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Ellipsometric Porosimetry Set-up and Study of Thin Films in the Nanometer Regime

Master's Thesis

to achieve the university degree of
Diplom-Ingenieur

Master's degree programme: Technical Physics

submitted to

Graz University of Technology

Supervisor

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Graz, September 2020

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ACKNOWLEDGEMENTS

I want to take this chance to thank every single one, who helped and supported me throughout the past years.

I wish to express my sincere thanks to my supervisor, Anna Coclite, for giving me the opportunity to write this Master thesis. Her patient guidance and the continuous encouragement during the last couple of months will never be forgotten.

Besides her, I want to thank the whole research group, especially Marianne Kräuter, who supported me during the formation of this thesis. She always lent me an ear and helped me with useful suggestions. At some points her never-ending effort to motivate me and her faith in this thesis were really needed.

I also want to express my gratitude to Alberto Perrotta, who brought the idea and plans of the ellipsometric porosimeter to TU Graz and who was always willing to help and advise me no matter the time or where he was.

And last, but not least I want to wholeheartedly thank my friends, my family and Michael for their support and encouragement. I want to express my gratitude for their faith in me, their effort to challenge me to become better and their unwavering love. Most of all, i want to thank my parents for everything they have done for me. They have made me, who I am today.

Ellipsometric porosimetry is a rather recently developed technique, used to characterise porous thin films concerning their porosity and pore size distribution. Ellipsometric porosimetry allows evaluating most of the features of thin films with pore diameters in the sub-nanometer regime. This is done by measuring the change in film thickness and of optical properties (e.g. the refractive index) using an ellipsometer throughout an adsorption and desorption cycle of a gaseous species within the pores.

Film porosity gains more and more importance in material science and has become a key element in many technology branches, e.g. to improve the switching speed in microelectronic devices, as barrier layers for organic light-emitting diodes or as components of selective gas- and biosensors.

The scope of this work is divided into three parts – realising the set-up of the vacuum system including the experimental chamber, developing a software to automate, and therefore speed up, the measurement and postprocessing process and testing the ellipsometric porosimeter by estimating the porosity of thin films. It is intended to use porous zinc oxide films created via molecular layer deposition as testing samples in this work.

Ellipsometrische Porosität ist eine junge Technik, um poröse Dünnschichtfilme bezüglich ihrer Porosität und ihrer Porengrößenverteilung zu charakterisieren. Ellipsometrische Porosität ermöglicht es, die meisten Eigenschaften von Dünnschichtfilmen mit Poren im Subnanometer-Regime zu untersuchen. Dies geschieht durch das Messen der Schichtdicke und optischer Eigenschaften (z.B. des Brechungsindex) mit einem Ellipsometer während eines Adsorptions- und Desorptionszyklus eines Gases innerhalb der Materialporen.

Die Porosität in Dünnschichtfilmen wird immer wichtiger in Materialwissenschaften und ist inzwischen ein Schlüsselement in vielen Technologiesparten geworden. Poröse Materialien helfen bei der Beschleunigung der Schaltgeschwindigkeit in Mikroelektronik und dienen als Barrierschicht in Organischen Leuchtdioden oder als Komponenten in Gas- oder Biosensoren, um nur einige wenige Einsatzgebiete zu nennen.

Die Masterarbeit lässt sich in folgende drei Teilaufgaben unterteilen. Zuerst wird der Aufbau, samt Reaktor und Vakuumsystem realisiert, dann werden die graphische Benutzeroberflächen geschrieben, um den Mess- und Auswertevorgang zu automatisieren und zu beschleunigen, und schließlich werden Testmessungen an porösen Dünnschichtfilmen vorgenommen. Zinkoxid-Filme, welche durch Moleküllagenabscheidung hergestellt wurden, sind als Testproben angedacht.

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The aim of this chapter is to give an overview of the fundamental physics behind the behaviour of porous materials and the possible ways to deposit and later characterise thin films thereof.

1.1 Porous Materials

Nearly every solid material is to some extent porous. Generally, porous materials consist of a solid framework and pores formed within this structure. There are numerous advantages to this material class, such as large surface areas and the possibility to include additional active species within the pore network. Most of the mechanical, physical and chemical properties of porous materials are based on the material's porosity. This section is used to give an insight into the concept of porous media and their properties [1].

1.1.1 Porosity

Usually, porous materials are characterised by the so-called porosity. It is defined as the fraction between the void volume and the total volume of the sample.

$$P = \frac{V_{void}}{V_{total}} \quad (\text{Eq. 1.1})$$

P ... porosity

V_{void} ... void volume

V_{total} ... total volume

Materials are classified into different porosity types based on their pore system, as it affects many of their physical and chemical properties. The distinction can be done due to the pore size.

According to the International Union of Pure and Applied Chemistry (IUPAC) porous solids can be grouped into micro-, meso- and macro-porous samples based on their pore size. The pore size is defined as the distance between two parallel pore walls. In case of cylindrical-shaped pores, this would be equivalent to the pore diameter, for slit-shaped pores it would be identical to its width [2]. In the following table the pore size related to the above-mentioned nomenclature is presented.

Table 1.1: Nomenclature of pore size based on the pore diameter d [2]

Denomination	Pore size
Microporous	$d < 2 \text{ nm}$
Mesoporous	$2 \text{ nm} \leq d \leq 50 \text{ nm}$
Macroporous	$50 \text{ nm} < d$

A comparison might be useful to put these sizes in perspective. Microporosity is given, if the pores are smaller than or have approximately the size of the fluids' molecules, which are used as adsorbent to examine the sample (e.g. water or toluene). Macro-pores are either comparable in size or larger than the mean free path of gas molecules in air at ambient pressure. This thesis focuses on meso- and microporous films (see section 4).

Another possible way to divide porous materials is based on their pore form and accessibility (depicted in figure 1.1). This distinction is especially important during specific characterisation methods for porous thin films (see section 1.3) and determines possible applications of the porous material (see section 1.1.2).

Some pores are completely surrounded by the solid framework of the material and therefore, isolated from each other and the outside. So-called 'closed pores' influence the mechanical strength and the thermal conductivity of the sample, but are not available to flows of liquids or gases.

The other main type of porosity is called 'open', as they are accessible to external adsorptives. Open pores can be classified into 'through pores', if they have two openings at the sample surface, or 'blind pores', if there is only one open end. Open pores can be further divided based on their shape (e.g. cylindrical-, ink-bottle-, funnel- or slit-shaped) [2].

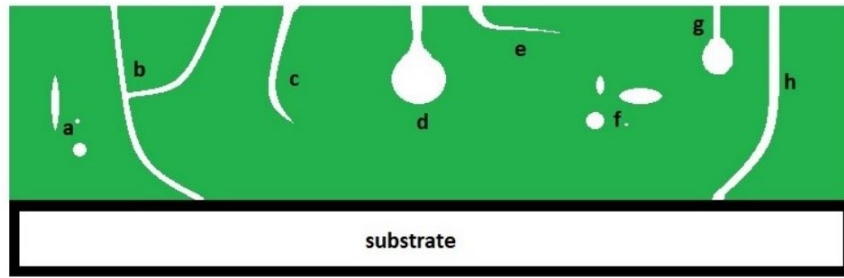


Figure 1.1: Schematic of different pore types based on their shape and accessibility [2]:
 a) f)...closed pores, b) c) d) e) g) h)...open pores, b) h)...through pores, c) d) e) g)...blind pores

Additionally to its porosity, it is highly likely, that the sample exhibits a certain roughness along its surface. Depending on the severity of the roughness, this may have an unwanted impact on the measurements' outcome, or even hinder an examination method completely. Therefore, it is also necessary to distinguish between surface roughness and blind pores. Conventionally, it is called a pore, if the depth of the surface irregularity is greater than its width [2]. This is depicted in figure 1.2.

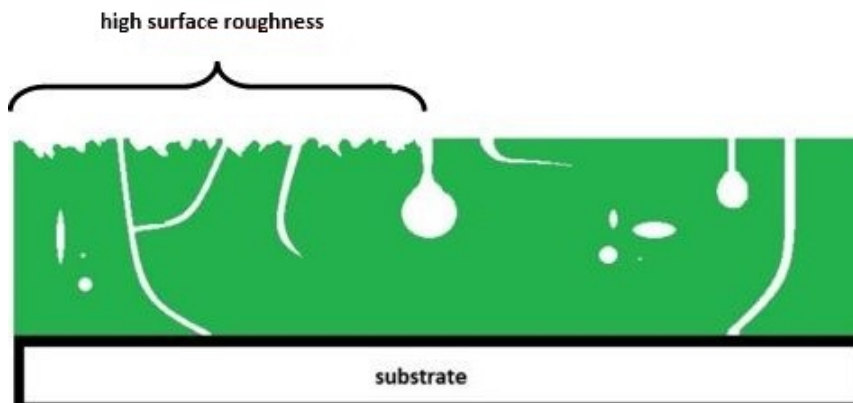


Figure 1.2: Schematic of a sample's surface: On the left, roughness can be seen.

1.1.2 Applications of Porous Materials

Most of the naturally occurring materials are porous to some extent. Not only stones and metals exhibit a certain porosity, but also the fauna and flora are based on pore systems within materials, e.g. bones and wood [3], [4]. During the last few decades different industry branches became more aware of the many advantages of porous materials and started researching and implementing them [5]. Therefore, this subsection will give a short overview into some of the many porous materials and their applications.

Porous samples have different physical and chemical properties compared to a dense body of the same material. The introduction of pores leads to a lower density and an increased specific surface area. Due to these changes, the samples gain new functional properties, which are mostly defined by the samples' pore type. For each industrial demand a certain type of pore morphology and therefore material characteristic is necessary [6].

Many applications require a high fraction of open porosity in a material, e.g. catalysts, filters and sensors. Depending on their additional pore characteristics, materials are chosen for a certain task [7]. Filters need a narrow pore size distribution, to hinder selected molecules of a mixture from entering through the sample's pores due to their large size [8]. For sensors a high interconnectivity and therefore a large surface area of the pore system is a must to obtain a low detection limit and an increased sensitivity [9], [10]. The chemistry of the pore walls can also be of great importance, for example during the interaction with adsorbing species in the catalysis process [11].

Materials with closed porosity, on the other hand, can be used as thermal and sonic insulators and low- κ -materials. The latter are used to reduce capacitance between interconnects and to improve the switching speed in ultralarge-scale integrated circuits. Introducing a certain porosity leads to a reduction of the dielectric constant, what will be important in future microelectronics [12].

Generally, uniformity within the pore morphology is needed to obtain superior and consistent functional properties for industrial applications. Concerning porous thin films, this uniformity is procured by choosing the right deposition method for each task. Hence, the following section 1.2 presents the working principle of several thin film deposition methods [13].

1.2 Film Deposition Methods

Numerous deposition methods for thin films have been developed over the past decades. Only some of them are suitable, if a controllable thickness and a certain uniformity of the film is needed. Vapour-based techniques have proven themselves to be especially suitable for the fabrication of porous thin films. They can be classified either as physical vapour deposition (PVD) or as chemical vapour deposition (CVD). As the latter is researched to a greater extent within the research group of Anna Coclite and also enables the introduction of porosity to the samples, this section is supposed to briefly explain the commonly used CVD methods.

1.2.1 Thin Film Growth during CVD

Generally, the film growth during CVD processes depends on atom diffusion on the surface and intra-layer, but also on the film precursor reactivity. This on the other hand depends strongly on the technique used for growing the thin film. The deposition technique determines most of the thin film's properties and therefore must be chosen depending on the future area of application [14].

During Chemical Vapour Deposition, the film is formed in the following way:

A gaseous compound of reactants and an inert gas are led into the vacuum chamber. There, chemical reactions in the gas phase take place to produce new reactive species, which are transported to the substrate surface, which is often heated. The film precursor is then adsorbed at the surface, where additional reactions, diffusion and desorption of these species finally lead to a film formation [14].

CVD has several advantages compared to PVD. The produced thin films exhibit a high conformity, tracking the morphology of the substrate and uniformly covering even its vertical sections. This happens with a rather high deposition rate and a good reproducibility. Counterbalancing these advantages, the processes usually require high temperatures and the source materials are often highly toxic or flammable [15].

1.2.2 Initiated Chemical Vapour Deposition

Through CVD, stable and conformal coatings in the nanometer-regime can be obtained. One of the most commonly used CVD processes refers to as initiated chemical vapour deposition (iCVD) [16]. It has been successfully used to deposit thin films of numerous polymers and co-polymers, e.g. hydrogels [17], insulating materials [18] and fluoropolymers [19].

The main advantage to other CVD processes is the initiating species, which flows into the vacuum chamber at the same time as the monomer. As soon as the initiator nears the heated filaments of the reactor, its labile azo- or peroxy-linkage decomposes generating free radicals. The initiator radicals generate monomer radicals by attacking the unsaturated bonds of the monomer. The substrate is cooled to a lower temperature compared to the filaments, what promotes the adsorption of the monomer. The initiator leads to a faster and more controlled polymerisation of the monomer molecules adsorbed on the substrate's surface. Monomer units are added to the polymer chains until the process is terminated [20].

The iCVD process can also be used to generate porous thin films, as done by Ran Tao. First, the initiator and the so-called cross-linker flow into the vacuum chamber to form a base layer on top of the substrate. Subsequently, the monomer and the porogen (material, which is supposed to dissolve later on in order to create pores) flows are additionally introduced. This leads to the formation of a thin film with trapped porogen within the polymerised monomer. After purging the chamber to remove volatile species, the film is annealed to remove the porogen from the film. This last step introduces a certain porosity to the thin film [21]. The process is depicted in figure 1.3.

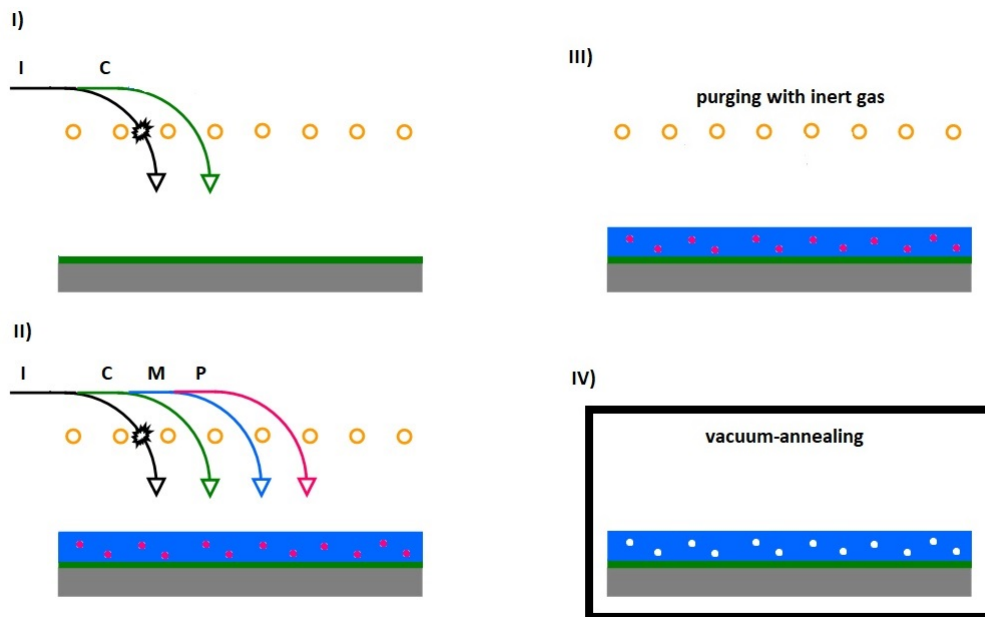


Figure 1.3: A schematic of the iCVD process: Initiator I and cross-linker C flow into the vacuum chamber and form a base layer. Monomer M and porogen P are introduced, which leads to the formation of the thin film. After purging the vacuum chamber, the thin film is annealed. This removes the trapped porogens and leads to the film's porosity [21].

