 2 and 3 wt%. A few of the more successful, but still failed, coating procedures for those concentrations are presented in Table 4.7.

Table 4.7: Dip coating procedures for PPMA solutions with toluene solvent and on Gold/silica substrates where the solution concentration is varied between 1 and 3 wt%.

	Polymer	Conc.	Withdrawal[mm/min]	T [°C]
<i>2a</i>	PPMA	1 wt%	150	50
<i>2b</i>	PPMA	2 wt%	150	50
<i>2c</i>	PPMA	3 wt%	150	50

The procedures in Table 4.7 yielded the polymer coating visible in Figure 4.3.

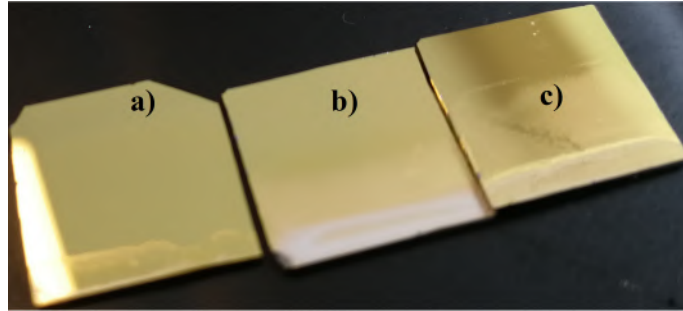


Figure 4.3: PPMA coating applied on gold/silica substrates. The solution concentration used in the dip coating procedures varied between 1,2 and 3 wt%. **a)** is the procedure corresponding to *2a*, **b)** to *2b* and **c)** to *2c*.

Figure 4.3 illustrates the polymer coatings produced by the coating procedures *2a-c*. The 2 and 3 wt% polymer solution coatings are clearly very non-uniform. This non-nuniformity is also present in the *2a* but to a lesser extent. Although it is not as easy to see the non-uniformity on the coating produced by the dip coating procedure *2a* in Figure 4.3, ellipsometry imaging confirmed that the surface was non-uniform.

4.2.3 Temperature

The following subsection concerns the relationship between the solution temperature and the coating properties. Starting with the dip coating procedures with varying temperatures for PVDF-HFP on silicon substrates. The procedures which were explored are detailed in Table 4.8.

Table 4.8: Dip coating procedures for PVDF-HFP on silicon substrates in acetone solutions with solution temperatures varying between 30 and 50 °C.

	Polymer	Conc.	Withdrawal[mm/min]	T [°C]
<i>1g</i>	PVDF-HFP	2 wt%	150	30
<i>1h</i>	PVDF-HFP	2 wt%	150	40
<i>1i</i>	PVDF-HFP	2 wt%	150	50

The procedures in Table 4.8 yielded the coating displayed in Figure 4.4. The reason a higher temperature than 50 °C was not tested was because the boiling point of acetone is 56 °C, which limited how high the solution could be heated.



Figure 4.4: 2 wt% PVDF-HFP coating applied on silicon substrates. Solution temperature during dip coating varied between 30 and 50 °C. **a)** corresponds to dip coating procedure *1g*), **b)** to *1h* and **c)** to *1i*.

Figure 4.4 illustrates how the temperature of the solution impacts the coating quality for PVDF-HFP polymer solutions in acetone on silicon substrates. The leftmost image is the result of *1g* and seems to be uniform. The middle image of the *1h* coating shows some darker areas around the sides suggesting that its non-uniformity manifests in regions of thicker coating there. The final image of Figure 4.4 displaying the *1i* coating illustrates the same increased thickness of the coating near the sides but a seemingly thinner middle area.

The same experiment as the one conducted with the dip coating procedures *1g-i* was replicated on silica substrates but with a few extra solution temperatures tested. These coating procedures are outlined in Table 4.9.

Table 4.9: Dip coating procedure for PVDF-HFP in acetone solutions on silica substrates with solution temperatures varying between 5 and 50 degrees.

	Polymer	Conc.	Withdrawal [mm/min]	T [°C]
<i>1j</i>	PVDF-HFP	2 wt%	150	5
<i>1k</i>	PVDF-HFP	2 wt%	150	20
<i>1l</i>	PVDF-HFP	2 wt%	150	30
<i>1m</i>	PVDF-HFP	2 wt%	150	40
<i>1n</i>	PVDF-HFP	2 wt%	150	50

The procedures detailed in Table 4.9 produced the coatings which are presented in Figure 4.5.

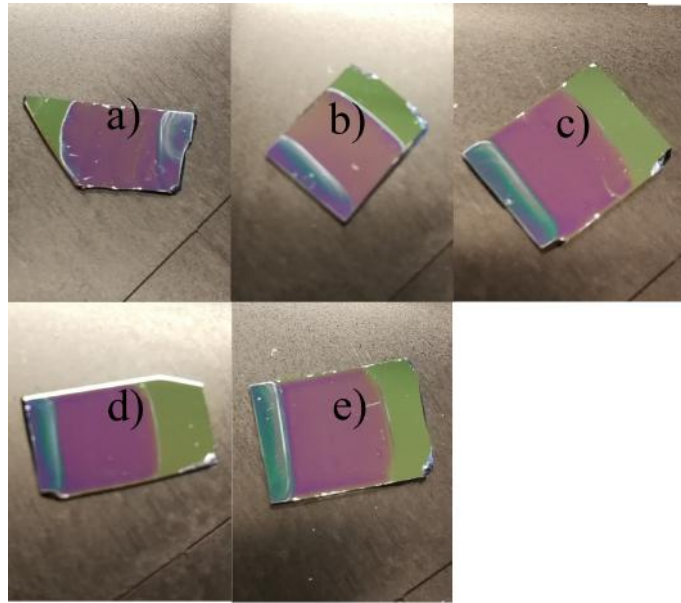


Figure 4.5: 2 wt% PVDF-HFP coating applied on silicon dioxide substrates. Solution temperature during dip coating varied between 5 and 50 °C. **a)** corresponds to dip coating procedure *1j*, **b)** to *1k*, **c)** to *1l*, **d)** to *1mk* and **e)** to *1n*.

The polymer coating can be observed to be non-uniform for the *1l* coating procedure as this coating contains the striped pattern characteristic for failed dip coating procedures. *1m* yields the most uniform coating as expected, *1n* and *1o* both show an increase in thickness compared to the procedure they preceded. They also share a faint non-uniformity that manifest in the increased thickness at the sides which was also observed for the silicon substrate coatings *1g-i*. The last polymer coating seen produced by *1n* has a lighter middle coating than *1m*. The similarities between *1n* and *1m* seem to mirror those between *1i* and *1h*.

The final temperature tests were those conducted with PPMA polymer coatings. The boiling point of its solvent toluene is a lot higher than that of acetone so a lot more solution temperatures could be tested. The coating procedures investigated are detailed in Table 4.10.

Table 4.10: Dip coating procedure for PPMA in toluene solutions on silica substrates with solution temperatures varying between 20 and 90 degrees.

	Polymer	Conc.	Withdrawal [mm/min]	T [°C]
<i>2d</i>	PPMA	3 wt%	150	20
<i>2e</i>	PPMA	3 wt%	150	30
<i>2f</i>	PPMA	3 wt%	150	40
<i>2g</i>	PPMA	3 wt%	150	50
<i>2h</i>	PPMA	3 wt%	150	60
<i>2i</i>	PPMA	3 wt%	150	70
<i>2j</i>	PPMA	3 wt%	150	80
<i>2k</i>	PPMA	3 wt%	150	90

The dip coating procedures in Table 4.10 yielded the coatings which are illustrated in Figure 4.6.