1.2.3 Atomic Layer Deposition

Micro-electronics is one of many application fields of atomic layer deposition (ALD). The nature of its self-limiting surface reactions ensures superb thickness control and great conformality of the thin films. Using ALD, it is possible to either generate porous thin films or to tune the porosity of pre-existing membranes and films [22], [23].

During an ALD process, the substrate is exposed to two or more precursors in a sequential manner. Unlike other CVD techniques, every step during the atomic layer deposition is self-limiting, because the precursor molecules can only react with a finite number of sites on the surface. Generally, an ALD consists of the alternation of the following four steps:

The substrate is exposed to precursor A, which forms a monolayer. Then, the chamber is purged using an inert gas to remove all volatile species. After that, precursor B is introduced leading to a second monolayer on top of the first one and resulting in a binary atomic layer. Subsequently, the vacuum chamber is purged again. Those four steps are repeated until the desired film thickness is finally reached. Each step requires enough time to achieve saturation to ensure a conformal film thickness [24].

ALD has been used by several scientists to produce porous metal oxides or to adjust the porosity of samples. E.g. J. Dendooven et al. used ALD to coat mesoporous silica films with TiO_2 to tune their accessible porosity, pore size distribution, thickness and mechanical properties. The experiments concluded, that ALD was suitable to reduce the average pore size and therefore adjust the films pore size distribution. Unfortunately, the porous film shrunk due to internal stresses within in the additional TiO_2 layers [22].

An other example are S. Karwal et al., who created nanoporous ultra-thin films by annealing them at $1000\text{ }^\circ\text{C}$ after the ALD process. The formation of the nano-pores was probably related to a densification of the films during a phase transition [23].

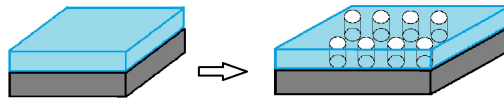


Figure 1.4: Formation of nanopores in an ALD thin film due to a phase transition during the annealing process [23]

1.2.4 Molecular Layer Deposition

Molecular layer deposition (MLD) resembles the previously elucidated technique of ALD, but it is not limited to inorganic coatings. Figure 1.5 shows the schematic of an MLD process, which usually consists of 4 or 6 steps.

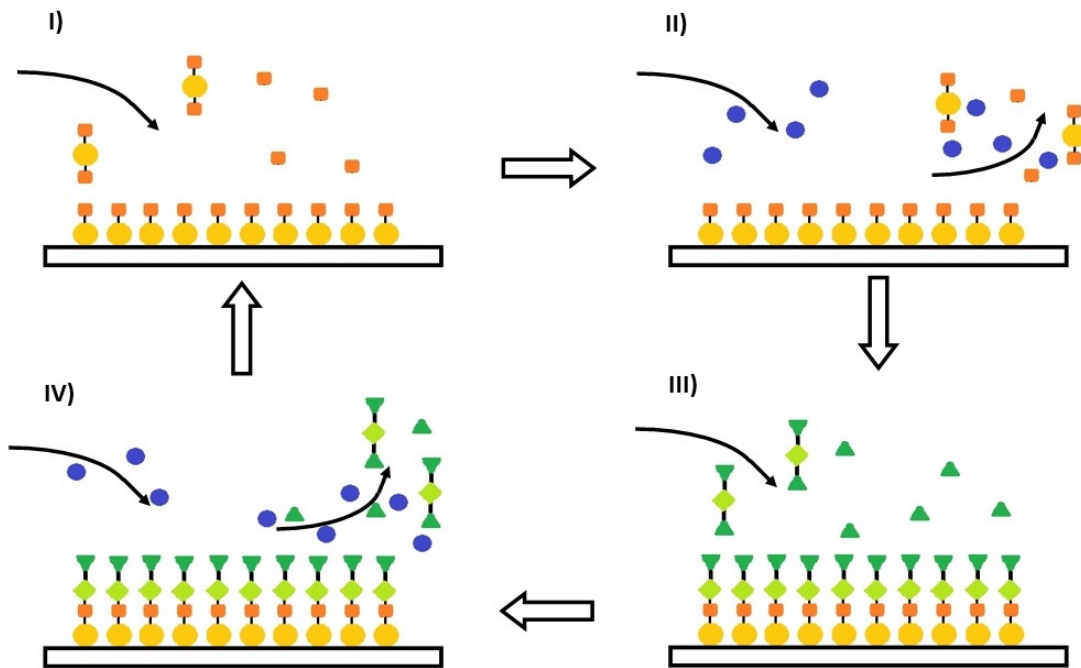


Figure 1.5: Process steps of the film development during a MLD process:

I) Self-limiting reaction of the inorganic precursor (yellow-orange molecule), II) purging step using an inert gas (blue molecule), III) self-limiting reaction of the organic precursor (green molecule) and IV) purging step using an inert gas (blue molecule) [25]

First, the inorganic precursor is pulsed to the reactor, where it reacts with the surface species. Once all adsorption sites are occupied, no additional precursor molecule can react. This self-limitation leads to a molecular monolayer and allows for ideal thickness control. During the next step, the excess precursor and possible by-products are removed from the reactor by purging with an inert gas. Then, the organic precursor is introduced, which reacts with the precursor molecules previously anchored to the surface. This surface reaction is again self-saturated and is followed by a second purging of the reactor. In an ideal case a monolayer of a hybrid material is formed. The MLD cycle can be repeated, thereby building up hybrid films one layer at a time. The resulting process enables coatings with good conformality and thickness control [26].

The combination of organic and inorganic molecules to form hybrid films, opens doors for new applications, like sensors, photonics and electronics [27], [28], [29]. Especially metal-organic materials can inherit advantageous mechanical, optical, chemical, and electrical properties from the combination of the organic precursor and the metal precursor [30].

The research group of Anna Coclite has shown that the generation of mesoporous ZnO thin films using a MLD process is possible. This was accomplished by depositing a zincone thin film, which was annealed at several 100 °C. This led to a calcination, which resulted in mesoporous ZnO [31]. Later, similar ZnO samples were produced by Martin Seiler, which were analysed during the scope of this thesis. The measurement data and results are shown in section 4.

Annealing of the Thin Film

As mentioned before, it is necessary to anneal the sample after finishing the ALD or MLD process. This enables the creation of porous thin films by getting rid of the organic parts.

During the annealing process the thin film is heated up to several hundred degrees. The oxygen surrounding the sample during the annealing tends to react with the organic parts of the thin film, resulting in their removal. The inorganic remains of the thin film resemble an amorphous structure and undergo atom rearrangement when heated further leading to a crystalline structure. Due to the rearranging of the atoms, an ordered stable crystal structure can be obtained. After the calcination of the thin film, a certain porosity is retained [32].

The properties of the porous thin film are influenced by the choice of heating parameters, like the duration of the annealing process and the maximum heating temperature. The latter is a determining factor concerning the thin film's porosity and the crystallite grain size, and therefore also its future applications [32].

M. Kubo et al. have proven, that both the morphology and the crystallinity are strongly effected by the choice of the maximum heating temperature of the annealing process. Due to phase transitions at certain temperatures, not only the film thickness, but also film's porosity and the mean pore size changed dramatically [33].

1.3 Porosity Characterisation Methods

To check, whether the created porous thin film has the desired characteristics, the sample needs to be examined thoroughly. Numerous methods have been developed over the years. Procedures on porous bulk materials have already been well-established and used to determine the void fraction of samples [34], [35]. Unfortunately, the structure of larger bulk materials differs generally from thin films. Therefore, it was necessary to develop other, more suitable, methods to examine porous thin films. Two of them were used during this thesis and are therefore explained in the following subsections.

1.3.1 In-situ Spectroscopic Ellipsometry

Ellipsometry measures the change in polarisation as light reflects or transmits from a material structure. The polarisation change is represented by an amplitude ratio, Ψ , and the phase difference, Δ , between the perpendicular and the parallel parts (s- and p-parts) of the electric field of the reflected light. The incident light is linearly polarised with both p- and s- components. The reflected light has undergone amplitude and phase changes for both p- and s- polarized light, and ellipsometer measures their changes (see figure 1.6) [36].

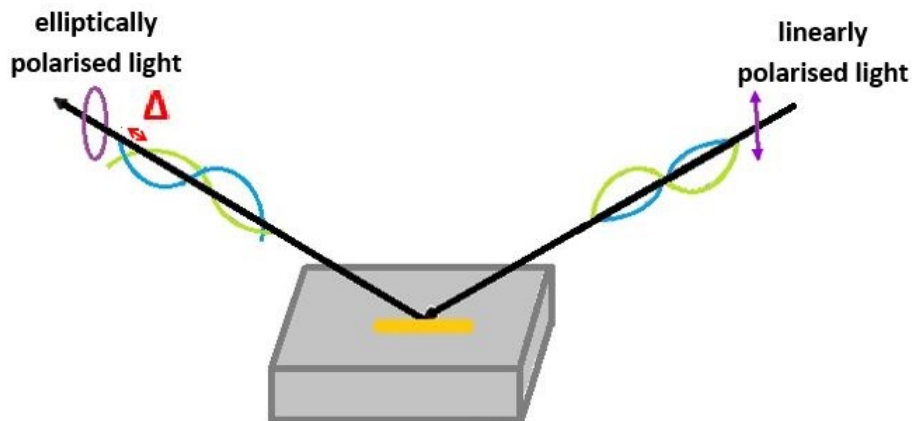


Figure 1.6: Schematic of an ellipsometric measurement:

The incident beam is linearly polarised and the reflected beam exhibits elliptical polarisation. The electric field components parallel (green curves) and perpendicular (blue curves) to the plane of incidence show a changed amplitude ratio and phase difference Δ before and after the reflection from the thin film [36].

The measured response can be used to retrieve information on optical properties, e.g. the refractive index, and thickness of individual material layers of the sample. The Fresnel equations relate Ψ and Δ with the complex index of refraction. By applying them to multiple reflections at different interfaces the thin film properties can be calculated based on the measurement data of the spectroscopic ellipsometry (SE) [36], [37].

After acquiring the measurement data, the next step is to find a fitting model for the measured sample, to retrieve information on the film thickness and the refractive index of the material. This is done by a regression analysis, as the answer is often over-determined by the amount of experimental data (see figure 1.7) [36].

The model is used to calculate the predicted response from Fresnel’s equations. The resulting values are then compared to experimental data. Any unknown material properties can then be varied to improve the match between experiment and calculation [36].

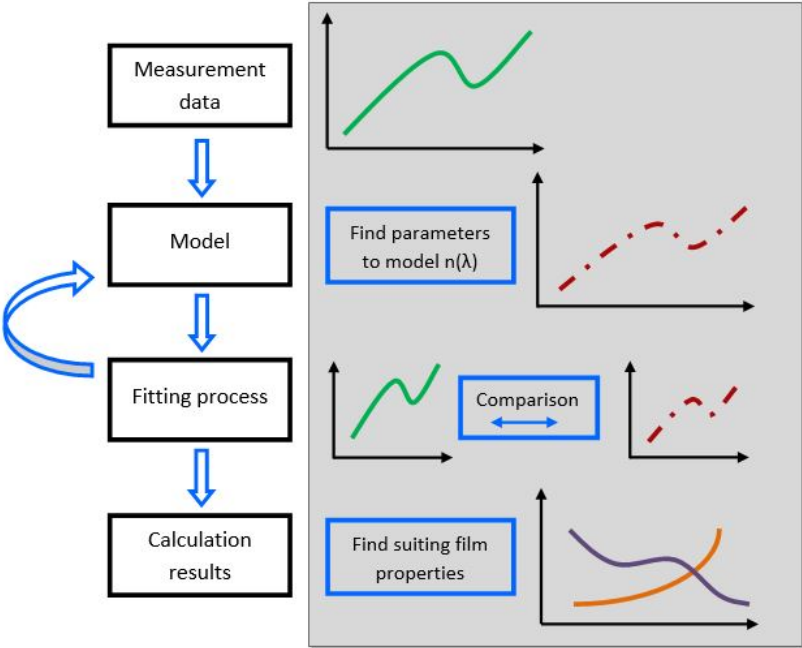


Figure 1.7: Flowchart of the ellipsometric data analysis [36]

Depending on the thin film’s composition certain models deliver the best results, therefore basic information concerning the sample’s properties should be provided. The films evaluated during this thesis’ scope of work were zinc-oxide thin films. Further information on them will be found in section 4.1. In the case of the zinc-oxide thin films, a Cauchy model was used to fit the data points.

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} + \dots \quad (\text{Eq. 1.2})$$

n ... refractive index

A, B, C ... material dependent coefficients

λ ... wavelength

The Cauchy model is commonly used to describe the wavelength dependency of the refractive index in isotropic, (ideally) transparent materials. Hence, the extinction coefficient k of the complex refraction index $n + ik$ must be sufficiently small. To describe the adsorption of light within only partly transparent materials, the extinction coefficient is included in the Cauchy model. If the thin film is perfectly transparent, k can be set to zero [38].

1.3.2 Ellipsometric Porosimetry

Ellipsometric porosimetry (EP) allows measuring the number of open, therefore accessible pores inside of a film. This is done by measuring the change in film thickness and of optical properties (e.g. the refractive index) using an spectroscopic ellipsometer throughout an adsorption cycle. As the ratio of the partial pressure of the adsorptive and its saturation pressure ($\frac{p_{ad}}{p_{sat}}$) is gradually increased from 0 to 1, the vapour begins to condense along the pore walls (see figure 1.8) [12].

The propagating adsorption of the adsorptive within the pores leads to an increase of the thin film's refractive index, because the probing liquid generally has a higher refractive index than air or inert gases. By applying the effective medium approximation the volume fraction of the condensed adsorbate vapour within the film's pore network can be calculated from the index of refraction. The open pore system is completely filled with the probing liquid, if its partial pressure is equal to its saturation pressure. At this point, the volume fraction of the adsorbate inside the film is identical to the fraction of open porosity [12].

The Kelvin equation is used to obtain the pore size distribution of the sample by relating a certain value of $\frac{p_{ad}}{p_{sat}}$ to the curvature of the adsorbate's surface at that moment. This enables the calculation of the pore size distribution within the thin film, if a suitable pore shape model is found [12].

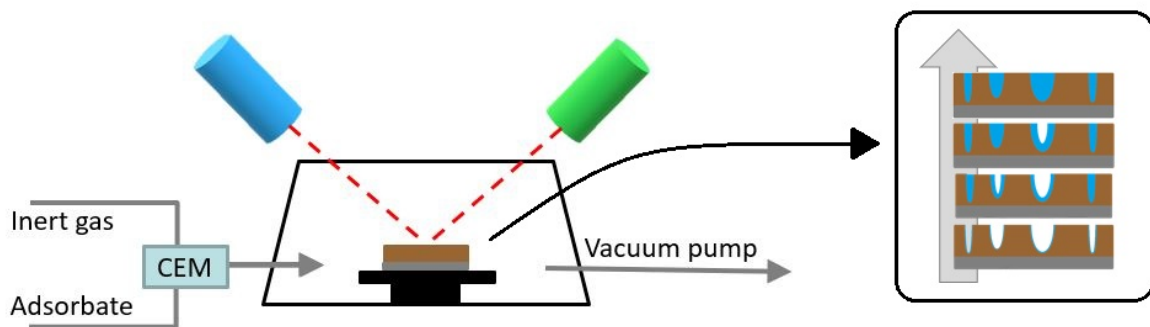


Figure 1.8: Schematic of an EP measurement:

As $\frac{p_{ad}}{p_{sat}}$ is increased, the probing vapour condenses along the pore walls and the pores are gradually filled with the adsorbate [39].

The following sections will be used to give a short introduction into the effective medium approximation and the calculations leading to the pore size distribution. Further information on EP and the post-processing of the obtained measurement data can be found in [12], [22], [40] and [41].

Effective Medium Approximation

The so-called effective medium approximation (EMA) is used to backcalculate the volume fraction of the condensed liquid inside a porous thin film. It relates the changing refractive index of the film during the propagating adsorption process to the increasing volume fraction of the adsorbate within the sample [12], [22].

Based on the Lorentz-Lorenz effective-medium expression for the effective dielectric function of a sample, which consists of two components, one can derive an expression for the volume fraction of the condensate inside the pores. In case of porous materials, the two components are the pores and the framework (see figure 1.9) [12], [42].

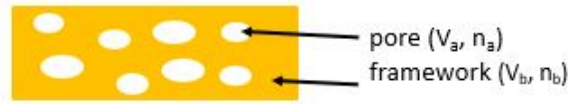


Figure 1.9: Porous thin films resemble a two-component material:

They consist of the framework and the pore system, each of which occupies a certain fraction of the total volume V_i and has a specific refractive index n_i [42].

For non-magnetic materials the expression for the refractive index of the sample is simplified, because μ_r is equal to 1.

$$n = \sqrt{\epsilon_r \mu_r} \quad \mu_r = 1 \quad n = \sqrt{\epsilon_r} \quad (\text{Eq. 1.3})$$

n ... refractive index

ϵ_r ... relative dielectric function

μ_r ... relative permeability

Included into the Lorentz-Lorenz effective-medium expression for the effective dielectric function, this relation leads to an expression for the refractive index:

$$\frac{\epsilon_{eff} - 1}{\epsilon_{eff} + 2} = \frac{V_a \epsilon_a - 1}{V \epsilon_a + 2} + \frac{V_b \epsilon_b - 1}{V \epsilon_b + 2} \quad n = \sqrt{\epsilon_r} \quad \frac{n_{eff}^2 - 1}{n_{eff}^2 + 2} = \underbrace{\frac{V_a n_a^2 - 1}{V n_a^2 + 2}}_{\text{pores}} + \underbrace{\frac{V_b n_b^2 - 1}{V n_b^2 + 2}}_{\text{framework}} \quad (\text{Eq. 1.4})$$

$n_{eff/a/b}$... refractive index of the total sample/ material a/ material b
 $\epsilon_{eff/a/b}$... dielectric function of the total sample/ material a/ material b
 $V_{eff/a/b}$... volume of the total sample/ material a/ material b

Equation 1.4 is transformed based on the atmosphere surrounding the sample. The refractive index of the framework material of a porous sample is often unknown and generally difficult to determine. However, the main advantage of EP in combination with the EMA is, that the volume of the pore system can still be easily estimated by combining two cases. On the one hand a dry air atmosphere with completely empty open pores and on the other hand a vapour-filled atmosphere, in which an adsorbate is already present in some pores (see figure 1.10).

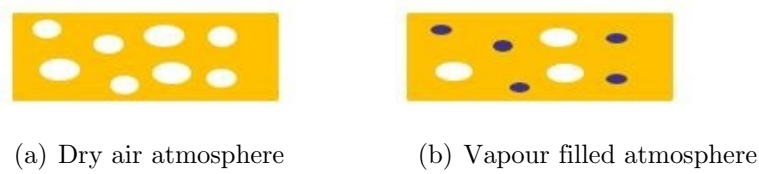


Figure 1.10: The filling status of the pores depends on the atmosphere surrounding the sample. The closer the partial pressure of the adsorbative is to its saturation pressure, the more open pores have been filled [42].

For the first case, the sample is evacuated and subsequently Argon is introduced, filling the complete open pore system with the inert gas. The literature value of the refractive index of Argon is around $n = 1.00028$ in the wavelength range of the used laser, which can be approximated by setting it equal to 1 [43]. This leads to a vanishing pore term in equation 1.4:

$$\frac{n_{eff,Ar}^2 - 1}{n_{eff,Ar}^2 + 2} = \frac{V_f n_f^2 - 1}{V n_f^2 + 2} \quad (\text{Eq. 1.5})$$

$n_{eff,Ar}$... refractive index of the total sample surrounded by Argon
 n_f ... refractive index of the framework
 V_f ... volume of the framework
 V ... volume of the total sample

For the second case, the sample is surrounded by the vapour, consisting of a mixture between Argon and the adsorbative. The exposure to the vapour leads to a partial filling of the open pore system with the condensed adsorbate. Therefore, two terms are necessary to describe the complete system at that point - the framework and the pores filled with vapour:

$$\frac{n_{eff,vapour}^2 - 1}{n_{eff,vapour}^2 + 2} = \frac{V_f n_f^2 - 1}{V n_f^2 + 2} + \frac{V_{ad} n_{ad}^2 - 1}{V n_{ad}^2 + 2} \quad (\text{Eq. 1.6})$$

$n_{eff,vapour}$... refractive index of the total sample exposed to the vapour

n_{ad} ... refractive index of the adsorbate

V_{ad} ... volume of the condensed vapour

Combining the equations 1.5 and 1.6 leads to the elimination of the term describing the framework and therefore to the final formula for the volume fraction of adsorbate inside the voids:

$$\frac{V_{ad}}{V} = \frac{\frac{n_{eff,vapour}^2 - 1}{n_{eff,vapour}^2 + 2} - \frac{n_{eff,Ar}^2 - 1}{n_{eff,Ar}^2 + 2}}{\frac{n_{ad}^2 - 1}{n_{ad}^2 + 2}} \quad (\text{Eq. 1.7})$$

The volume fraction of the condensed adsorbate inside the open pore system is now only described by already known or measurable quantities. Estimating the volume fraction $\frac{V_{ad}}{V}$ for the whole adsorption curve is the first step of post-processing the measurement data of the EP [12].

Pore Size Distribution

Based on the results obtained using the EMA, the maximum radius of the open pores, which are already filled with condensed adsorbate at a certain partial pressure, can be determined. This enables the calculation of a pore size distribution (PSD).

Dealing with zinc-oxide thin films, micro- and mesoporous structures are present and different analysis approaches are valid for each pore size. Since microporosity would have required Density Functional Theory simulations, only the mesoporosity was analysed during this thesis work. Generally, the Kelvin equation is applied for pore size distributions in the mesoporous regime:

$$\frac{1}{r_1} + \frac{1}{r_2} = \frac{RT}{\gamma V_m} \ln\left(\frac{p}{p_0}\right) \quad (\text{Eq. 1.8})$$

$r_{1/2}$... curvature radii of the liquid on two perpendicular trajectories along the surface
 R ... gas constant
 T ... temperature
 γ ... surface tension
 V_m ... molar volume
 p ... vapour pressure of a liquid with a curved surface
 p_0 ... vapour pressure of a liquid with a flat surface

It relates the liquid's curvature, described by r_1 and r_2 , to its vapour pressure. In other words, $\frac{p_{ad}}{p_{sat}}$ can be related to the radii of open pores, in which the adsorbate of the gas mixture has already condensed [22].

This together with a suitable model for the shape of the pores allows for the calculation of the pore size distribution inside the film. For zinc-oxide films, cylindrical pores were assumed (see figure 1.11).

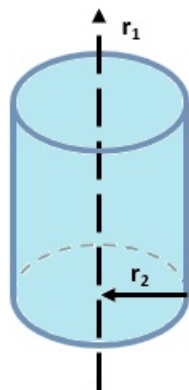


Figure 1.11: Geometry of a cylindrical pore

Cylindrical pores have a convex curvature with $r_2 < 0$ and a infinitely large r_1 compared to r_2 , what simplifies the equation 1.8, since the first term can be neglected.

$$r_1 \rightarrow \infty \quad \& \quad r_2 = -r_{pore} \quad (\text{Eq. 1.9})$$

r_{pore} ... radius of the cylindrical pore

$$-\frac{1}{r_{pore}} = \frac{RT}{\gamma V_m} \ln\left(\frac{p}{p_0}\right) \quad (\text{Eq. 1.10})$$

Equation 1.10 indicates, that a lower partial pressure is needed for the vapour to condense within small pores than within wider pores. This suggests, that the pores are filled with adsorbate subsequently according to their radii. The higher the vapour pressure gets, the bigger the radii of the pores are, which are filled with adsorbate.

In EP $\frac{p}{p_0}$ refers to the ratio between the adsorptive's partial pressure and its saturation pressure $\frac{p_{ad}}{p_{sat}}$. At its saturation pressure the adsorbate is completely condensed and therefore the liquid has a flat surface.

For water at room temperature in cylindrical pores, this relation between $\frac{p_{ad}}{p_{sat}}$ and the radius of pores, in which the probing vapour has already condensed, is shown in figure 1.12. If water is used as probing liquid, $\frac{p_{ad}}{p_{sat}}$ is equal to the relative humidity (RH). Using a proper sensor, relative humidity can be easily measured during an EP experiment.

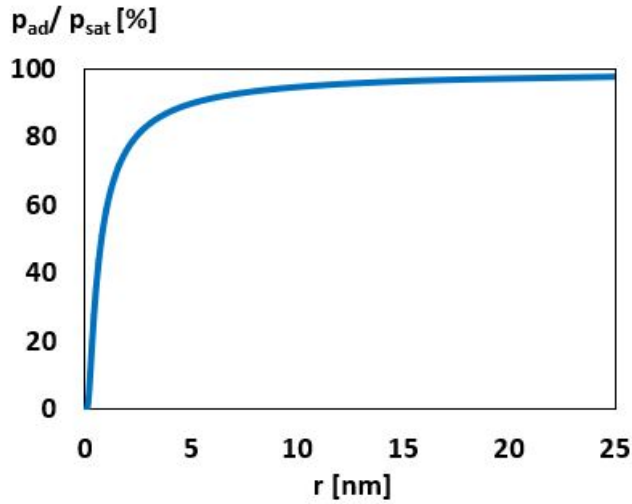


Figure 1.12: Prediction of the Kelvin equation for water at room temperature in cylindrical pores

Small changes in $\frac{p_{ad}}{p_{sat}}$ have a great impact on the pore sizes affected by the adsorbate as one is approaching the saturation pressure. Therefore, fine measurement steps are necessary in this region.

As before mentioned, ellipsometry calculates the refractive index of the thin film at each $\frac{p_{ad}}{p_{sat}}$ setpoint. After applying equation 1.7 and the Kelvin equation 1.10 to the measurement results, the cumulative volume of the adsorbed probing liquid within pores with a radius $r < r_{pore}$ is obtained. The final step in calculating the pore size distribution is to differentiate $V_{ad}(r_{pore})$ according to 1.11:

$$dV_{ad}(r_{pore}) = \frac{\partial V_{ad}(r_{pore})}{\partial r_{pore}} dr_{pore} \quad (\text{Eq. 1.11})$$

$dV_{ad}(r_{pore})$... adsorbed probing liquid volume in pores with a radius $r \in (r_{pore}, r_{pore} + dr_{pore})$
 $V_{ad}(r_{pore})$... adsorbed probing liquid volume in pores with a radius $r < r_{pore}$

The pore size distribution resembles the change in the volume fraction of adsorbate within the pore system at a certain vapour pressure and therefore pore radius. The equations 1.10 and 1.11 can only be applied to the adsorption curve of the ellipsometry measurement. To analyse the desorption curve another pore form model must be applied, since the adsorbate-air interface then rather resembles a capillary [22].

Unfortunately, suitable models for the desorption process are usually more complicated and do not always deliver trustworthy results, if water is used as an adsorbate [12], [22]. Hence, the results, which are shown in this thesis (see section 4), were all calculated from the adsorption regime of the ellipsometry measurements.

The first step of this thesis was to finalise the set-up after the assembly of all necessary parts and to get accustomed with each component's principle of operation. A schematic of the whole ellipsometric porosimeter set-up is depicted in figure 2.1.

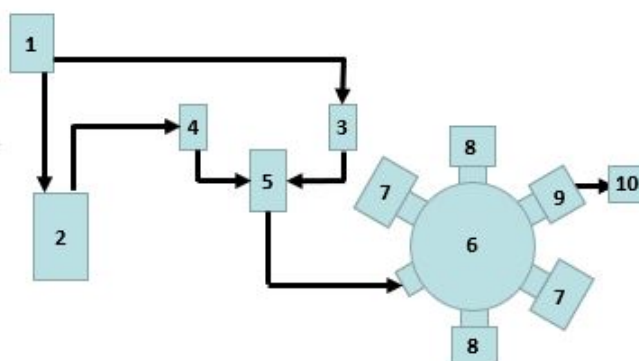


Figure 2.1: Schematic of the ellipsometric porosimeter set-up:

1) Inert gas source, 2) Bubbler, 3) Flowmeter for gases, 4) Flowmeter for gases and liquids, 5) Controlled Evaporator Mixer, 6) Reactor, 7) Ellipsometer mounts, 8) Pressure sensors, 9) Pressure control unit and 10) Vacuum pump

In principle, the set-up consists of an experimental chamber, which is connected to a rotary vane vacuum pump through a pressure control unit and to the controlled evaporator mixer (CEM). The CEM is the link between the reactor and the flowmeters, which are controlling the inert gas flow and the adsorbate vapour flow coming from the bubbler. Additionally to the gas inlet and outlet, two pressure sensors and the ellipsometer's laser and detector are mounted onto the reactor.

A recent photograph of the set-up is shown in figure 2.2.



Figure 2.2: Photograph of the ellipsometric porosimeter set-up

In the following chapter, the individual units are described based on their functionality and properties.

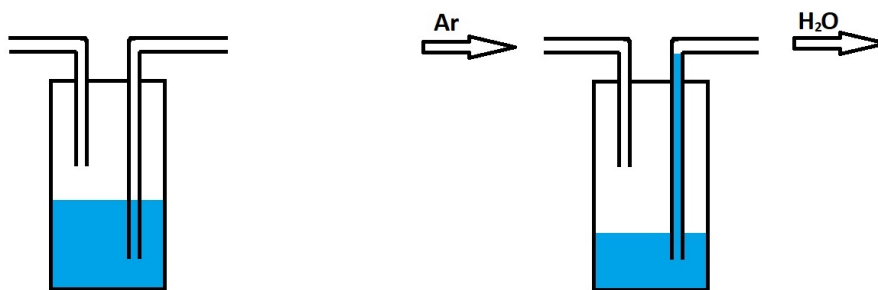
2.1 Argon Pipe and Bubbler

As described in subsection 1.3.2, an inert gas is needed to vary the partial pressure of the adsorbate throughout the measurement process of the ellipsometric porosimeter. The volume ratio between the adsorbative and the inert gas within the vacuum chamber is the basis to create the adsorption and desorption curves.