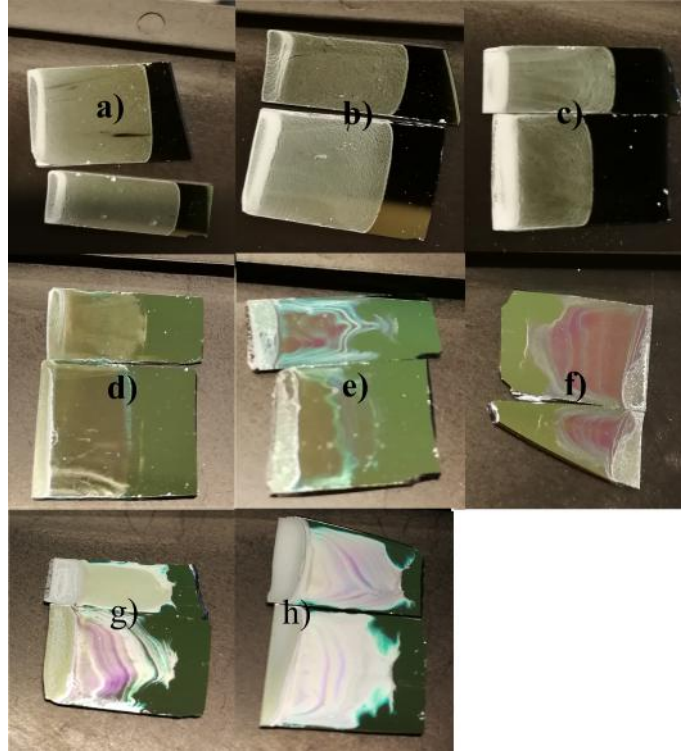


Figure 4.6: 3 wt% PPMA coating applied on silicon dioxide substrates. Solution temperature during dip coating varied between 20 and 90 °C. **a)** corresponds to dip coating procedure 2d, **b)** to 2e, **c)** to 2f, **d)** to 2g, **e)** to 2h, **f)** to 2i, **g)** to 2j and **h)** to 2k.

The coatings produced from procedures 2d-f display a spotted white opaque surface that seems to consist of several smaller crystals. It is possible that the temperatures at which these dip coating procedures were conducted, were not enough to completely solvate the polymer. The rest of the coating procedures 2g-k starting with the procedure with a solution temperature of 50 degrees show proper solvation but nevertheless a clear non-uniformity that is exacerbated at higher temperatures. This non-uniformity looks to be due to uneven crystallization during withdrawal/drying of the coating.

Both PVDF-HFP and PPMA are crystalline polymers. Due to the results observed across this subsection of the report, it is of interest to note how the crystallinity impacts coating uniformity. Crystal growth occurs at temperatures between the glass transition temperature and the melting temperature of the polymer. Crystallization consists of two processes with rates that vary with temperature in this region. The first is the crystal nucleation rate, which is the rate at which new crystal grains in the material are nucleated. The second is the crystal growth which is the rate at which the nucleated sites grow in the material. The nucleation rate is dominant at lower

temperatures closer to the glass transition temperature whereas the crystal growth rate is dominant at higher temperatures closer to the melting temperature [48]. The following paragraphs will evaluate the crystallization of the best coating procedure with regards to solution temperature for each polymer and what this might imply for polymeric dip coating in general. To start with, the glass transition temperature and melting point of PVDF-HFP and PPMA are displayed in Table 4.11.

Table 4.11: Glass transition temperature and boiling point of PVDF-HFP and PPMA.

Polymer	T _g [°C]	T _m [°C]
PVDF-HFP	-40	130-136
PPMA	-10	156

The manufacturer of the PPMA did not list the glass transition temperature of the polymer but it was assumed to be similar to normal polypropylene which is roughly -10 °C. A rough sketch of the nucleation rate, crystal growth rate and overall crystallization rate for PPMA are presented in Figure 4.7. The nucleation and growth rate graphs outlined in this section are sketches meant to illustrate where in the crystal growth regions the dip coating takes place for the optimal dip coating procedures. The rates have not been measured so they are merely estimations of how the relative rates change as the temperature is varied. The relationship between melting temperature, and crystal growth- and nucleation rate can be found in the article *Glass Transition, Crystallization of Glass-Forming Melts, and Entropy* [49].

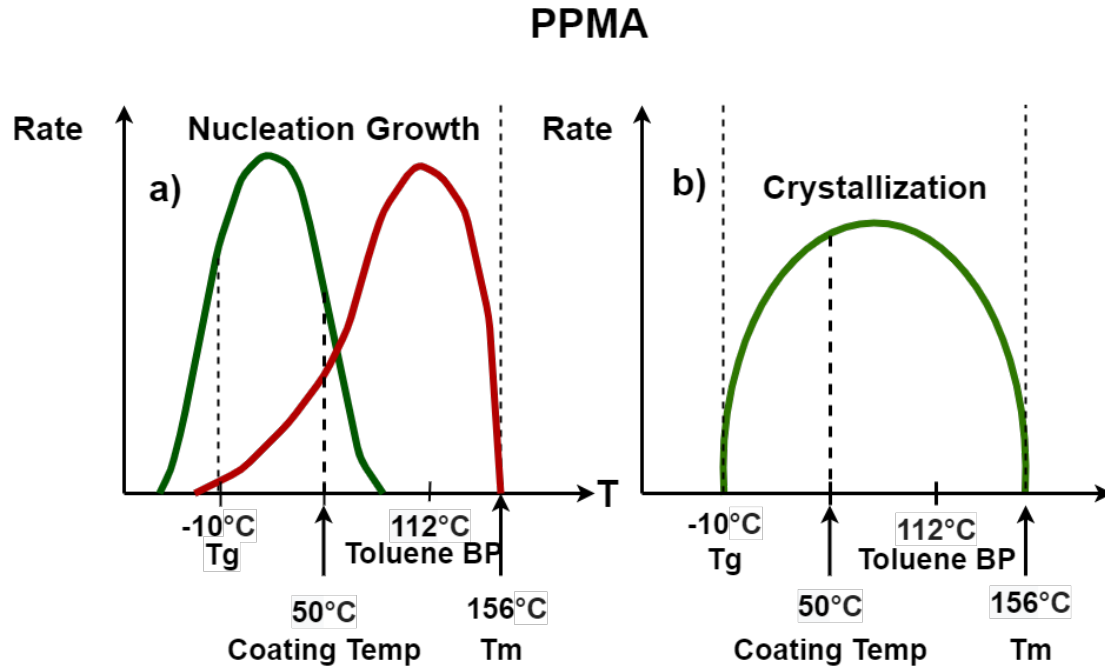


Figure 4.7: Rough sketch of the crystallization behavior of PPMA as it relates to polymer temperature. **a)** shows how the nucleation and crystal growth rate depends on the polymer temperature and where in this diagram the best solution temperature for dip coating has been shown to be. **b)** shows how the overall crystallization rate depends on polymer temperature

Looking at Figure 4.7, a possible reason for the apparent crystallization problem with the higher solution temperature dip coating procedures from Figure 4.6 becomes apparent. The growth rate of the crystals is higher at these temperatures, meaning that the overall crystallization will have fewer and larger grains which probably causes the white-ish colour on the *2h-k* polymer coatings. The crystallization rates for PVDF-HFP are presented in Figure 4.8.

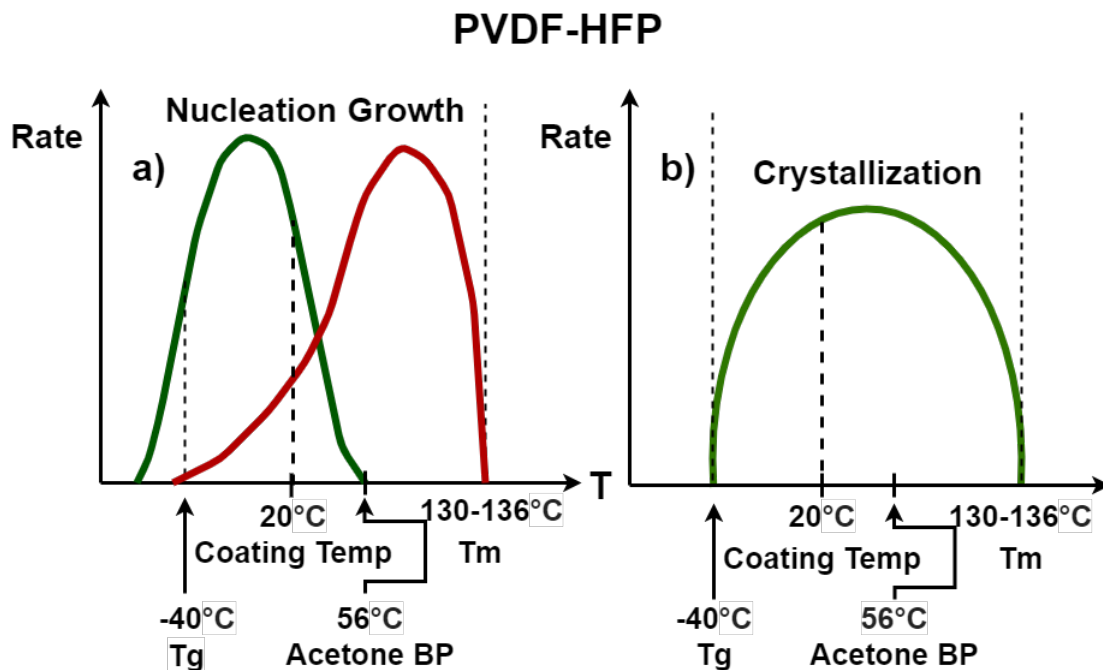


Figure 4.8: Rough sketch of the crystallization behavior of PVDF-HFP as it relates to polymer temperature. **a)** shows how the nucleation and crystal growth rate depends on the polymer temperature and where in this diagram the best solution temperature for dip coating has been shown to be. **b)** shows how the overall crystallization rate depends on polymer temperature.

The optimal dip coating solution temperature seems to be roughly in the same spot for PVDF-HFP as PPMA when it comes to growth rate, nucleation rate and overall crystallization rate. There is a clear preference for a lower growth rate and a higher nucleation rate. It is possible however that if PPMA had a solvent which could solvate it better at temperatures below 50 degrees that the optimal coating temperature might be lower, but that is for future work in this field to determine.

This subsection has primarily discussed the crystallization as an explanation for the observed change in the coatings as the solution temperature was varied. Another important factor that has not been discussed is the viscosity change. Viscosity tends to decrease as solution temperatures increase. This might be an argument for why viscosity changes probably are not the cause of the increases in thickness and lack of uniformity seen for the increased solution temperatures in this subsection. Since the viscosity decreases with increased temperature, the polymer coating thickness would decrease as well according to the relation between coating thickness and viscosity laid out in Equation 2.3. Since this was not the case, the more likely explanation for the increase in thickness as the solution temperature is increased becomes the

variation in crystal nucleation- and growth rate.

4.2.4 Withdrawal speed

The withdrawal speed was an important parameter in the creation of uniform coatings and a general trend between concentration and withdrawal speed was observed during the course of the project. A higher withdrawal speed was preferable in PVDF-HFP dip coating procedures where the concentration was at or below 2 wt%. Conversely, a lower withdrawal speed was necessary to yield uniform coatings when the concentration was at 3 wt% or above. This latter case is illustrated in Figure 4.9.

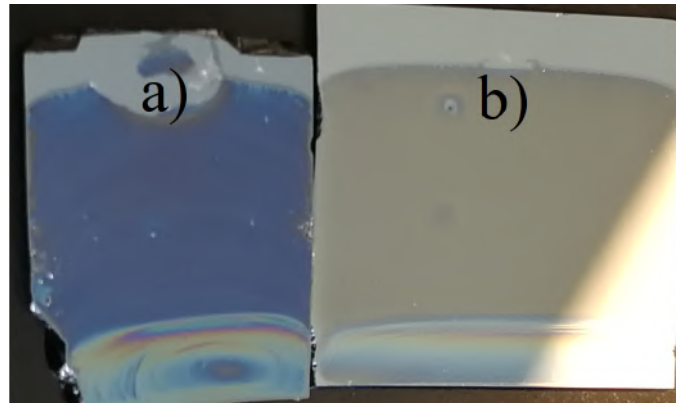


Figure 4.9: PVDF-HFP coating on two silicon substrates dip coated in a polymer solution with a concentration of 3 wt%. **a)** corresponds to a dip coating created using the withdrawal speed 150 mm/min and **b)** to 60 mm/min.

The polymer coating on the leftmost substrate in Figure 4.9 contains the thicker stripes which are consistent with the type of non-uniformity that occurs at higher coating thicknesses. The coating which is applied at higher withdrawal speeds is thicker, which is also in accordance with the relationship between withdrawal speed and coating thickness brought forth in Equation 2.3. This relationship is as previously mentioned valid for withdrawal speeds at or above 60 mm/minute, at which the dominant forces of the dip coating are the viscous drag forces.

Due to the PPMA coatings being very obviously non-uniform for all tested concentrations which were thought to yield a coating of the desired thickness, very little time was spent testing different withdrawal speed for those solutions. Both high and low withdrawal speeds were briefly tried but yielded no uniform coatings so more attention was spent to instead optimize the PVDF-HFP coating procedures.

4.2.5 Substrate material

The influence of the substrate material on the coating quality varies depending on which polymer was used. For the PVDF-HFP coating there was barely any dis-

cernible change between the coatings produced at room temperature on the different flat substrates. This holds true both with regards to thickness and uniformity. This was not the case for PPMA. There was a discernible difference between the quality of the polymer coating on the silicon substrates as compared to the silica and gold substrates. However, the silicon substrate coatings were still not uniform enough to be viable.

The silicon substrates are as previously mentioned hydrophobic whereas the silica and gold substrates are hydrophilic. The PPMA dip coating procedures yielded more uniform coatings on the hydrophobic silicon substrates. The cause of the lack of uniformity on the hydrophilic substrates might be due to the toluene solvent not being polar enough to sufficiently wet these surfaces. A solvent with a higher dipole moment such as 1,2,4-Trichlorobenzene might be needed to fix this and would be the logical next step if further experimentation with PPMA dip coating procedures are to be conducted.

4.3 Final polymer coating procedure

This section details the polymer coating procedure which produced the overall best results of those tried throughout the project.

The polymer solution was made by weighing 0.3130 grams of PVDF-HFP in a vial. 19.821 ml of Acetone was then added to the vial along with a stirrer. The solution was then stirred for 2 hours at room temperature and 300 rpm until the polymer was completely dissolved, yielding a 2 wt% PVDF-HFP solution.. A substrate was then cleaned by first placing it in a flat beaker filled with IPA which was placed in a sonicator bath full of water and sonicated for 10 minutes. The substrate was then dried and placed inside the tray of the UV/Ozone cleaner. The UV/Ozone cleaning was conducted over a 10 minute period. The substrate was then quickly placed in a closed container and transported to the dip coater.

The dip coater was set to a submersion and withdrawal speed of 150 mm/min and a hold and drying time of 3 seconds. The cleaned substrate was then fastened vertically to the dip coater clamp and coated in the solution by following the set parameters. After the substrate had been withdrawn it was placed hanging inside a preheated vial through a hole drilled into the lid while fastened by a clamp. The vial was then placed inside the preheated oven and was dried at 100 °C for 10 minutes.

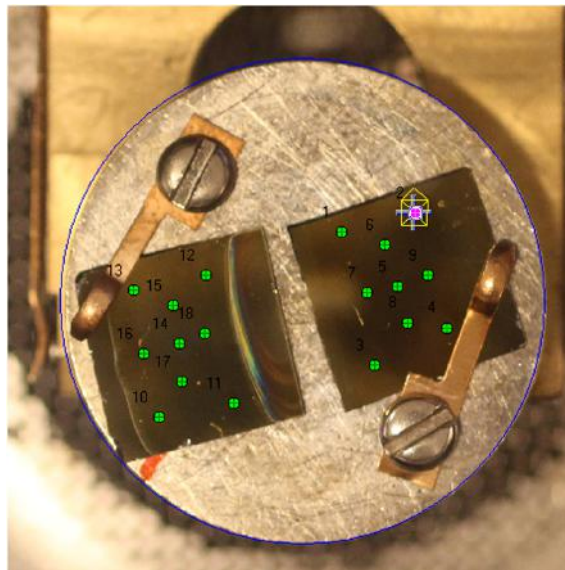
4.4 Uniformity measurements utilizing XPS

The XPS measurements were performed to evaluate the uniformity of the polymer coatings. XPS is a costly analysis to perform, meaning that the number of samples analyzed had to be limited. It was decided that two polymer coatings would be investigated, one made from a PVDF-HFP dip coating procedure and another made from FP1, which is a polymer that Insplorion has worked with previously. They were prepared according to the procedures illustrated in Table 4.12.

Table 4.12: Dip coating procedure for PVDF-HFP and FP1 coatings on silicon substrates used in XPS measurements.

	Polymer	Conc.	Solvent	Withdrawal[mm/min]
<i>1o</i>	PVDF-HFP	2 wt%	Acetone	150
<i>3a</i>	FP1	3 v%	FP1 solvent	40

The thickness of PVDF-HFP coated silicon substrates made using the dip coating from the above formulation is between 35-42 nm, which was measured by ellipsometry. The thickness of the coating yielded by the FP1 formulation above was measured to be 40 nm. The penetrating depth of the XPS used to measure the samples is 3 nanometers. Therefore, if the polymer coating is thinner than 3 nanometers due to some kind of non-uniformity, the XPS spectrum will include silicon peaks from the substrate underneath the polymer coating. The XPS sample setup can be seen in Figure 4.10.