The set-up is attached to an Argon line. Argon was chosen for the first experiments, as it is easily accessible in the laboratory and because the flowmeters have both been gauged using Argon. If another inert gas is used instead, an additional gas factor has to be applied during pre-processing of the setpoints and post-processing of the measured data due to the flowmeters' principle of operation, which will be further discussed in the flowmeter section 2.2.

After the inert gas is introduced into the set-up, its line is split and led towards a flowmeter on the one hand and the bubbler on the other hand.

The bubbler is a metal vessel, which can be easily refilled with various probing liquids and tightly sealed afterwards. It contains two lines, an input line, which ends slightly above the liquid's surface and an output line, which is nearly reaching to the ground of the vessel. As parts of the inert gas are pumped into the bubbler, the presence of the additional gas forces parts of the liquid out off the bubbler. The excessive fluid is sent from the bubbler to the second flowmeter (see fig. 2.3).



(a) Before the start of the experiment

(b) During the measurement process

Figure 2.3: Schematic of the working principle of a bubbler:

(a) First, the outlet line reaches into the liquid without it being pressured towards the flowmeter. (b) Then, the inert gas is let into the bubbler, forcing the fluid out.

2.2 Flowmeter

The flowmeters play a key role during an EP measurement, as they are used to create the adsorption and desorption curves. This is done by setting suitable flows for the inert gas and the liquid to reach various volumetric ratios, which translate to certain partial pressures of the adsorptive vapour. As the amount of the adsorptive vapour within the experimental chamber is increased, the partial pressure rises from zero to nearly the saturation pressure of the evaporated adsorptive. This leads to the gradual filling of the porous sample's pores depending on their size, as explained in section 1.3.2.

Depending on the state of matter of the materials passing through, the flowmeters have to work based on different techniques. Concerning this set-up, one flowmeter only handles inert gases, while the other one deals with saturated vapours and also liquids. Therefore, two types of flowmeter were installed, the EL Flow and the Cori Flow. They have different working principles, which are briefly explained in the following subsections.

Both flowmeters are connected to the computer using a serial port. This enables the user to set and control the flows of the EL Flow and the Cori Flow using the Measurement GUI, which is elucidated in chapter 3.

2.2.1 EL Flow

One part of the inert gas flows through the EL Flow, a thermal mass flowmeter. Within this device, only a small portion of the gas stream runs through a sensor capillary, which consists of a heater and two temperature measurement points (T1 and T2), one before and one after the heating.

As long as no flow passes through the bypass capillary, the sensors T1 and T2 measure the same temperature, as the capillary heats up evenly. If a flow is introduced into the flowmeter, the temperature at the first measurement point decreases, because the heat convects from the capillary surface to the fluid. This even leads to a temperature increase at the second measuring point. A greater flow results in a higher temperature differential between the two measuring points. The working principle of a thermal mass flowmeter is depicted in figure 2.4 [44].

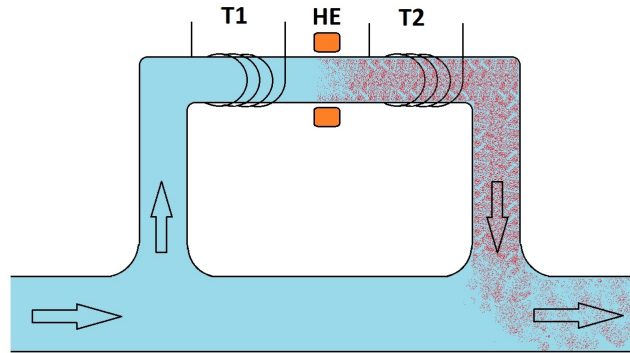


Figure 2.4: A schematic of the working principle of a thermal mass flow based flowmeter [44]: The flow splits into the main tube and the sensor capillary, where the gas passes a temperature sensor (T1), a heating element (HE) and a second temperature sensor (T2). Through the temperature difference between the two sensor positions the current flow can be calculated.

The measurements of thermal mass flowmeters are dependent on the physical properties of the gas. It only measures the volumetric flow and not the mass flow, which requires the inclusion of gas factors for each material different from the gauge gas. Additionally, it is also affected by pressure and temperature changes. The application of the Antoine equation is therefore necessary to calculate the right setpoints for the thermal mass flowmeter (see chapter 3).

2.2.2 Cori Flow

The liquid or saturated vapour leaving the bubbler, flows towards the Cori Flow, which is a so-called Coriolis flowmeter. Similar to the EL Flow, it also contains a bypass capillary, which is being vibrated at a fixed frequency. If a stream passes through the capillary, the mass flow momentum will cause this vibration to change. The altered movement of the capillary is then compared to the initial vibration and the flow is derived. The working principle of the Cori Flow is shown in figure 2.5.

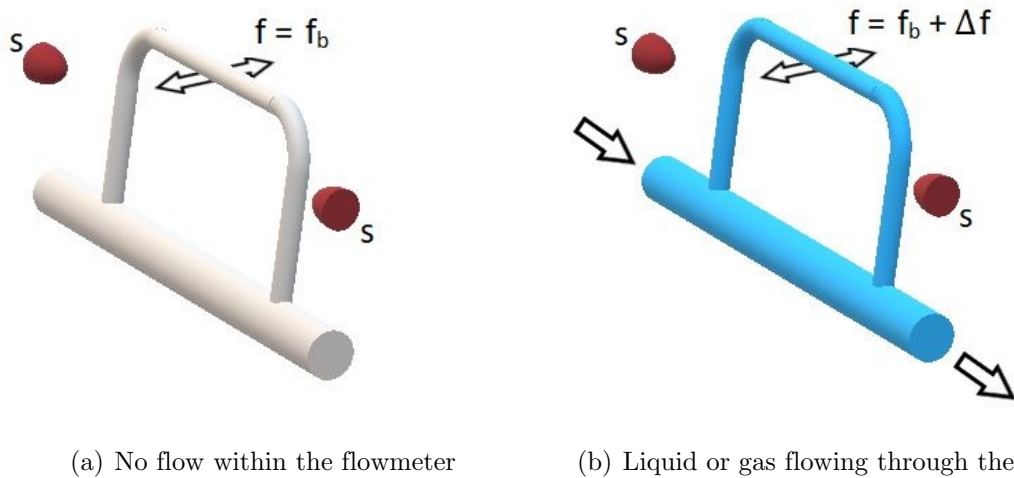


Figure 2.5: A schematic of the working principle of a Coriolis force based flowmeter [45]:

(a) If no flow passes the flowmeter, the capillary is vibrated with a fixed frequency f_b . (b) If a flow enters the flowmeter, a part of it runs through the capillary and changes the vibrational frequency to $f = f_b + \Delta f$. The deviation in frequency is measured by two external sensors S.

Contrary to the thermal mass flowmeters, Coriolis flowmeters measure the real mass flow. This makes it suitable to measure gases and liquids independently from the temperature and pressure of the medium. The mass flow can later be calculated, if the density of the gas or liquid is also known.

2.3 Controlled Evaporator and Mixer

Both flowmeter direct their exiting flows towards the Controlled Evaporator and Mixer unit. The main task of the CEM is to create a gaseous mixture between the probing liquid and the inert gas, which is then sent to the experimental chamber.

The CEM consists of a control valve, a mixing chamber and a heat exchanger. It is fed with a liquid or saturated vapour from the Cori Flow and an inert gas from the EL Flow. The latter is also called carrier gas, as its purpose is to serve as conveyor of the adsorptive after the mixing process. The control valve atomizes the probing liquid, mixes it with the inert gas and creates an aerosol. Subsequently, the aerosol is heated within the CEM, until it transforms into a consistent vapour. Figure 2.6 shows, how this process works [46].

Additionally, the CEM contains a temperature sensor to monitor its internal temperature. This temperature can be risen up to 200 °C using an external control unit. Due to the limited pressure range of the pressure control unit (for further explanation see subsection 2.5), it can be necessary to heat certain mixtures, to measure a full adsorption-desorption cycle. To prevent the vapour's premature condensation within the outgoing line the reactor, this sections of the set-up will be attached to heating wires and thermally isolated using Aluminium foil.

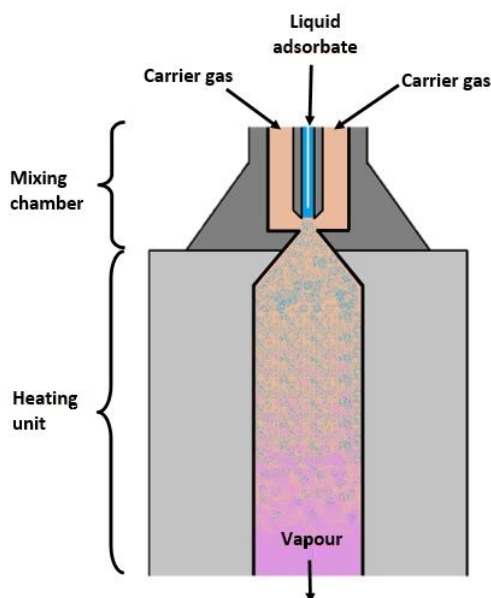


Figure 2.6: A schematic of the working principle of a CEM [47]

2.4 Reactor and Ellipsometer Installation

The reactor was designed by the university's workshop team and costum-built by Vacom (see figure 2.7). It is made of stainless steel and has eight ports, which are reserved for the following purposes:

- one gas inlet coming from the CEM
- two mounts for the ellipsometer
- two pressure sensor positions
- one gas outlet towards the vacuum pump
- two ports for future additions (e.g. temperature sensor)

The ellipsometer mounts are on exact opposite sites of the chamber and are fixed at an angle of 70° . On one reactor arm the laser source is mounted, on the other the detector is positioned. The tilt of both parts can be adjusted with several screws, which are attached to springs.

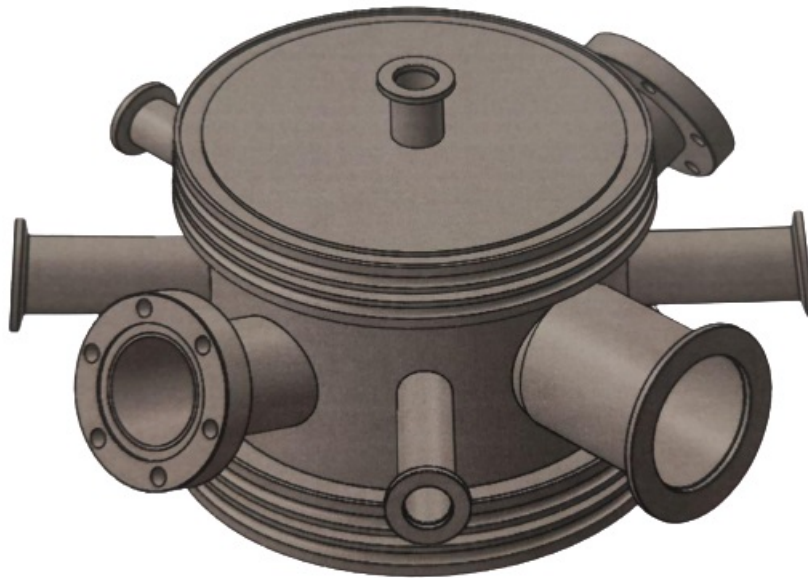


Figure 2.7: The computer-aided design (CAD) drawing of the reactor

2.5 Pressure Control Unit

The reactor is connected to the rotary vane vacuum pump through a pressure control valve. In combination with a pressure sensor and a PID valve controller, this pressure control valve can maintain a certain pressure within the reactor. This pressure control system is indispensable for EP measurements under vacuum, due to the necessity of a constant pressure environment.

The pressure control system works in the following way: The pressure sensor detects a certain pressure within the reactor. The pressure controller compares this value to the desired setpoint and sends a command to the control valve to open or close to obtain the right process pressure. The schematic below shows the work principle of the pressure control system (fig. 2.8).

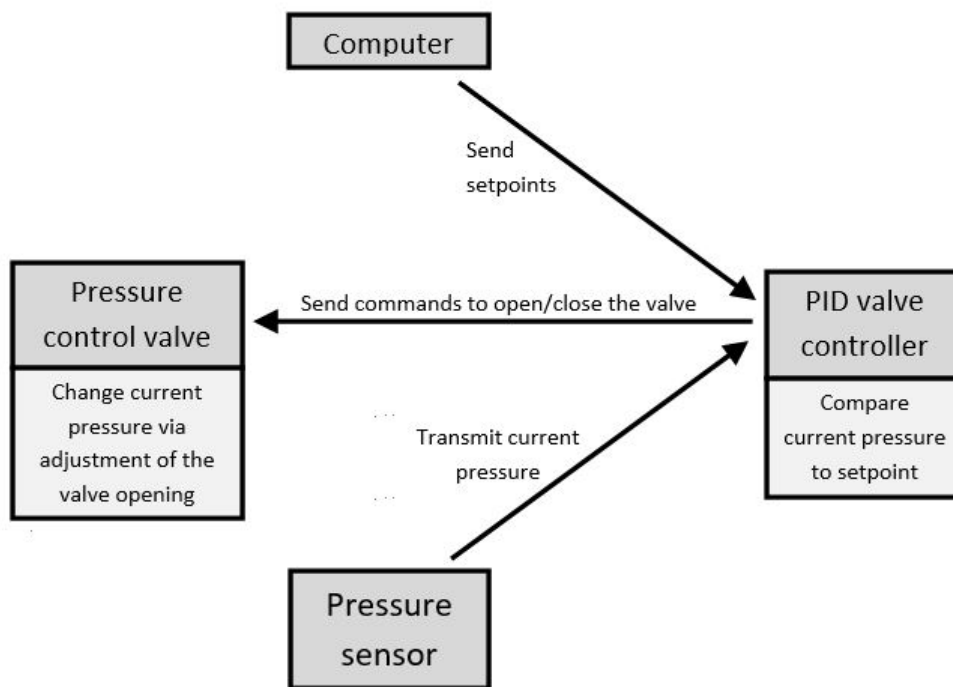


Figure 2.8: The working principle of the pressure control system

This pressure control system can be operated manually using the input field of the pressure controller or remotely using a serial port, which enables the inclusion into the Measurement GUI in the future for simpler handling.

2.6 Set-up Evaluation

Before any measurements can be done, the set-up has to be evaluated concerning its main properties. These include the reactor's volume and the set-up's total leak rate. Depending on the volume, certain time steps are chosen during the adsorption-desorption-cycle, to ensure stable conditions. The leak rate limits the vacuum level, that can be achieved using the set-up, and should therefore be as low as possible.

2.6.1 Reactor Volume Calculation

Every small modification of the experimental set-up leads to a change in the reactor's volume. Since device exchanges and other adjustments are rather common, it is necessary to find a quick way to calculate the new volume.

The easiest option is to decouple the vacuum pump from the reactor and to introduce a constant flow of inert gas, e.g. Argon. Depending on the pressure increase per unit of time, which is measured by the pressure sensor, it is possible to calculate the reactor's volume according to [44]:

$$\frac{\Delta p}{\Delta t} = \frac{Q}{V} \quad (\text{Eq. 2.1})$$

$\frac{\Delta p}{\Delta t}$...pressure increase per unit of time

Q ...gas flow rate

V ...reactor's volume

Equation 2.1 states, that the pressure increase inside the chamber caused by a constant gas flow relates to its volume. The leak rate of the set-up can be neglected, as its effect is very small in comparison to the incoming gas flow. Hence, the reactor's volume can be estimated by applying a linear fit to the pressure data recorded over time and taking the first derivative, as shown in figure 2.9. The measurement details and results of the reactor volume estimation can be found in table 2.1.

Table 2.1: Measurement details and results of the reactor volume estimation

Gas flow rate [l/min]	$\Delta t_{Measurement}$ [s]	dp/dt [Torr/s]	Volume [l]
2.5	40	4.474	6.987

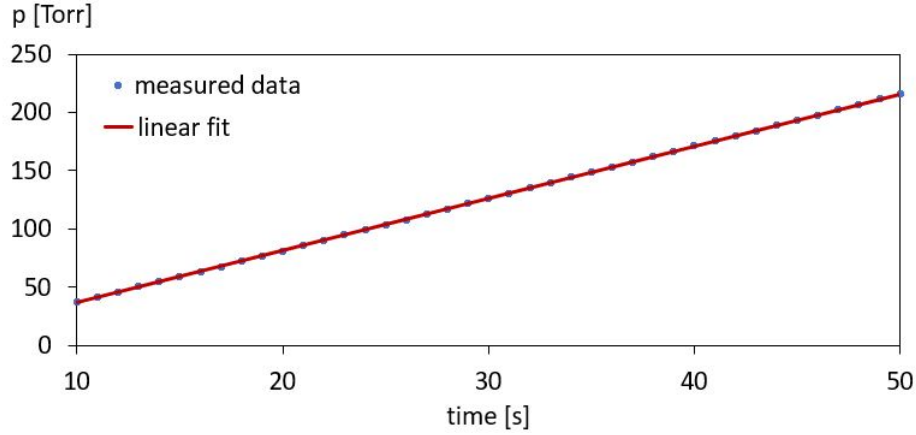


Figure 2.9: Pressure increase over time during a constant flow into the reactor for the calculation of its volume

For the current set-up, the reactor volume is estimated to be around $V = 7.0$ l.

2.6.2 Leak Rate Estimation

After estimating the reactor's volume, the leak rate of the set-up can be obtained. To this end, the pressure increase within the system is measured, while the vacuum pump is disconnected from the reactor after its evacuation. As the amount of particles inside the evacuated set-up is relatively small in comparison to the surrounding atmosphere, the number of particles going out of the reactor is negligible compared to the ones going into the reactor. Therefore, the leak rate formula is rather similar to equation 2.1:

$$q_l = V \frac{\Delta p}{\Delta t} \quad (\text{Eq. 2.2})$$

q_l ...leak rate

V ...reactor's volume

For the leak rate estimation, a LabView program written by Katrin Unger is used. It only requires the reactor's volume and the starting point and duration of the linear regime of the recorded pressure increase. Based on this information, it calculates the leak rate using equation 2.2.

Table 2.2: Measurement details for the reactor's leak rate estimation

Volume [l]	$\Delta t_{Measurement}$ [s]	Leak rate [mbar l/s]	Leak rate [sccm]
7.0	300	0.0097	0.582

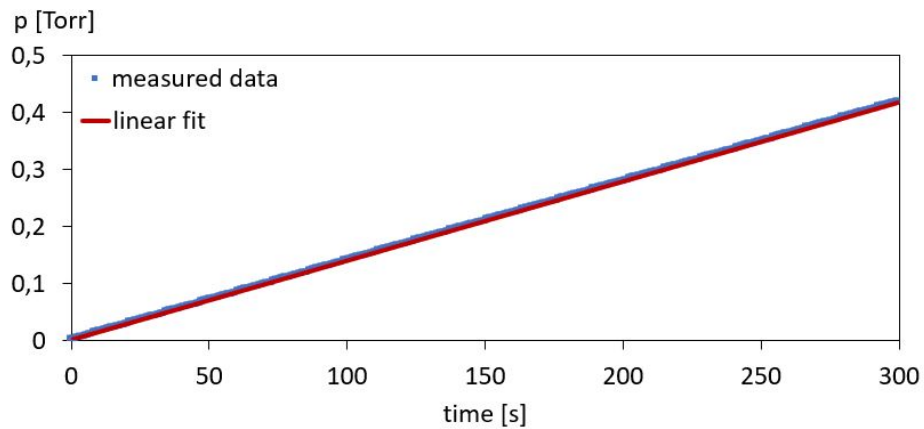


Figure 2.10: Calculation of the set-up's leak rate

Using this approach the estimated leak rate of the set-up was $q_l = 0.6 \text{ sccm}$. The measurement details are presented in table 2.2 and in figure 2.10. This rate is small enough to ensure a sufficient vacuum level and little material loss.

2.7 The formerly used Set-up

Porosimetry measurements have already been done at the Institute of Solid State Physics at TU Graz, before the ellipsometric porosimeter was built. They were realised using a specialised sample stage of the spectroscopic ellipsometer, which consists of a closed chamber, which can be heated up to several 100 °C. Additionally to the heating system, a bubbler system is attached to the stage, which is used to introduce vapour into the sample chamber. The level of saturation of the vapour is controlled by two needle valves, which regulate the ratio between inert gas and water vapour within the gaseous mixture (see figures 2.11 and 2.12).

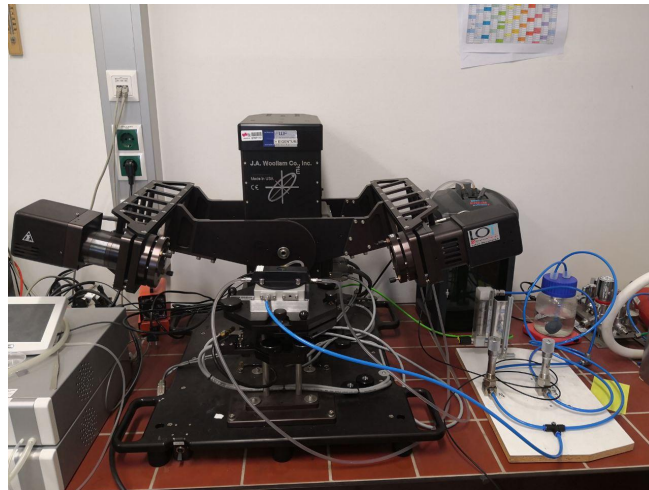
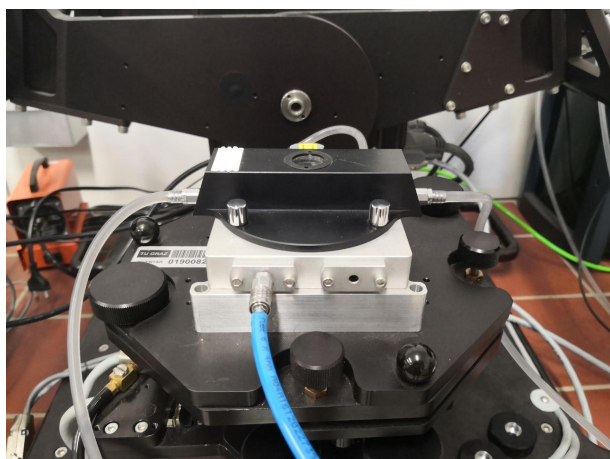


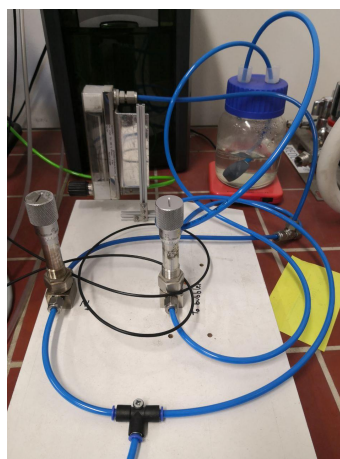
Figure 2.11: Photo of the formerly used set-up for porosity measurements

Since this set-up is far from a closed system and all pipes are made out of plastic, only water is used as an adsorbate for safety reasons. Other chemicals could damage the pipes or leak through the hood of the sample stage. Hence, a simple humidity sensor can be used to measure and record the temperature and the level of relative humidity within the chamber throughout the adsorption-desorption-cycle.

The fact, that only water can be used as an adsorbate during measurements, unfortunately limits the range of porosity and the materials, that can be examined. Additionally, the pipe guiding the vapour from the bubbler to the chamber is quite long and neither straight, nor thermally isolated, which sometimes leads to a formation of water droplets. These on the other hand plug the pipe and lead to a short relative humidity drop during the measurement. Besides, the humidity sensor has a rather long response time, which also complicates the piloting of the setpoints using the needle valves and the post-processing of the measurement data.



(a) The sample chamber



(b) The bubbler-flowmeter system

Figure 2.12: Close-ups of the formerly-used set-up

CHAPTER 3

GRAPHICAL USER INTERFACES

The second step of this thesis was to script two graphical user interfaces (GUI) to automate and speed-up the measurement procedure and post-processing of the obtained data. The Python binding Tkinter was used to code both of them. Additionally, a library document was created, containing material data of different carrier gases and probing liquids, which is used by both GUIs. In this chapter the workflow of the two GUIs leading from the input data to the resulting actions and outcomes is described.

3.1 Set-up and Measurement Control

The first GUI controls the whole measurement process through communicating with both the valves of the flowmeters and the pressure control unit using a RS232 connection. The workflow is explained in the following pages and summarised in a flowchart (see 3.2). The source code is shown in the appendix (section 12).

3.1.1 General Workflow

After starting the GUI through the command window, it automatically takes several actions. It connects itself with both flowmeters and the pressure control unit, which were described in the chapter 2. The flowmeters' functionalities are checked and the reactor is evacuated by opening the control valve completely. Simultaneously, the software CompleteEase, which is controlling the ellipsometer, is opened. Besides, two txt-files are created, one for all measurement setpoints and the other one for the immediate results of the ellipsometer measurements, the film thickness and the refraction index of the film.

After completion of these initial tasks,, the next window opens and the inert gas and the adsorptive, which are used during the measurement, can be chosen from two drop down menus. All necessary properties of each material are provided by a material library, which is further described in section 3.2.

The next window requests the working temperature within the set-up to be entered. Based on the data given to the GUI - the materials and the temperature - the saturation pressures of both the carrier gas and the adsorptive is calculated and printed. This is done by applying the Antoine equation:

$$p_{sat} = 10^{A - \frac{B}{C+T}} \quad (\text{Eq. 3.1})$$

p_{sat}...saturation pressure

A, B, C...Antoine coefficients

T...temperature

The Antoine equation uses different Antoine coefficients for each material, which are only valid for a certain temperature range. Multiple sets of Antoine coefficients have been stored in the material library to ensure the calculation of the saturation pressure, which is closest to the working temperature.

Subsequently, the working pressure of the set-up is entered, set at the pressure control unit and should not be changed throughout the whole measurement cycle. The working pressure must be chosen in a way, that enables the recording of the whole adsorption curve. Then, the flowmeters are checked once again. The valve controlling the inert gas flow is set to a certain opening and the other flowmeter is sealed. This allows a reference measurement of the sample with emptied pores.

The following step prepares the measurement setpoints for the adsorption and desorption curves. Based on the before set working pressure and carrier gas flow, the flow of the probing liquid is calculated for several setpoints $\frac{p_{ad}}{p_{sat}}$. The setpoints can be chosen between the values 0 and 1. These setpoints correspond to the ratio between the partial pressure of the adsorptive and its saturation pressure. 0 is a closed liquid flowmeter, ergo no adsorptive molecules being present within the chamber and 1 corresponds to the complete condensation of the adsorbate within the pores of the sample, ergo the saturation pressure being reached.

The GUI is given a minimum and a maximum value in percentage of the saturation pressure and the number of steps between the two values. It extrapolates all entered setpoints and calculates the needed volume of the adsorptive vapour, which relates to the certain volume of the adsorbate liquid, using equation 3.2.

$$q_w = \frac{\frac{p_{ad}}{p_{sat}} * M_g * q_g}{V_{M,ad} * \frac{T}{T_0} * \frac{p_w}{p_{atm}}} \quad (\text{Eq. 3.2})$$

q_w ...water flow [$\frac{g}{h}$]

p_{ad} ...partial pressure of the adsorbate [mbar]

p_{sat} ...saturation pressure of the adsorbate [mbar]

M_g ...Molar mass of the carrier gas [gmol]

q_g ...carrier gas flow [$\frac{l}{h}$]

$V_{M,ad}$...Molar volume [$\frac{l}{mol}$]

T ...working temperature [K]

T_0 ...temperature at freezing point [K]

p_w ...working pressure [mbar]

p_{atm} ...standard atmosphere [mbar]

This liquid volume is translated to the necessary valve opening of the Cori Flow. Every setpoint within this tranche is then saved as partial pressure to one of the txt-files, which were created at the beginning, and as valve position to an array (see figure 3.1). Additional setpoint series with different step sizes can be appended, if it is needed.

1	Setpointlist			
2	Flow Argon	Flow Water	Pressure Water	Setpoint
3	9.5 l/min	0.486 g/h	1.186 mbar	2.5 %
4	9.5 l/min	0.972 g/h	2.371 mbar	5.0 %
5	9.5 l/min	1.458 g/h	3.557 mbar	7.5 %
6	9.5 l/min	1.944 g/h	4.743 mbar	10.0 %
7	9.5 l/min	2.431 g/h	5.928 mbar	12.5 %
8	9.5 l/min	2.917 g/h	7.114 mbar	15.0 %
9	9.5 l/min	3.403 g/h	8.3 mbar	17.5 %

Figure 3.1: Example of the generated list of setpoints

After all the setpoints of the adsorption curve are fed into the GUI, it will automatically create the setpoints for the desorption curve by reversing the setpoints of the adsorption before. This can be done several times depending on the number of cycles demanded from the GUI.

Then the in-situ measurement of the ellipsometer is started and the first setpoint is transmitted to the flowmeter, which changes the position of its valve to allow the desired adsorbate flow. After a sufficiently long period of time, the stabilized new values of the refractive index and the film thickness can be saved to the second txt-file and the next setpoint is sent to the flowmeter. This is done until the last setpoint of the desorption curve is reached and the Cori flow is sealed again.

During all the steps it is possible to check on the momentary flow of both the carrier gas and the adsorbate.

The GUI can be easily divided into certain inputs and outputs and the calculations and actions leading from one to the other. The following flowchart (see figure 3.2) is supposed to facilitate the GUI's comprehensibility.