**Figure 4.10:** XPS spectroscopy sample setup with marked points for where the sample will be analysed. The sample to the left (points 10-18) is PVDF-HFP and the one to the right (points 1-9) is FP1.

4.4.1 PVDF-HFP measurements

PVDF-HFP is a copolymer that consists entirely of carbon, hydrogen and fluoride atoms. The technique is not capable of detecting hydrogen so the XPS spectrum should therefore only contain peaks characteristic to carbon and fluoride [28]. The peak positions of substrate *1o* are displayed in Figure 4.11.

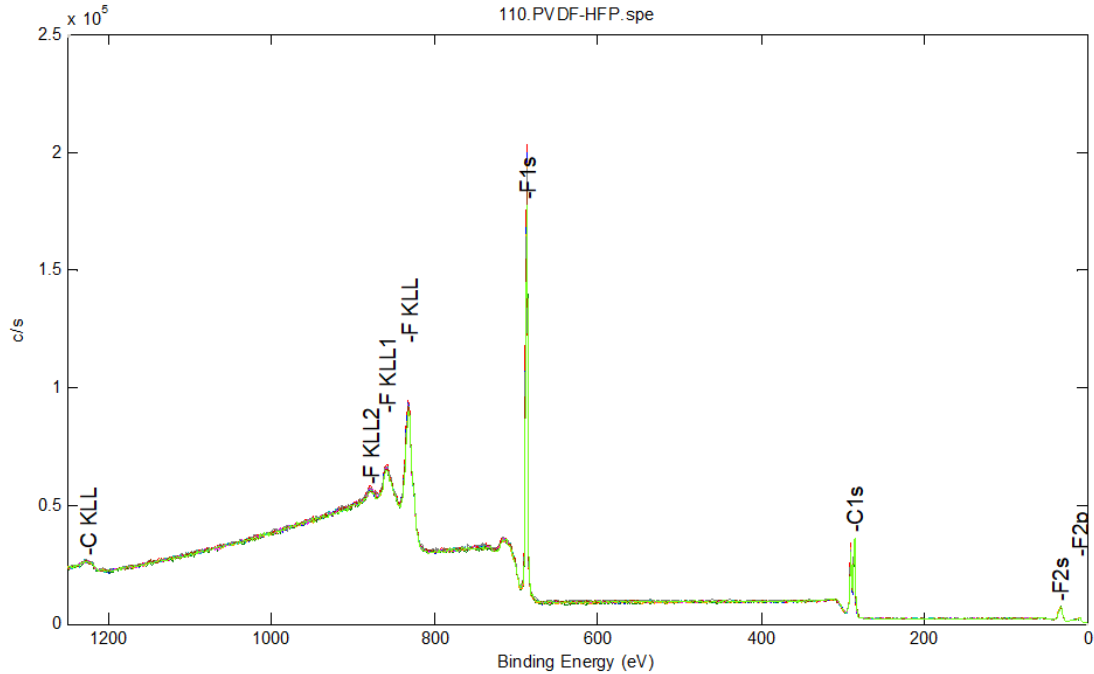


Figure 4.11: XPS spectrum for PVDF-HFP featuring detected coulomb per second on the Y-axis and Binding energy of the electrons to the atomic core on the X-axis. The diagram features measurements from points 10-18 overlapped onto each other.

Figure 4.11. clearly displays the elemental peaks of carbon and fluoride. The carbon peak present is the C1s peak and the Fluoride has the F1s, F2s and F2p peaks. No other elemental peaks are present in the sample. The atomic percent and weight percent composition of the sample are presented in Table 4.12.

Table 4.13: 2 wt% PVDF-HFP coating composition as analysed by XPS spectroscopy.

Concentration	
<i>Atomic percent (at%)</i>	C 47.5 at%, F 52.5 at%
<i>Weight percent (wt%)</i>	C 36.5 wt%, F 63.5 wt%

The concentrations of elements above details the ratio of elements present in the 3 nm deep layer analysed by the XPS spectrometer. As the results of this analysis only show the presence of carbon and fluoride atoms, it is safe to say that the polymer coating is uniform to the degree that it at least covers the entire surface with a coating layer thicker than 3 nanometers.

4.4.2 FP1 measurements

FP1 is a fluoropolymer that consists of fluoride, oxygen and carbon atoms. Peaks belonging to these three compounds are therefore the only ones that should appear in Figure 4.12, which displays the peak positions of the substrate dip coated according to procedure 3a.

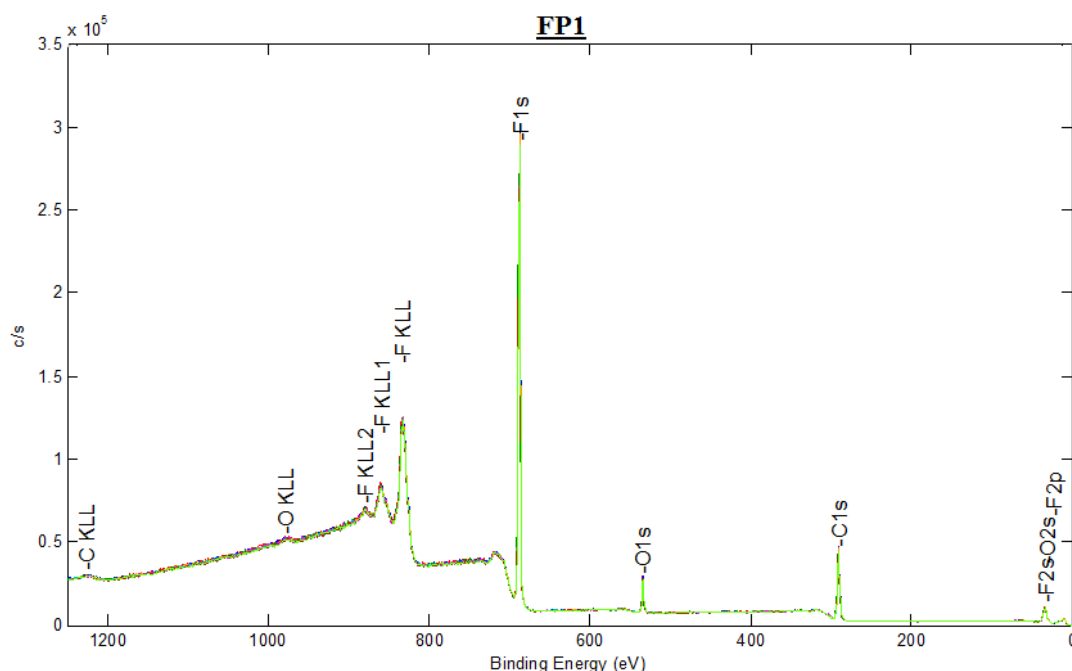


Figure 4.12: XPS spectrum for FP1 with detected coulomb per second on the Y-axis and Binding energy of the electrons to the atomic core on the X-axis. The diagram features measurement from points 1-9 overlapped onto each other.

The peaks present in Figure 4.12 show that only carbon, oxygen and fluoride are present in the analysed area of the sample. C1s belongs to carbon, O1s and O2s belongs to oxygen and F1s, F2s and F2p belongs to fluoride. The ratio between the elements is presented in Table 4.14.

Table 4.14: 3 v% FP1 coating composition as analysed by XPS spectroscopy

Concentration	
Atomic percent (at%)	C 33.5 at%, O 6 at%, F 60.5 at%
Weight percent (wt%)	C 24.5 wt%, O 6 wt%, F 69.5 wt%

Table 4.14 displays a high concentration of fluoride atoms in the coating, a smaller

concentration of carbon and an even smaller concentration of oxygen. As these elements are the only ones present in the sample it can be assumed that the top 3 nanometer thick layer of the substrate is comprised entirely of FP1. That is to say that the uniformity of the FP1 polymer coating is at least good enough to not leave any non-uniform areas thinner than 3 nanometers on the sample.

4.5 Gold etch testing

Gold etching was used to investigate the uniformity and permeability of the polymer coating, specifically if it was uniform enough or had a sufficiently low free volume to not allow the etchant solution to reach and etch the gold layer underneath the coating. The effects of the etching are clearly visible with the naked eye as the substrate loses its golden colour when it is etched. There is therefore no need to utilize any analytical instruments for the gold etch test. This did however mean that no quantifiable information about whether it was a problem with uniformity or free volume which had caused the etching. However, it can be assumed that gaps in the coating is likely the cause for instantaneous etching since permeation is diffusion controlled and should thus be slow enough as to not instantaneously etch any sample.

A clear difference between the etching behaviour on flat substrates and fiber substrates was observed. The results of the gold etching results are therefore separated based on substrate type.

4.5.1 Flat substrates

The gold etching tests were conducted with polymer coatings of all polymer types, including PPMA, PVDF-HFP and FP1. No PPMA coating had been produced for which a thickness value could be obtained with an MSE below the acceptable limit, meaning that the model used to evaluate the thickness did not fit the curve well enough to be able to provide an accurate thickness measurement. Nevertheless, it was of interest to see if the non-uniform coating would still provide protection against the gold etchant.

The gold etching results were evaluated by the time it took for the substrate to begin etching after it was first submerged, how long the etching experiment went on and what the status of the substrate was when the experiment was stopped. The last one was necessary because the experiment was suspended if the substrates were not completely etched after an hour or so. The polymer coating procedures for the PPMA fibers which were used in the etching experiments are found in Table 4.15.

Table 4.15: PPMA polymer dip coating procedures with toluene solvent at solution temperatures of 70 °C used for gold etching tests.

	Polymer	Conc.	Substrate	Withdrawal[mm/min]
<i>2l</i>	PPMA	1 wt%	Si	150
<i>2m</i>	PPMA	1 wt%	SiO ₂	150
<i>2n</i>	PPMA	2 wt%	Si	150
<i>2o</i>	PPMA	2 wt%	SiO ₂	150
<i>2p</i>	PPMA	3 wt%	Si	150
<i>2q</i>	PPMA	3 wt%	SiO ₂	150

The results of the etching tests performed on these substrates can be presented in Table 4.16.

Table 4.16: Gold etching tests performed on PPMA dip coated substrates.

	Etching starts [minutes]	Stopping time [minutes]	End status
<i>2l</i>	immediately	immediately	completely etched
<i>2m</i>	immediately	immediately	completely etched
<i>2n</i>	immediately	immediately	completely etched
<i>2o</i>	immediately	0,5	completely etched
<i>2p</i>	immediately	immediately	completely etched
<i>2q</i>	immediately	immediately	completely etched

As can be observed in Table 4.16, almost all of the PPMA dip coated substrates were etched immediately. The only one which was not completely etched in an instant was *2o*, but it still only took half a minute. The PPMA dip coated substrates were all visibly non-uniform and the fact that they were almost all etched in an instant was therefore not surprising.

The next etching tests were performed on PVDF-HFP and FP1 coated substrates. The substrates were dip coated according to the procedures *1o* and *3a* detailed in Table 4.17.

Table 4.17: Gold etching tests performed on PVDF-HFP and FP1 dip coated substrates.

	Etching starts [minutes]	Stopping time [minutes]	End status
<i>1a</i>	5	48	Partially etched
<i>2a</i>	4	62	Partially etched

The PVDF-HFP polymer coating *1o* started etching after 5 minutes. The etching started as a grey smudge on the higher more uniform part of the coating that slowly grew. After a while a part of the bottom of the substrate which had a thicker but less uniform polymer coating also started to become grey. The grey etching spread

very slowly over 48 minutes until the experiment was halted. By then it had spread over a wide area in the upper part without seemingly etching any particular area that intensely, while the bottom had a very small area that seemed to have been extensively etched.

The FP1 coated substrate *3a* started etching after 4 minutes and this manifested by the surface turning slightly greyer and small flecks appearing on the surface. This continued for 62 minutes until the experiments were stopped. The extent to which this actually etched the sample seemed to be minor.

4.5.2 Fibers

The gold etching experiments were also performed on coated fiber sensors. Among the fibers etched were the ones prepared according to the procedures detailed in Table 4.18.

Table 4.18: Dip coating procedures for gold/silica fiber sensors that were subjected to gold etching.

	Polymer	Conc.	Withdrawal[mm/min]
<i>1p</i>	PVDF-HFP	1 wt%	60
<i>1q</i>	PVDF-HFP	2 wt%	60
<i>1r</i>	PVDF-HFP	3 wt%	60
<i>1s</i>	PVDF-HFP	5 wt%	60
<i>1t</i>	PVDF-HFP	7 wt%	60

PVDF-HFP polymer coatings made with solvent concentrations varied between 1,2,3,5 and 7 wt% were coated on Au/SiO₂ fibers according to the dip coating procedures detailed in Table 4.18. These were all etched immediately with the exception of the optical fiber which was coated using a 7 wt% dip coating solution when they were subjected to a gold etching solution. That coating immediately etched the middle of the deposited gold on the optical fiber, but the gold at the ends of the gold coated region remained intact for 20 minutes before it too was completely etched.

Gold etching had not been performed on any polymer coated flat substrates produced with the dip coating procedures in Table 4.18. This meant that no direct comparison between the etching behavior on flat and optical fiber substrates was available. However, instead of conducting gold etching tests with flat substrates coated according to the procedures in Table 4.18, an optical fiber coating coated using dip coating procedure *1o* was subjected to gold etching instead. As was established in Section 4.5.2, this dip coating procedure produced a polymer coating on a flat gold/silica substrate that was able to withstand gold etching for 48 minutes without being completely etched. The coated optical fiber produced from procedure *1o* was also immediately etched. This indicated that there was a difference in the dip coating behavior on flat substrates compared to fibrous substrates, with the latter producing less uniform coatings for the PVDF-HFP coatings. The reason

behind this difference could reasonably be expected to be due to one of the following parameters, substrate width or geometry.

As was discussed in Section 2.2 of this report, the width of the substrate should only play a dominant roll in determining the coating thickness of the polymer coating at withdrawal speeds below 0,1 mm/second in the capillary regime. As *1p-t* all had withdrawal speeds of 1 mm/second the width of the sample should not have been that big of a factor. With that said, 1 mm/second is just at the threshold between the viscous drag- and intermediary regime. In the intermediary regime the capillary forces which are dependent on the width still play a significant part so this might be the explanation. But when the etching was performed on a dip coated fiber similar to *1q* with the exception that it had been withdrawn at a speed of 2.5 mm/second it was still immediately etched. Since this is quite far outside the regime where the width is supposed to influence the thickness, this indicated that the problem might instead be the geometry, which the dip coating equations in Section 2.2 does not account for.

4.6 Hydrofluoric acid treatment and FTIR measurements

An important property of the polymer coating is its chemical resistance to hydrofluoric acid. This is tested by submerging a polymer coated substrate into an HF solution and analysing it. In this specific case the substrates were submerged for 10 minutes into a 2 v% HF solution. The analysis method needed to be able to detect a change in the surface makeup of the sample and give a rough estimate of how the presence of carbon and fluoride atoms on the substrate surface had changed. FTIR was suitable for this task as the peak intensities of the FTIR spectrum could be used to loosely quantify how the presence of polymer had changed after HF treatment. Because no PPMA dip coating procedures had produced any uniform coating the HF treatment was only performed on PVDF-HFP coated substrates and FP1 coated substrates. The dip coating procedures used are detailed in Table 4.19.

Table 4.19: Dip coating procedures for PVDF-HFP and FP1 coatings on silica substrates used in FTIR measurements.

	Polymer	Conc.	Solvent	Withdrawal[mm/min]
<i>1o</i>	PVDF-HFP	2 wt%	Acetone	150
<i>3a</i>	FP1	3 v%	FP1 solvent	40

After these substrates had been subjected to HF treatment, they showed obvious signs of having been etched. The reason that the etching was so clearly visible is because of how HF removes the hydroxide groups attached to the SiO₂ surface [50]. The area that had been etched included the coated area of the substrate, it was therefore assumed that the HF had either penetrated the polymer coating by going through it or by starting to etch the uncoated part of the substrate and then traveling under the coating from that direction.

4.6.1 PVDF-HFP measurements

The chemical resistance to HF for PVDF-HFP polymer coatings is evaluated in this section. Figure 4.13 displays the way the PVDF-HFP coated substrate surface was impacted by HF treatment.