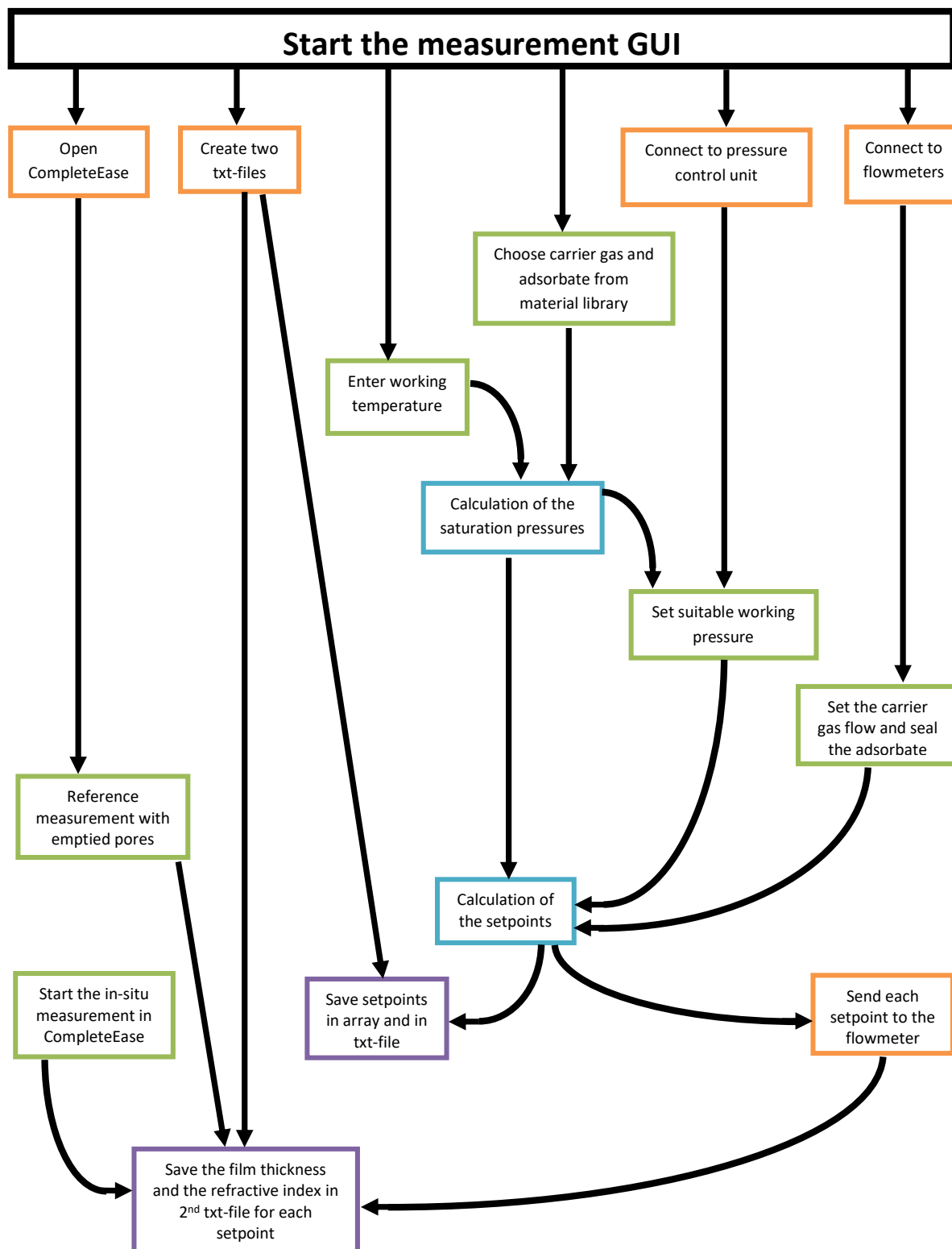


Figure 3.2: Flowchart of the set-up and measurement control:
 User input is marked as green, GUI actions as orange, GUI calculations as blue and outputs as purple.

3.1.2 Communication with Flowmeter

One of the main functions of the GUI is the communication with both flowmeters, which stay closed after powering up, until the instruments receive a setpoint from an active setpoint source. The flowmeters are controlled internally by a number of digital parameters, most of which can only be accessed via digital communication. Each communication protocol uses its own methods for communicating with instruments and accessing parameters [48].

Using a RS232 connection the communication protocol is called ProPar ASCII, in which the parameters are identified by a combination of process and parameter numbers. To communicate with each instrument, the comport number must be known, as well as its node number, if one comport is connecting several instruments at the same time. Besides the process and the parameter number, the parameter type is needed, to control the flowmeters.

If all of this is known, the ProPar ASCII protocol enables the following tasks according to the manual for the RS232 interface [49]:

- request a status update of the flowmeters
- send or request a parameter to the flowmeters
- start, stop, claim or unclaim processes of the flowmeters

The figure 3.3 presents an example of the ProPar communication protocol in use. It depicts the action of reading the current setpoint. An ASCII code is send to the instrument requesting a parameter - the setpoint defining the flow passing through the flowmeter. The answer is then translated from ASCII to an integer to improve the readability.

```
def read_setpoint(self, nodenumber, max_setting):
    """ Read the current setpoint """
    read_setpoint = ':06' + nodenumber + '0401210121\r\n' # Read setpoint
    response = self.comm(read_setpoint)
    response = int(response[11:], 16)
    response = (response / 32000.0) * max_setting
    return response
```

Figure 3.3: Example of the communication with the flowmeters: Reading the current setpoint

3.2 Material Library

As it is planned to use several probing liquids and different inert gases for ellipsometric porosimetry, it was necessary to include the properties of these possible combinations during the scripting of the GUIs. This was done by creating an external data sheet, the so-called Material library, which contains information on the gas phase of several materials.

The main characteristics included into the Material library are:

- Name of the material
- Chemical formula
- Coefficients for the Antoine equation for two temperature ranges
- Gas factor
- Density

The data sheet can be extended easily with additional entries for new liquids and gases. Up to now the Antoine coefficients were found using the database of the National Institute of Standards and Technology [50], while most of the gas factors were taken from the database of MKS [51].

3.3 Calculations and Evaluation

The second GUI controls and accelerates the post-processing of the measured data by applying the Kelvin equation and the effective medium approximation. The workflow is explained in the following pages and summarised in a flowchart (see 3.2). The source code is shown in the appendix (section 12).

3.3.1 General Workflow

After starting the GUI, a window with several entry fields is opened. It is fed with the list of setpoints and their corresponding refractive index and thickness, which were estimated by the ellipsometer software. The setpoints are entered in percentage of the saturation pressure of the adsorbate and the thickness in nanometer.

As even small derivations can have an impact on results of the subsequent calculations, the data is presented to the user, after finishing the input of the ad- and desorption curve. It is possible to adjust the list, if mistakes or missing data is found. To include additional data, the user simply needs to choose the lines before and after the new data point and type the setpoint in. Specific lines can also be deleted or corrected in a similar manner. The correct data of the film thickness and the refractive index is then plotted against $\frac{p_{ad}}{p_{sat}}$.

Once all entry mistakes are fixed, the GUI uses the before explained EMA (see section 1.3.2) to calculate the volume fraction of adsorbate inside the voids for every setpoint. The volume fraction is subsequently plotted against the percentage of the saturation pressure of the adsorbate. The figure is saved to the folder, which contains the GUI, for later use.

Then the GUI requires the user to enter the molar volume and the surface tension of the adsorbate as well as the working temperature during the measurement. This input is necessary to calculate the pore size distribution using the Kelvin equation. The pore size distribution is plotted and the figure is saved. In the end the GUI plots every data combination the user needs, either on a linear or logarithmic scale, and prints a table containing the setpoints, the film thickness, the refractive index, the volume fraction and the pore size distribution to a text-file.

Also the postprocessing GUI can be easily divided into certain inputs and outputs and the calculations and actions leading from one to the other. Like the previous one, the following flowchart (fig. 3.4) is supposed to break down the GUI's workflow into single actions to make it intelligible.

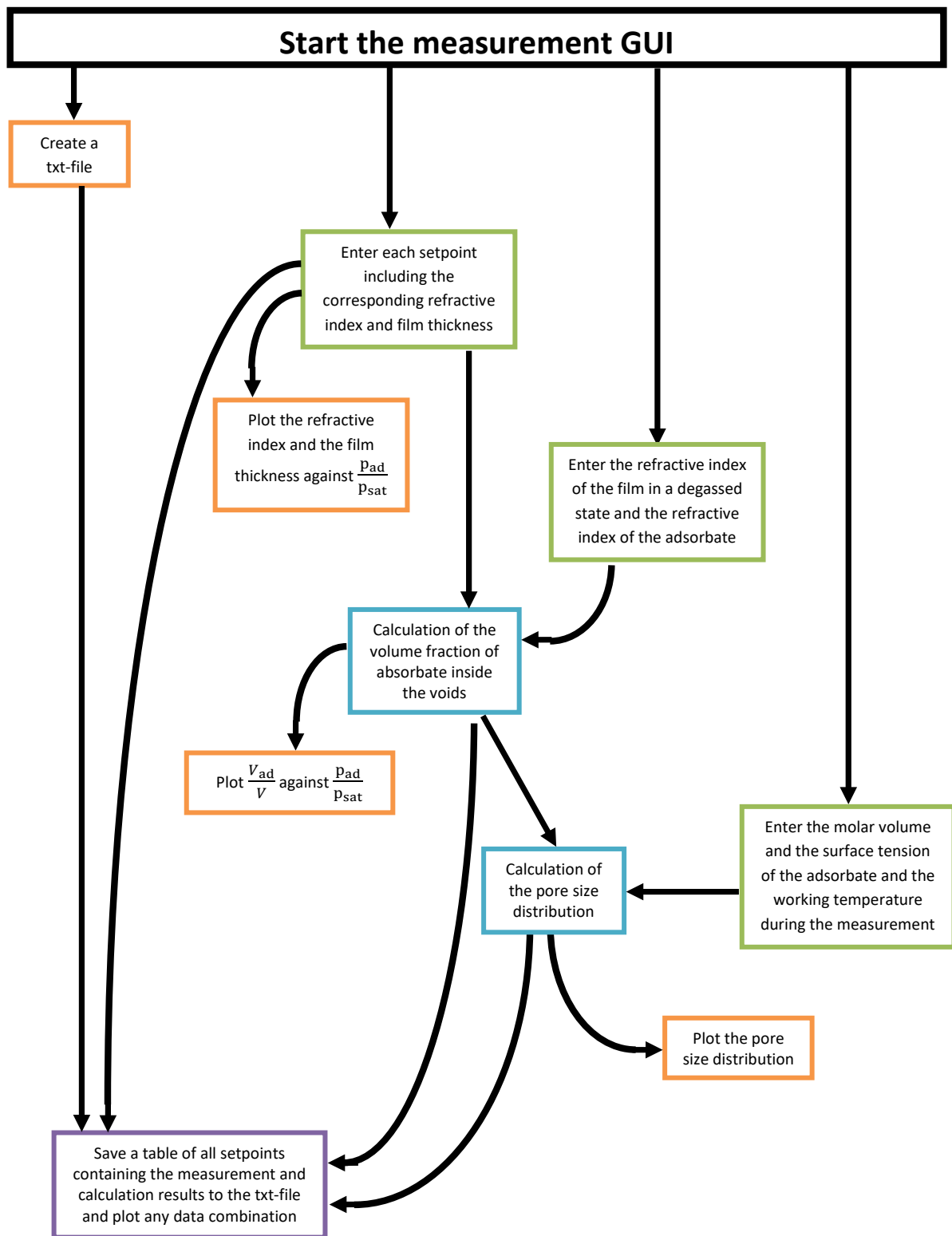


Figure 3.4: Flowchart of the postprocessing:

User input is marked as green, GUI actions as orange, GUI calculations as blue and outputs as purple.

CHAPTER 4

MEASUREMENTS AND RESULTS

This chapter addresses the final step of this thesis, the results obtained using spectroscopic ellipsometry and ellipsometric porosimetry on various samples. Both measurement techniques are explained in section 1.3. Further, the comparison between the results of the formerly used set-up and the new ellipsometric porosimeter are presented.

4.1 Samples

The set-ups functionality was tested by studying several possibly porous samples produced by Richard Berger and Martin Seiler using either plasma enhanced-ALD or MLD. Since the focus of this thesis lies with mesoporous thin films and their analysis by spectroscopic ellipsometry and ellipsometric porosimetry, only measurements of such samples are presented within this chapter. Hence, solely thin films produced by MLD, which were subsequently annealed, are presented. The four samples are from two different batches and are described in table 4.1.

Table 4.1: Description of the samples

Denomination	MLD process	<i>Date_{Production}</i>	<i>Date_{Annealing}</i>
AB	AB	September 2018	October 2018
ABC ₁	ABC	November 2019	February 2020
ABC ₂	ABC	November 2019	February 2020
ABC ₃	ABC	November 2019	February 2020

Single-side polished Si-wafers with an native oxide of around 1.3 nm were used as a substrate for all thin films. They were deposited by a costum-built MLD reactor and later calcined in air within the heating stage of the spectroscopic ellipsometer.

While the AB thin film was created using only two precursors (AB process), the ABC-batch of samples was produced using an ABC-MLD process, which means, that the substrate was sequentially exposed to three different precursors. In both cases, the reactor was purged with Argon after each precursor step, to keep the precursors and possible by-products from interacting with one another anywhere other than the sample's surface. Diethyl zinc (DEZ) and ethylene glycol (EG) served as metalorganic and organic precursor for the AB-thin film. The ABC-batch's MLD-process on the other hand consisted of DEZ as a metal-organic precursor and maleic anhydrate (MA) and ethanolamine (EA) as organic precursors.

To create the desired porosity, the zinc-oxide films underwent an annealing process after the demanded film thickness was reached by the MLD. Several maximum annealing temperatures were tested to investigate the influence on the film's later porosity and thickness (see table 4.2).

Table 4.2: Characteristics of the annealing process

Denomination	Maximum temperature [° C]	Heating rate [° C/h]
AB	600	200
ABC ₁	400	200
ABC ₂	500	50
ABC ₃	600	200

The main purpose of the annealing process is the removal of the organic linker within the thin film. Upon removal, the residuary zinc and oxide is forced to structurally reorganise to maintain stable. While three of the samples were annealed at a rather low pace to enable the film's reorganisation, ABC₂ was heated even slower at only 50 °C per hour. Not only the heating rate was varied, but also the influence of the maximum temperature reached during annealing was examined.

Both the annealing rate and the maximum annealing temperature can influence the final porosity and conformality of the thin film. An example of the in-situ SE measurement is given under the section 4.2.1. The SE results of the refractive index and the film thickness before and after the annealing process are shown in section 4.2.2.

4.2 Spectroscopic Ellipsometry Measurements

The spectroscopic ellipsometry measurements were done on both setups, obtaining the same or nearly identical results. The ellipsometer was used to do fast data acquisitions and for in-situ measurements during the annealing process. On the spectroscopic ellipsometer the former were done by averaging over the measurements at four different angles to reduce the measurement uncertainty. All ellipsometry results presented in this thesis were achieved at a wavelength of 623.8 nm.

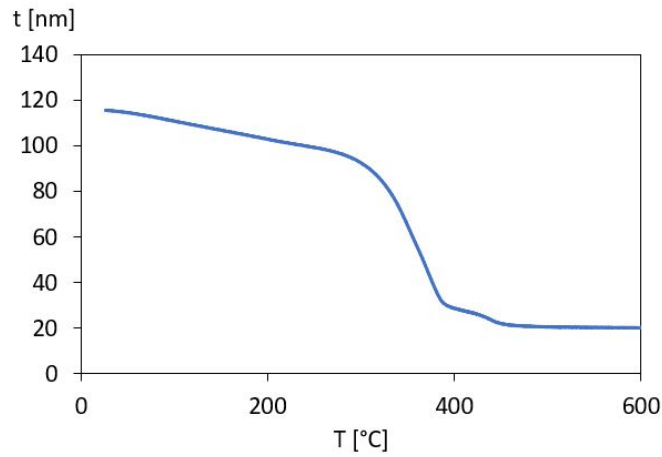
4.2.1 In-situ Measurements of the Annealing Process

Due to the use of a special heating stage of the spectroscopic ellipsometer it is possible to measure the film's properties (e.g. film thickness and roughness and the refractive index) as a function of temperature throughout the whole annealing process. This enables the instantaneous observation of every structural change within the thin film. An example of this in-situ SE measurement is shown in the figure 4.1.