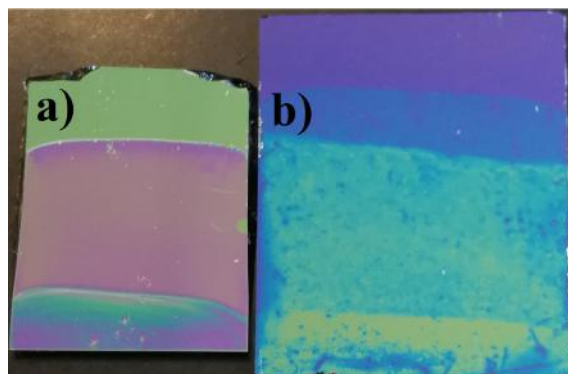


Figure 4.13: PVDF-HFP dip coated silica substrates, reference and HF treated. **a)** is the reference sample and **b)** has been subjected to an HF treatment.

When the two substrates from Figure 4.13 are compared it is evident that the HF treated polymer coated substrate has undergone some etching of the silica, both in the uncoated area and underneath the coated area. During the HF treatment an error was made, the entirety of the substrate was submerged in the HF solution even though only the coated part was supposed to be evaluated. The etching underneath the polymer coating could therefore have been caused by hydrofluoric acid diffusing through the silica layer underneath the coating [51]. It is therefore not possible to evaluate if the hydrofluoric acid etched the substrate beneath the coating by diffusing through the non-coated silica or penetrated the PVDF-HFP coating. However, whether or not the polymer coating had been damaged by the HF treatment could still be evaluated using FTIR, the results of which is presented in Figure 4.14.

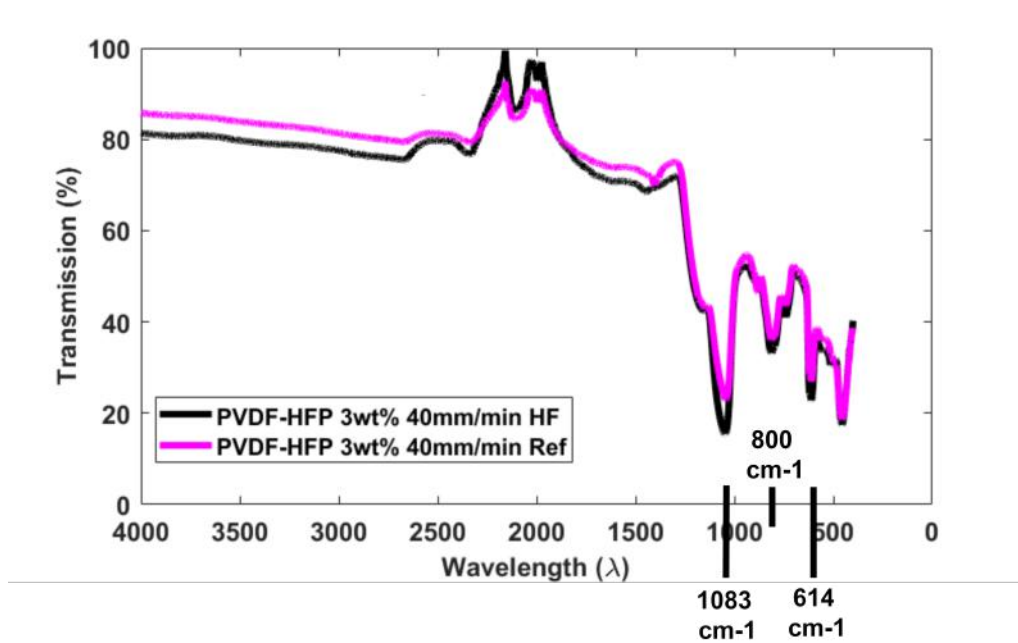


Figure 4.14: FTIR spectra for PVDF-HFP coated silica substrates. The graph with the magenta line is the reference substrate and the black line is the HF treated substrate.

The FTIR spectra in Figure 4.14 features 3 marked absorption peaks. Two of which belong to the silica substrates. These are the 1083 cm^{-1} and 800 cm^{-1} , which correspond to Si-O-Si stretching and Si-O bending respectively [52]. The 614 cm^{-1} absorption peak is characteristic to CF₂ bending for PVDF-HFP [53]. The intensity of the absorption peak at 614 cm^{-1} seems to be the same for both the reference and the HF treated sample, this would suggest that the polymer coating was able to withstand the HF treatment without deteriorating.

4.6.2 FP1 measurements

The chemical resistance to HF for FP1 polymer coatings is evaluated in this section. Figure 4.15 displays the way the FP1 coated substrate surface was impacted by HF treatment.

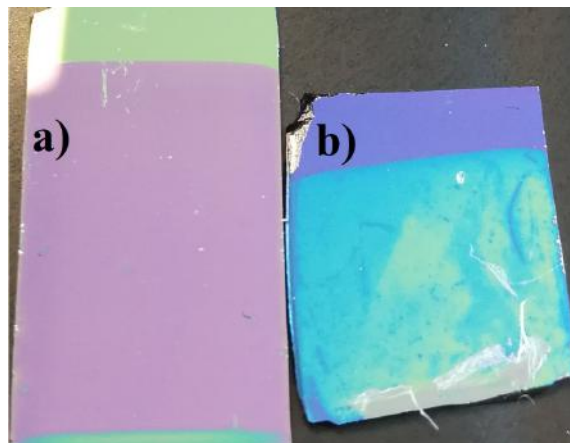


Figure 4.15: FP1 dip coated silica substrates, reference and HF treated. **a)** is the reference sample and **b)** has been subjected to an HF treatment.

The same HF treatment procedural error was repeated on the FP1 coated substrate during HF treatment as was done for the PVDF-HFP coated substrate. Meaning the uncoated substrate was subjected to the HF. The etching underneath the polymer coating could therefore be due to HF diffusion through the silica from the uncoated region. The bottom of the HF treated substrate was accidentally scratched with a tweezer, the scratch seen in Figure 4.15 **b)** should not be confused with degradation due to the HF treatment itself. This scratch was made after HF treatment so it should not have any bearing on the FTIR results, which are displayed in Figure 4.16.

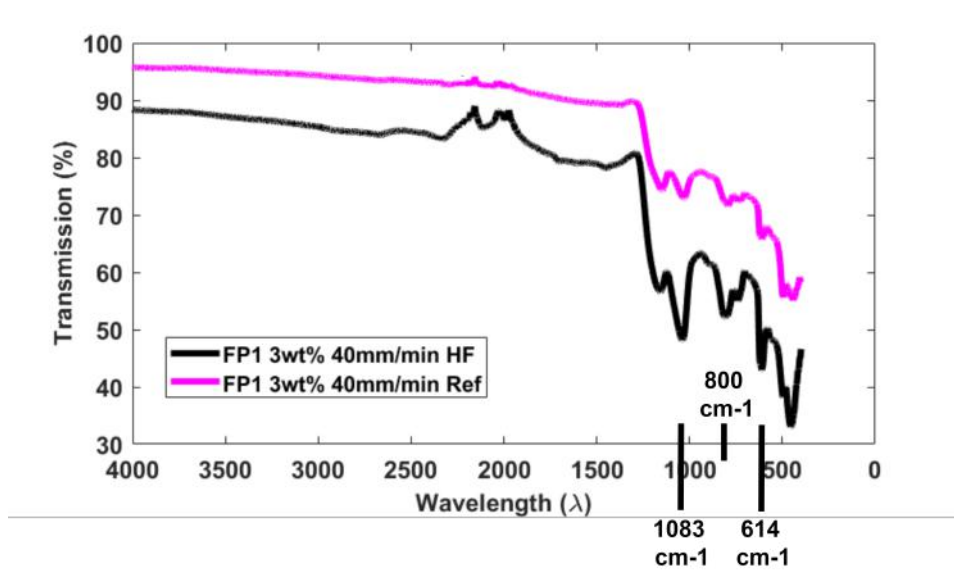


Figure 4.16: FTIR spectra for FP1 coated silica substrates. The graph with the magenta line is the reference substrate and the black line is the HF treated substrate.

Figure 4.16 features the same absorption peaks as Figure 4.14 does. FP1 is a fluoropolymer just like PVDF-HFP and therefore has a CF₂ bending peak at about the same position as the PVDF-HFP. The peak intensities observed in the FTIR analysis of the FP1 polymer coating are all increased for the HF treated sample as compared to the reference. For the silica peaks at 1083 cm⁻¹ and 800 cm⁻¹ this could mean that the polymer coating had been degraded and allowed the IR radiation to be more readily absorbed by the silica underneath. However, in that case we would expect to see a decrease in the FP1 absorption peak at 614 cm⁻¹, which is not the case. The peak instead displays an increased intensity, suggesting that the results might contain some error to cause the increase in peak intensity for the HF treated samples. A conclusion can therefore not be drawn from these results.

4.7 Impact of polymer coating on sensor sensitivity as measured by BRIS

The polymer coating adds an extra layer between the NPS gold film and the solution whose optical properties it is supposed to interpret. This will obviously affect the sensitivity of the sensor, which could be correlated to the thickness of the polymer coating. This impact was evaluated using BRIS. Testing was done on PVDF-HFP- and FP1 coated fibers as well as uncoated fibers. All fiber sensors were taken from the same batch and they were all cleaned in the same way before the coating was

applied. The FP1 and the uncoated fiber were tested a month after the PVDF-HFP coated fibers. An example of how the resonance peak position is redshifted as the refractive index is increased is presented in Figure 4.17.

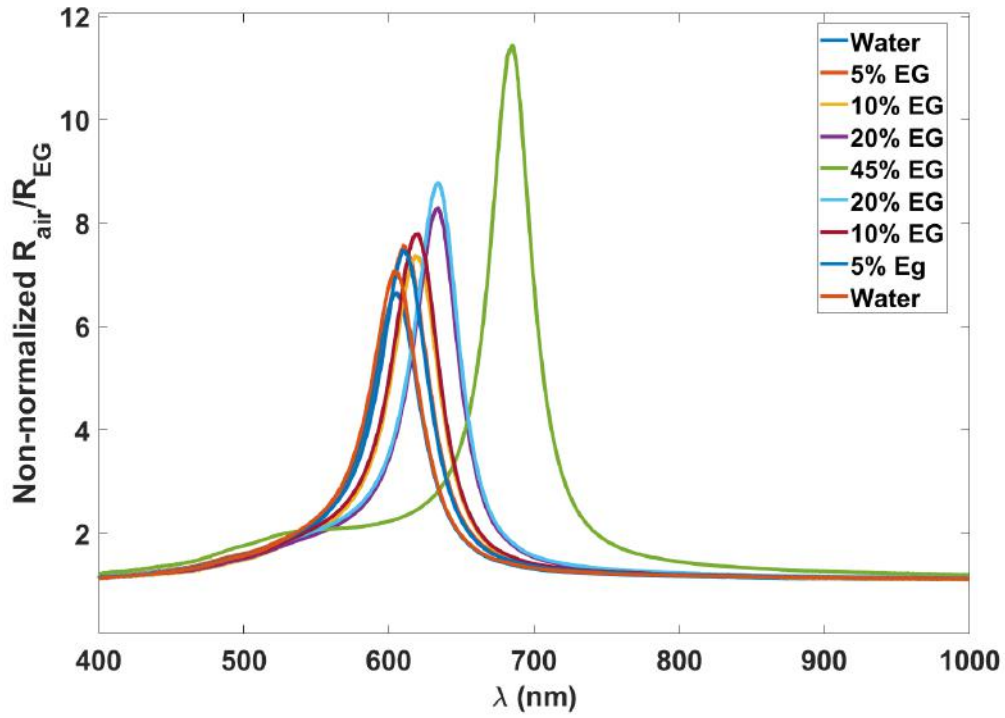


Figure 4.17: BRIS extinction spectra for an NPS fiber sensor measured in a number of EG/water solutions.

Figure 4.17 illustrates how an increase in the EG concentration, i.e. an increase in the refractive index of the dielectric material surrounding the NPS fiber sensor, redshifts the resonance peak position. The linear relationship between the resonance peak positional shift and the refractive index is presented in Figure 4.18.

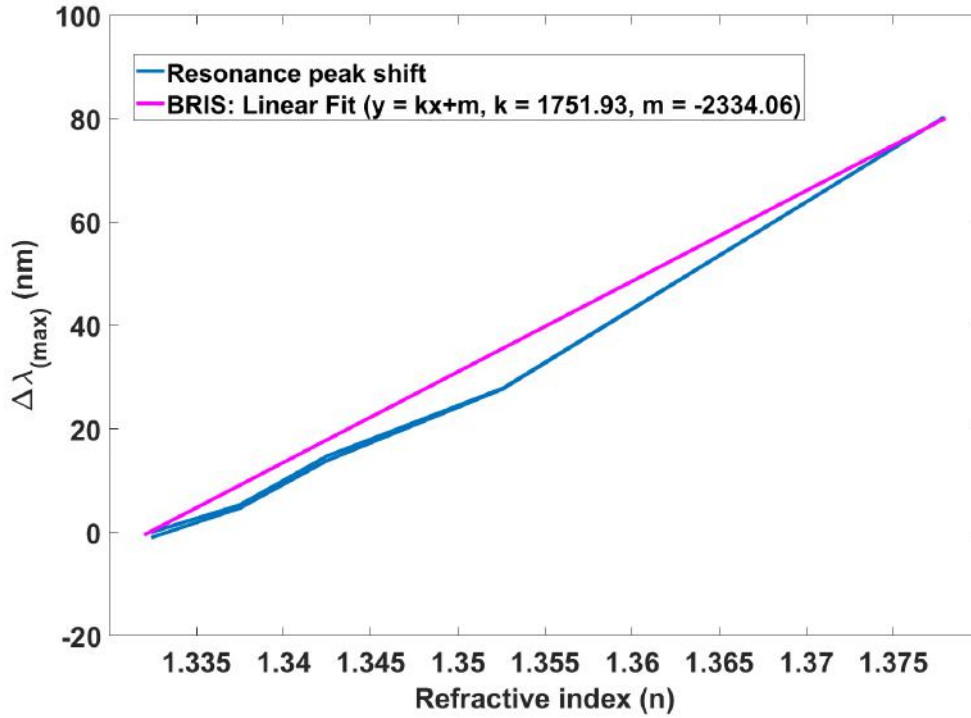


Figure 4.18: The resonance peak shift data and a linear model plotted against the refractive index.

The BRIS is defined as the incline of the linear fit to the resonance peak shift against refractive index plot. In Figure 4.17, this corresponds to the variable k , meaning that k is the BRIS value. The ability to construct this model is contingent on the refractive index of the solution being known. Given that the relationship between EG concentration and refractive index is known, BRIS can be calculated. In this project this was done using the programming platform matlab.

Since one of the most important areas of testing in this case was how the thickness of the coating influences the sensitivity, various polymer solutions of different concentrations were used to coat the fibers whose sensitivity was tested. Their coating procedures and the resulting sensitivity is detailed in Table 4.20.

Table 4.20: Fiber coating procedures and sensitivity of dip coated gold/silica fibers measured using BRIS. The PVDF-HFP coatings were produced using acetone solutions.

	Polymer	Conc.	Withdrawal[mm/min]	BRIS $[\Delta\lambda_{Max}/\Delta n]$
<i>1p</i>	PVDF-HFP	1 wt%	60	1970.5
<i>1q</i>	PVDF-HFP	2 wt%	60	1960.1
<i>1r</i>	PVDF-HFP	3 wt%	60	1919.5
<i>1s</i>	PVDF-HFP	5 wt%	60	1856.4
<i>3a</i>	FP1	3 v%	40	1751.9
<i>Uncoated</i>	-	-	-	1902.6

The sensitivity of the fibers coated with PVDF-HFP show a clear trend of decreased sensitivity as the solution concentration of the dip coating solution is increased. The sensitivity of the uncoated fiber was meant to be used as a baseline to which the loss of sensitivity for the polymer coated fibers could be compared. However, as can be observed in Table 4.20, the sensitivity of the uncoated fiber is lower than that of the majority of the PVDF-HFP coated fibers. Some error must therefore have occurred to cause that sensor to have a lower sensitivity. This could have been anything from measurement errors to contaminated fiber surfaces to faulty gold deposition. Either way, it is not suitable to use as a baseline.