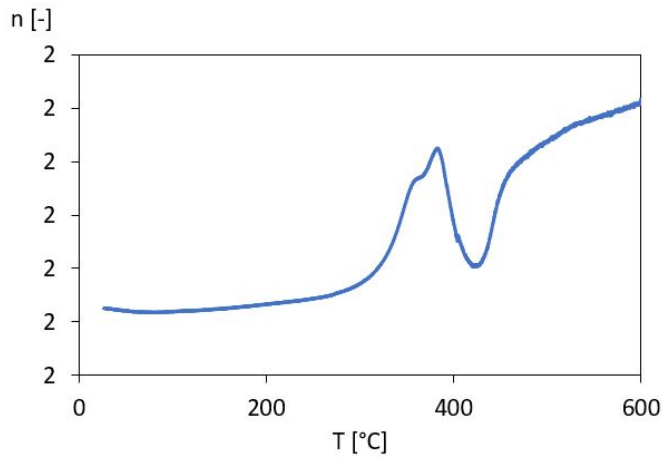
The heating stage is operated by a system control unit and cooled using an external liquid nitrogen pump. The ellipsometer software CompleteEASE is given a specific temperature ramp defined by the minimum and maximum temperature and the duration of the heating process.

The same software is subsequently used to create a proper model to fit the measured data of the SE. For all the zinc-oxide films the model consisted of two layers. The first one represented the substrate, the Si wafer with its native oxide (SiO_2), and the second one was supposed to model the zinc-oxide thin film deposited on top of the former. A precast fitting model called Si_Temp_JAW from the software library was used for the substrate. The metal-organic thin film was modelled using the Cauchy equation 1.2, by fitting the film's thickness and the parameter A and B, while setting parameter C to zero, throughout the whole measurement. Since the zinc-oxide films are supposedly transparent within the pre-set wavelength limits of the laser, the adsorption coefficient k was also set to zero.

Figure 4.1(b) shows the refractive index at $\lambda = 632.8nm$ and figure 4.1(a) the thickness of the sample ABC_3 during the annealing process. As stated in table 4.2, the sample was heated up to $600^\circ C$ at a pace of $200^\circ C$ per hour in ambient air atmosphere. After reaching the maximum temperature it was cooled down to room temperature. To observe the changes in the thin film, its properties were measured as functions of temperature with the aid of SE.



(a) Film thickness versus temperature



(b) Refractive index at 632.8 nm versus temperature

Figure 4.1: SE calculation results of the ABC_3 thin film during the annealing process

The measurements performed on samples of batch ABC, which were produced using DEZ, MA and EA, showed a distinct drop in film thickness and a clear rise of the refractive index at around 300 °C (see figure 4.1). Consequentially, it can be assumed, that only small parts of the organic film content are removed until that temperature.

The simultaneous increase of the refractive index and the decrease in film thickness between 300 °C and 380 °C indicate a collapse of the film's structure due to absence of the organic content, which is followed by a structural reorganisation and the crystallisation of the zinc-oxide thin film (from 380 °C to 420 °C).

Following this regime of massive structural changes, the thin film experiences only little decrease in thickness up to the maximum annealing temperature. Due to the more or less

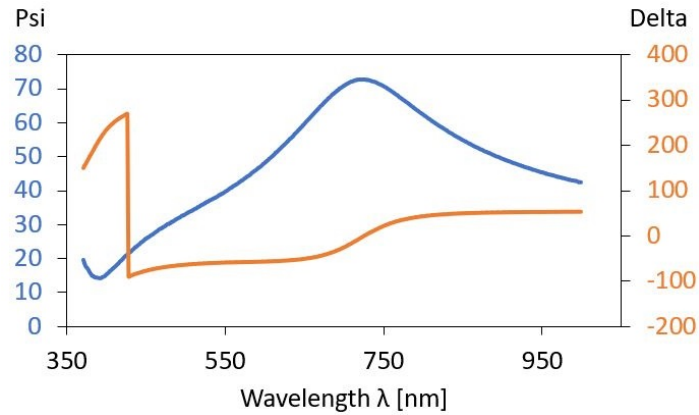
constant film thickness, it can be assumed that no additional components are lost during the higher temperature regime. The refractive index on the other hand decreases starting at 380 °C until 420 °C and increases again at around 430 °C. Until now, no clear explanation for the peculiar behaviour of the refractive index has been found.

Then, both the film thickness and the refractive index experienced only slight changes, until the maximum annealing temperature was reached.

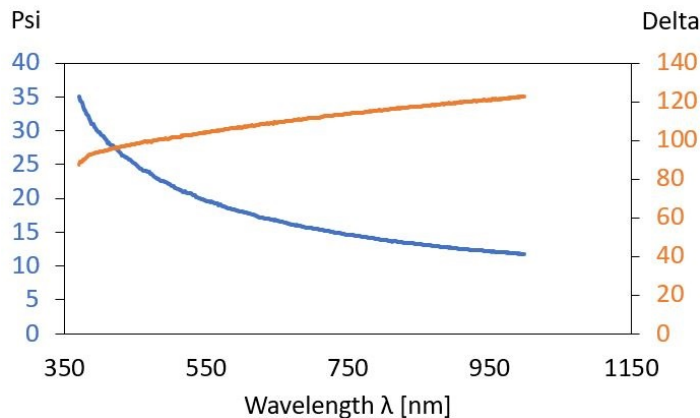
While cooling the sample back down to room temperature, the thickness is not further reduced, which indicates a stable zinc-oxide thin film after crystallisation. Although the cooling process seems to have little to non effect on the porous structure, the refractive index decreased slightly. The following section presents the initial and final thickness and refractive index of all samples before and after the annealing process.

4.2.2 Spectroscopic Ellipsometry Measurements before and after the Annealing Process

The ellipsometry software based its calculations of the thin films' properties on the SE measurements. An example for the measurement data before and after the reconstruction of the thin film is shown in figure 4.2.



(a) Before annealing



(b) After annealing

Figure 4.2: Spectroscopic measurements of sample ABC₃ before and after the annealing process

As explained in the section 1.3.1, the SE measurements of samples are based on the change in polarisation of the laser light, which is described by the amplitude ratio, Ψ , and the phase difference, Δ . Using the Fresnel equations, these two parameters can be translated to the thin film properties through the application of a proper material model. For the zinc-oxide thin films, a Cauchy model was used to fit the measurement data. During the fitting process the Cauchy parameter, A and B, and the film thickness was modified until the calculated Ψ and Δ curves matched the measured ones best.

Based on similar measurements on all four samples, their thickness and refractive index before and after the annealing were summarised in table 4.3. Richard Berger provided the properties of sample AB. The measurements of the samples ABC_1 and ABC_2 shown above were done by Martin Seiler. It can be observed, that the removal of the thin film’s organic contents resulted in an increase of the refractive index and a noticeable decrease in its thickness. While the AB sample lost around 50% of its thickness, the samples of the B-batch were reduced to only a fourth of their original thickness.

Table 4.3: Description of the samples’ properties (thickness t and refractive index n) before and after the annealing process in air at atmospheric pressure

Denomination	t_{before} [nm]	n_{before}	t_{after} [nm]	n_{after}
AB	49	1.57	27.7	1.78
ABC_1	83	1.55	21.1	1.69
ABC_2	75	1.56	18.8	1.72
ABC_3	116	1.56	27.2	1.68

To check the validity of the SE measurements of the new set-up, the porous samples were analysed a second time. Since the new set-up is only able to work at a fixed angle of 70° , the acquisition time is lower. Due to the same reason, the mean square error of the measurement is slightly higher, because it cannot average over several angular positions of the ellipsometer during one measurement cycle. Regardless, the estimated values of the film thickness and the refractive indices are in good agreement with the ones calculated based on the measurements on the old set-up (see table 4.4). The minor differences are always within the measurement uncertainty of the ellipsometer software.

Table 4.4: Comparison between the results obtained with the old set-up and the new set-up: Thickness t and refractive index n after the annealing process in air at atmospheric pressure of the sample batch ABC

Denomination	$t_{oldsetup}$ [nm]	$n_{oldsetup}$	$t_{newsetup}$ [nm]	$n_{newsetup}$
ABC_1	21.1	1.69	21.3	1.69
ABC_2	18.8	1.72	19.1	1.73
ABC_3	27.2	1.68	27.1	1.69

4.3 EP Measurements

In order to validate the functionality of the newly-built ellipsometric porosimeter set-up, several measurement cycles were done on both the formerly used set-up and the one described in chapter 2. The evaluated samples were produced by two different MLD processes. The following results are ordered according to the deposition set.

4.3.1 Thin Film of the AB-batch

The porosity of the AB-batch sample was primarily analysed by Richard Berger during the scope of his Master thesis 'Nano-Porous Zinc Oxide via Molecular Layer Deposition'. As stated in table 4.2, the thin film was heated up to 600 °C during the annealing process. After a successful crystallisation of the film's structure, an EP measurement was done. The relative humidity of the sample chamber was increased from 0% to 95% and again reduced to 0%. From the adsorption and desorption curve, it could be deduced, that the zinc-oxide film was indeed mesoporous [52].

Based on this promising analysis, the new ellipsometric porosimeter set-up was tested using the AB sample. Two EP measurements were carried out to test various aspects of the new set-up. Both were done using distilled water to simplify the comparison between the data obtained with the formerly used set-up and the new one. The main difference between the two measurements was the working pressure (shown in table 4.5)

Table 4.5: Experimental details of the EP measurements on sample AB

No.	Set-up	Adsorbate	RH _{max} [%]	Working pressure [mbar]
AB _{prime}	former	distilled water	95	1000
AB _{2020,1}	new	distilled water	95	1000
AB _{2020,2}	new	distilled water	95	650

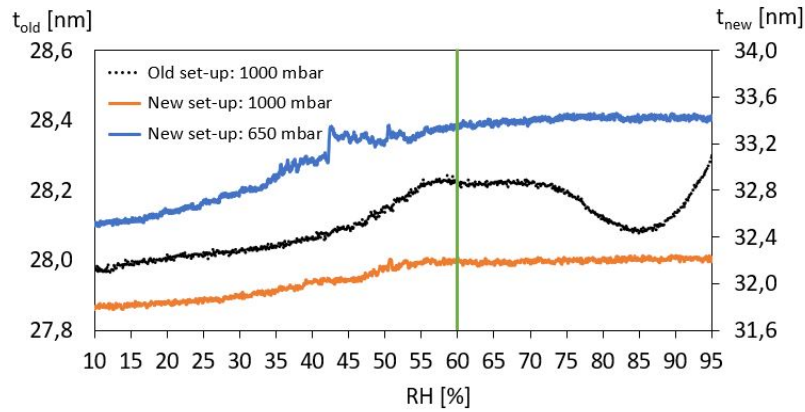
The first measurement done on the new set-up was supposed to emulate the primary experiment as much as possible. The same adsorbate was used and the working pressure was set to atmospheric pressure. The second measurement was intended to showcase the ability to work at various pressure levels.

Since the deposition and the annealing process happened in 2018 and the new measurements were performed 1.5 years later, SE measurements were done to check for primary indicators of structural degradation of the thin film (see table 4.6).

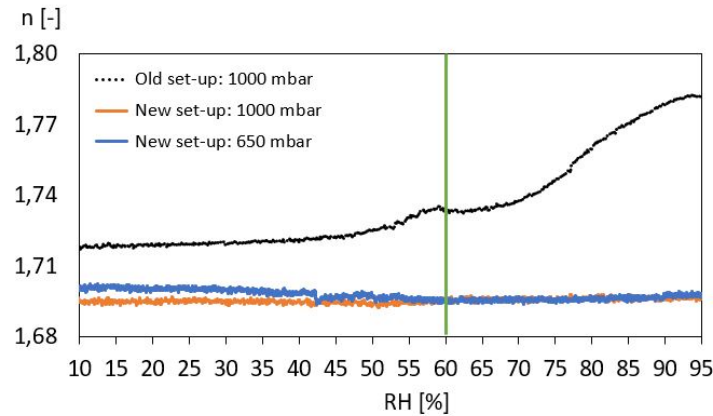
Table 4.6: Results of the film thickness t and the refractive index n obtained from SE analysis on sample AB ahead of the three EP measurements

No.	date _{experiment}	t [nm]	n [-]
AB _{prime}	October 2018	27.95	1.717
AB _{2020,1}	August 2020	31.78	1.695
AB _{2020,2}	August 2020	32.31	1.697

Although the film thickness slightly increased and the refractive index decreased a little, it seemed reasonable to assume, that the film kept its integrity due to its stable crystal structure, and the EP measurements were performed. The obtained results of the refractive index and the film thickness are presented in figure 4.3.



(a) Refractive index vs. relative humidity



(b) Film thickness vs. relative humidity

Figure 4.3: Results of the adsorption curve for each EP measurement of sample AB:

The AB_{prime} measurement using the old set-up (black dotted line), the AB_{2020,1} measurement using the new set-up at 1000 mbar (orange line) and the AB_{2020,2} measurement using the new set-up at 650 mbar (blue line). The green line marks the beginning of the mesoporous regime.

Figure 4.3 consists of two subplots, which contain three measurement curves each. One shows the change in refractive index, the other one the film thickness versus the relative humidity during the adsorption regime. The black dotted line represents the primary measurement soon after the annealing process in 2018 done by Richard Berger. The orange and blue lines mark the measurements done on the new EP set-up at a working pressure of 1000 mbar and 650 mbar in 2020.

Since the Kelvin equation relates the relative humidity to the radii of open pores, in which the adsorbate of the gas mixture has already condensed, the higher humidity regime is obviously of greater interest. A relative humidity of 60% corresponds to filled pores of a 2 nm diameter. This is the starting point of the mesoporous regime and therefore the Kelvin equation's validity. A green line indicates this threshold between micro- and mesoporosity in figure 4.3.

Due to the crystallinity of the ZnO after the annealing process, the film thickness is not expected to change drastically during the ellipsometric porosimetry measurement. All three curves show a similar increase of only a few tenths of a nanometer until 60% relative humidity. The film thickness has increased by approximately 4 nm since the primary measurement and after the 60% RH threshold, the film thickness of both measurements done on the new set-up converges. This leads to the assumption, that no pores with a radius over 1 nm are available for the vapour to condense in. This indicates either a structural change within the film or the formation of a top-layer blocking the formerly open mesoporosity.

While the two recent measurements of the refractive index of sample AB stay more or less constant throughout the whole adsorption curve, the primary analysis shows a strong rise after the 60% RH mark. At that point, the gas mixture begins to condensate in the mesopores. The closer the adsorbate's partial pressure is to its saturation pressure, the bigger the pore width of the filling pores should be within a porous material according to the Kelvin equation. During the recent EP measurements, the refractive index did not increase as the relative humidity approached 95 %. This is also a strong indication, that the film structure might have degraded over the last months.

As hoped, the thickness increases according to the step-function, modelled by the subsequent changing of the flowmeter's setpoint (see figure 4.4). This shows, that the GUI is properly interacting with the flowmeters and that the whole set-up works according to plan.

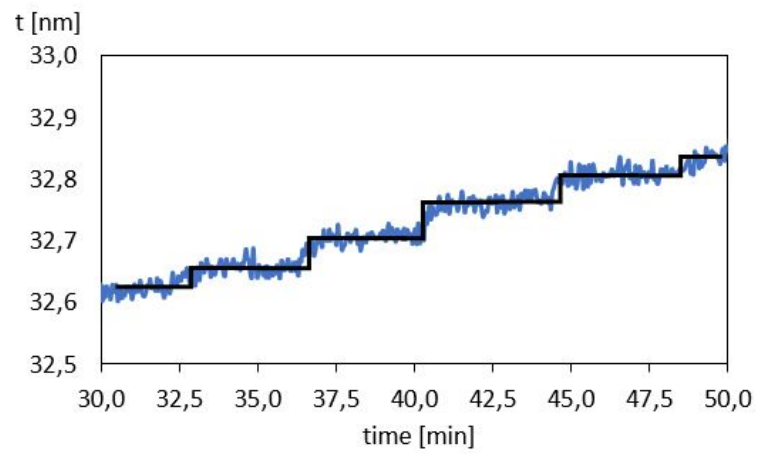


Figure 4.4: Close-up of a section within the adsorption curve of sample AB at 650 mbar working pressure: The stepwise increase of the film thickness is based on the rising relative humidity surrounding the sample.