The thickness of the FP1 polymer coating and the 2 wt% PVDF-HFP polymer coating should both be around 40 nm. Yet there is a very large difference in the sensitivity of these coated fibers sensors. The FP1 coated fiber sensor can be observed to have a significantly lower sensitivity than that of the 2 wt% PVDF-HFP one. The lowered sensitivity of the FP1 is in line with what is to be expected of a fiber sensor that has been coated. The gold etching experiments indicated that the PVDF-HFP coatings were not uniform on the fiber sensors. The seemingly small decrease in sensitivity for the PVDF-HFP coated fiber sensors seem to strengthen this assumption. The coating likely does not cover the entirety of the fiber sensor, meaning that the sensitivity is not affected as much as for the FP1 coated fiber sensors.

5

Conclusion

The result of the project shows that a dip coating procedure utilizing PVDF-HFP can consistently achieve polymer coatings thickness around 35-42 nm. The uniformity of the coatings produced by this procedure has with XPS been proven to be acceptable on flat substrates. Gold etch experiments have however indicated that the uniformity of the polymer coating might not be that great on the fiber sensor substrates, which is something that warrants further investigation.

Dip coating procedures utilizing a mixed solvent solution with the solvents DMSO and Acetone were investigated but ultimately disregarded due to the resulting coatings having a high degree of non-uniformity. The solvent which provided the most uniform coatings in single solvent solutions was acetone. The optimal solution temperature during dip coating with PVDF-HFP solutions was found to be room temperature and the polymer solution concentration yielding the most uniform coating is 2wt%. A dip coating procedure with the previously mentioned concentration, solution temperature and solvent has an optimal withdrawal speed of 150 mm/min. However, it was confirmed that a slight increase in concentration meant that the withdrawal speed had to be decreased in order to prevent localized polymer coating non-uniformity in the shape of stripes on the coating surface.

Bulk refractive index measurements have shown that the concentration of the polymer solution used to coat the nanoplasmonic optical fibers has a direct influence on the sensitivity of the fiber. However, the influence was rather small for the 2 wt% PVDF-HFP coating, which suggest that it might not meaningfully affect the sensitivity of the fiber optic sensor. This is thought to be because the coating does not uniformly cover the NPS surface of the fiber sensor.

Attempts to produce a dip coating procedure utilizing PPMA were unsuccessful. The cause of this failure is thought to be that toluene was chosen to be the solvent. Toluene likely does not have a high enough polarity to properly adhere and wet the Au/SiO_2 surface, which causes problems with the adhesion between the polymer coating and fiber sensor surface. Future projects should try a dip coating procedure for PPMA using 1,2,4-trichlorobenzene as a solvent, since it has a much higher dipole moment and is therefore more likely to adhere to the fiber sensor surface.

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A

Appendix 1 - Calculations

The solution vessels most suitable for use both to store the solutions and to dip into during dip coating that were available at Insplorion were 20 ml vials. The total volume V_t used for the basis of the concentration calculations was therefore set to 20 ml. The concentrations for the PVDF-HFP and PPMA solutions were calculated in weight percentage (wt%) concentration whereas the FP1 solution was calculated in volumetric percentage (v%) as it came pre-prepared in a 7 v% solution along with solvent which made dilution into lower concentrations convenient.

A.1 Single-solvent wt% concentration calculations

For the *wt%* calculations there were two types of solutions used, the solution utilizing a single solvent and the solution using two solvents. This subsection concerns the former case. The starting point for the calculations is the volume of the solution which is made up of the volumetric contributions from the polymer and solvent according to the relation in Equation A.1.

$$V_t = V_p + V_s = 20[ml] \quad (\text{A.1})$$

Where V_t is the total volume, V_s is the volume of the solvent and V_p is the volume of the polymer. Given a desired concentration of c_{wt} , the mass of the polymer can be expressed as the concentration times the weight of the solution in accordance with Equation A.2, where the volume of the polymer has been substituted for the difference between the total volume and the volume of the solvent.

$$\rho_p(V_t - V_s) = V_t c_{wt} \rho_t \quad (\text{A.2})$$

Where ρ_t is the total solution density and ρ_p is the polymer density. This equation can then be simplified to give an expression of ρ_t in Equation A.3.

$$\rho_t = \frac{\rho_p(V_t - V_s)}{c_{wt} V_t} \quad (\text{A.3})$$

The mass contributions in the solution from the solvent and polymer are described in Equation A.4.

$$m_t = m_p + m_s \rightarrow \rho_t V_t = \rho_p V_p + \rho_s V_s \quad (\text{A.4})$$

The expression for ρ_t from Equation A.3 is then substituted into the ρ_t in Equation A.4, yielding Equation A.5.

$$V_t \frac{\rho_p(V_t - V_s)}{c_{wt} V_t} = V_s \rho_s + (V_t - V_s) \rho_p = V_s(\rho_s - \rho_p) + V_t \rho_p \quad (\text{A.5})$$

The terms dependent on V_s are then placed on one side of the equation while the others are on the other side.

$$V_s(\rho_s - \rho_p + \frac{\rho_p}{c}) = \frac{\rho_p V_t}{c} - V_t \rho_p \quad (\text{A.6})$$

Both sides are then multiplied by c , yielding Equation A.7.

$$V_s(c\rho_s + \rho_p - c\rho_p) = \rho_p V_t - cV_t \rho_p \quad (\text{A.7})$$

The equation is then solved for V_s , yielding Equation A.8.

$$V_s = \frac{\rho_p V_t (1 - c)}{(c\rho_s + \rho_p (1 - c))} \quad (\text{A.8})$$

Equation A.8 contains known variables and a solvent volume can therefore be calculated. This volume can then be inserted into Equation A.9 to yield the mass of polymer that needs to be dissolved in the solvent to get the desired polymer solution.

$$m_p = \rho_p (20 - V_s) \quad (\text{A.9})$$

A.2 Double-solvent wt% concentration calculations

The double-solvent concentration calculations start with an expression similar to that of Equation A.1, with the difference being that a second term for the second solvent and an index differentiating the two is added. The new expression for the total volume is displayed in Equation A.10.

$$V_t = V_p + V_{s,1} + V_{s,2} = 20ml \quad (\text{A.10})$$

The term $V_{s,1}$ is chosen to be the solvent with the lower volume in the solution and $V_{s,2}$ being the one with the higher volume. k , i.e. the volumetric ratio between the solvents, is introduced in Equation A.11. As the ratio between the solvents is adjusted according to the specifications of the person making the solution, the value of k is known.

$$k = \frac{V_{s,2}}{V_{s,1}} \quad (\text{A.11})$$

Calculations analog to what was done in Equations A.2-A.8 are then performed for the double-solvent solution yielding the expression for $V_{s,1}$ in Equation A.13.

$$V_{s,1} = \frac{\rho_p V_t (1 - c)}{c\rho_{s,1} + ck\rho_{s,2} + ((k + 1) - (c(k + 1)))\rho_p} \quad (\text{A.12})$$

The expression for $V_{s,1}$ is comprised entirely of known variables and can therefore be calculated to a numerical value. This value can then be inserted into Equation A.13 to solve for the polymer mass to be weighed and solvated in the polymer solution.

$$m_p = \rho_p (20 - V_{s,1}(k + 1)) \quad (\text{A.13})$$

A.3 Single-solvent v% dilution calculations

The simplest calculations by far were those performed to yield the volumetric concentration for the FP1 solution. Equation A.14 yields the volume of the 7v% solution that needs to be added to the desired solution.

$$V_1 = \frac{C_f V_f}{C_1} \quad (\text{A.14})$$

C_f denotes the desired final solution concentration and V_f denotes the total volume, which is the same as for the other solutions; 20 ml. C_1 is the concentration of the master solution. The rest of the total volume is made up of the solvent that is added to dilute the polymer solution. The expression describing the amount necessary is displayed in Equation A.15.

$$V_{1,s} = V_f - V_1 \quad (\text{A.15})$$

B

Appendix 2 - Polymer properties

The following table details the properties of the polymers investigated in this project as well as their CAS numbers and suppliers.

Table B.1: Properties and details of used polymers.

	Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP)	Polypropylene-graft-maleic anhydride (PPMA)
M_w ¹	400000	9100
M_n ²	130000	3900
ρ ³	1.77	0.934
T_g ⁴	-40	-10
T_m ⁵	130-136	156
CAS:	9011-17-0	25722-45-6
Supplier	Sigma-Aldrich	Sigma-Aldrich

¹ Weight average molecular weight (*g/mol*)

² Number average molecular weight (*g/mol*)

³ Density at 25 ($^{\circ}C$)

⁴ Glass transition temperature ($^{\circ}C$)

⁵ Melting temperature ($^{\circ}C$)