4.3.2 Thin Films of the ABC-batch

The sample batch ABC was produced by Martin Seiler during the scope of his Master thesis 'Deposition and characterization of coatings by Molecular Layer Deposition'. The porous thin films were deposited by a MLD ABC-process and subsequent annealing at different heating rates up to various maximum temperatures (see table 4.2)[53].

As part of this thesis annealing processes were done and the measurement data of one of them is shown in section 4.2.1. Following the annealing, an SE and an EP measurement were done on the thin films using the old set-up on the spectroscopic ellipsometer. The experimental details of each EP adsorption-desorption-cycle is presented in table 4.7. Since only water can be used as adsorbate within the bubbler of the old set-up and the sample chamber is not intended to be sealed from its surroundings, all three measurements were conducted in the same way.

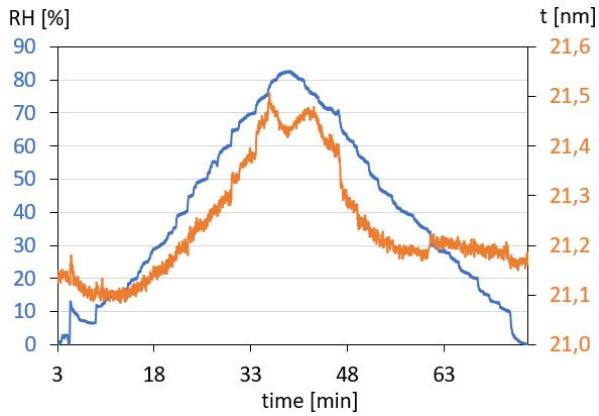
Table 4.7: Experimental details of the EP measurements on sample batch ABC measured on the old set-up

Sample	RH _{max} [%]	Working pressure [mbar]	Working temperature [°C]
ABC ₁	82.5	1000	26.0
ABC ₂	83.0	1000	25.6
ABC ₃	84.0	1000	25.5

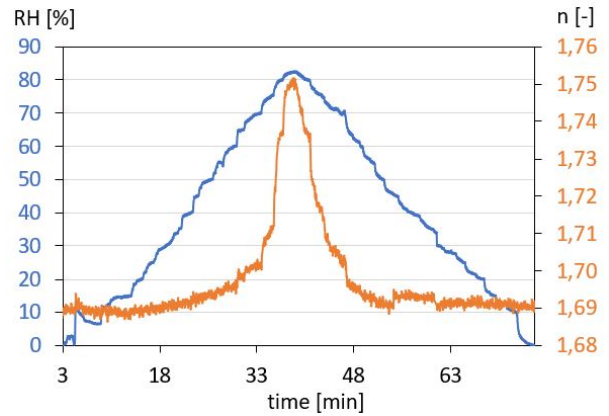
Each sample was analysed up to the highest relative humidity, which could be reached on the set-up on that day. The RH and the temperature were measured using a sensor, which was inserted into the sample chamber. CompleteEase estimated the film thickness and refractive index of the ZnO-layer during the whole measurement. The obtained data is shown in figure 4.5.

The graphs on the left show the change in film thickness and the relative humidity throughout the whole measurement. The behaviour of the refractive index compared to the relative humidity is shown in the graphs on the right side. Due to limitations concerning the set-up, all three samples were only evaluated up to a relative humidity between 83% and 84%, which relates to 2.8 nm and 3.0 nm.

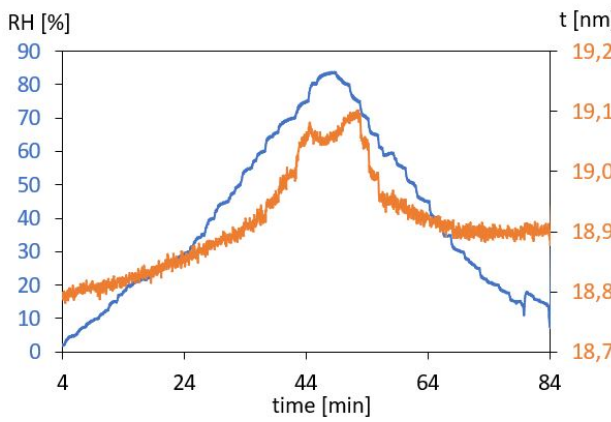
Similar to the thin film of batch AB, the film thickness t changed only in tenths of a nanometer during the measurement, which is negligible, since it translates to 1% film growth. The refractive index n , on the other hand, increased quite a lot, what generally points to a porous structure, which steadily fills with adsorbate.



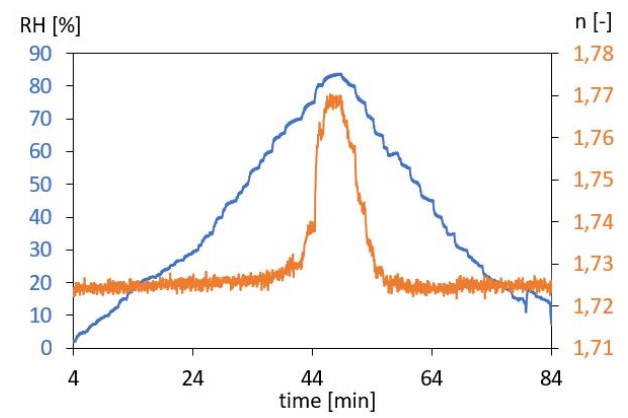
(a) ABC₁: t and RH vs. time



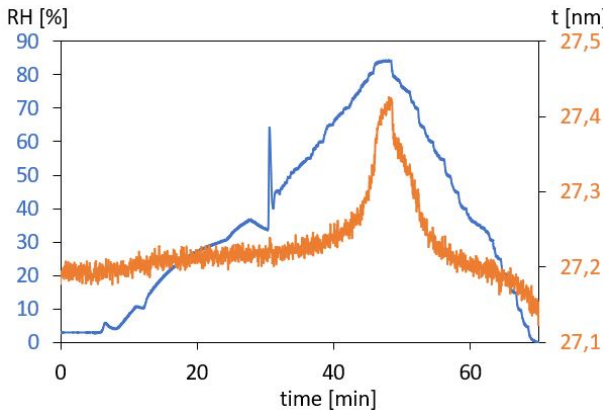
(b) ABC₁: n and RH vs. time



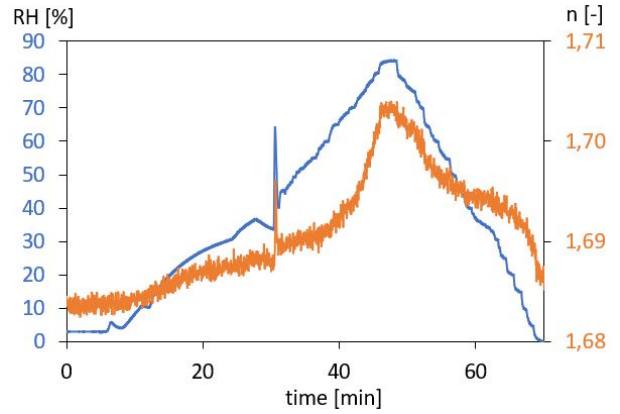
(c) ABC₂: t and RH vs. time



(d) ABC₂: n and RH vs. time



(e) ABC₃: t and RH vs. time



(f) ABC₃: n and RH vs. time

Figure 4.5: EP measurement data of all three samples:

The evolution of the film thickness t and the refractive index n during an increase of the relative humidity RH over time.

The samples ABC_1 and ABC_2 show only little change in the refractive index until a relative humidity of 70% and experience a sharp rise after that threshold. The refractive index of the thin film ABC_3 on the other hand gradually increases from 30% RH to 60% RH and then rises slightly steeper from there until the end of the adsorption. This suggests a higher percentage of open nanoporosity in thin film ABC_3 . The sample ABC_1 experiences the highest increase in refractive index by percentage, which indicates the highest mesoporosity in comparison to the other two samples of the ABC-batch.

These results of the refractive index should be seen in the context of the details of each annealing process (shown in table 4.2). Generally it is assumed, that the crystallinity of a thin film structure increases with the maximum annealing temperature. ABC_3 was annealed at the highest temperature, 600 °C, and hence should be the 'most' crystalline. But it appears that, during the crystallisation process, mesoporosity is lost due to the structural changes, leading to an increased nanoporosity.

Concerning the change in film thickness, the samples ABC_1 and ABC_2 also behave similar. They experience their maximum at around 75% RH and decrease a little until the end of the adsorption curve. The ABC_3 film has a constant thickness until 65% RH and finds its maximum thickness at the maximum RH.

According to section 1.3.2, the effective medium approximation was used to backcalculate the volume fraction of the condensed liquid inside of the samples ($\frac{V_{ad}}{V}$) during the increase and subsequent decrease of the relative humidity. The results are presented in figure 4.6. The blue curve is the so-called adsorption curve and the orange curve represents the desorption curve.

The different mechanisms of ad- and desorption lead to a hysteresis-like shape of the $\frac{V_{ad}}{V}$ curve. While for both, the ABC_1 and the ABC_2 sample, the curve part during adsorption looks quite similar to the one in the desorption regime, the thin film, which was heated up to 600°C shows a different behaviour. Apparently the RH was reduced too fast for the humidity sensor to respond properly. The gap between the initial value of $\frac{V_{ad}}{V}$ and the one after the finished desorption process indicates a residual fraction of adsorbate within the pore system.

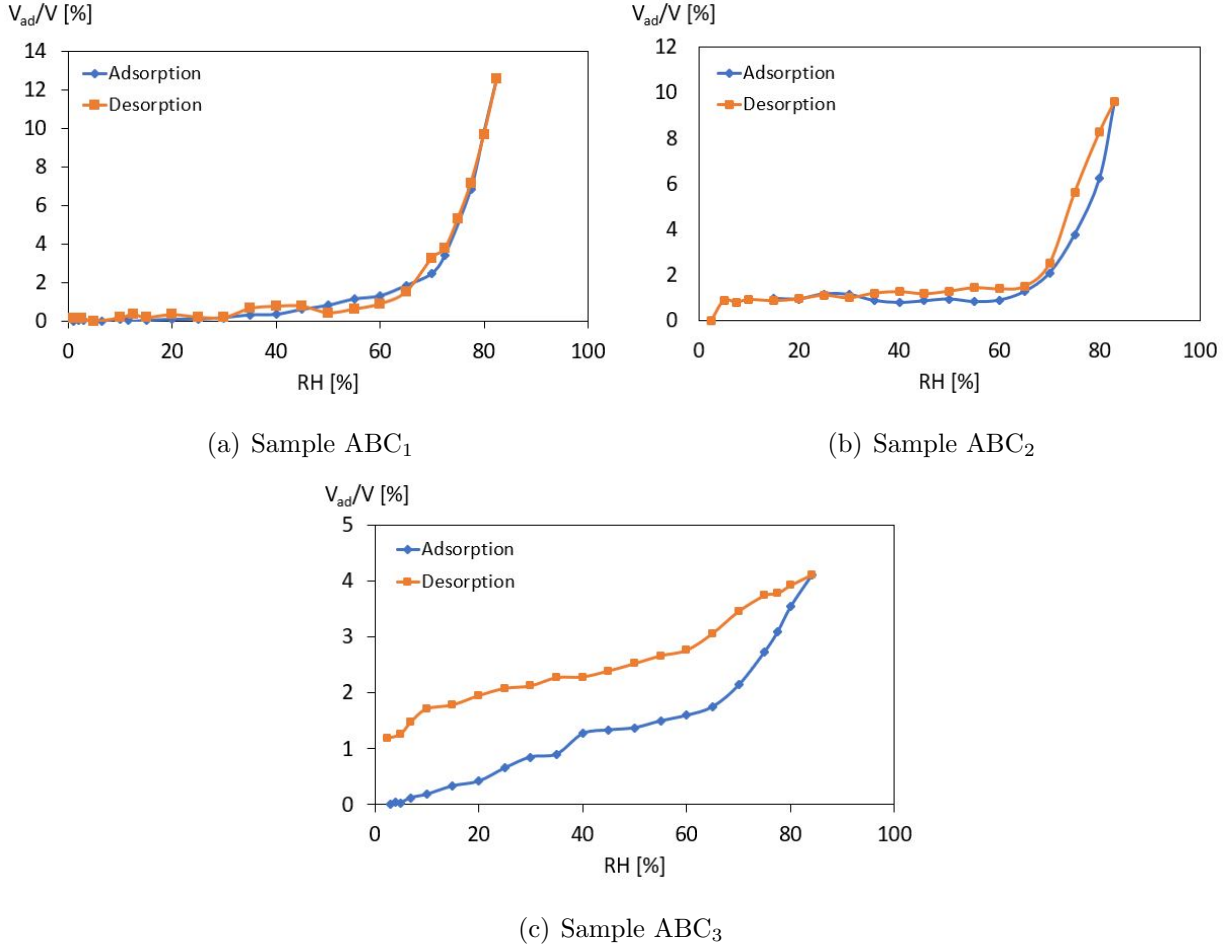


Figure 4.6: Evaluation of the EP measurement data of all three samples:

The volume fraction of the adsorbate within the pore system ($\frac{V_{ad}}{V}$) during an increase and subsequent decrease of the relative humidity.

Since the desorption curve of sample ABC₃ is not completely trustworthy and generally harder to analyse, only the adsorption curves were used to estimate the pore size distribution. To check whether the total open porosity of the film was filled with adsorbate, the calculated data of $\frac{V_{ad}}{V}(r)$ was extrapolated using fitting curves. These curves are shown in the graphs on the left in figure 4.7 and represent the cumulative distribution of the thin film's open pores as function of the pore radius. The fitting curves reveal an open porosity of the thin films ABC₁, ABC₂ and ABC₃ of approximately 24%, 10% and 4%.

The fit indicates, that the mean pore size of the sample ABC₁ is larger compared to the other samples of the batch and that a smaller fraction of its total open pore system was filled with condensed adsorbate at the maximum relative humidity, which could be achieved during the EP measurement.

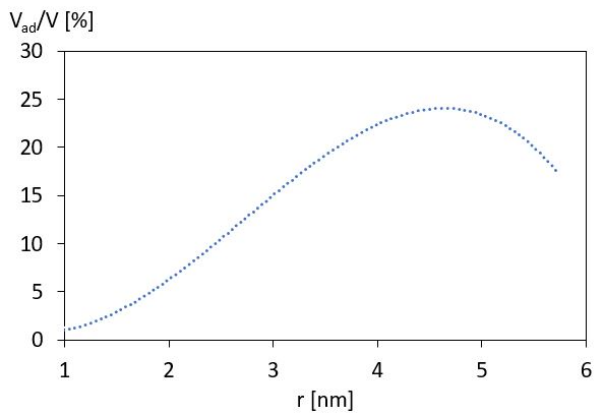
The right side of 4.7 shows the derivative of $\frac{V_{ad}}{V}(r)$, the so-called PSD, for the data range examined during the EP measurement. Every result surpassing the maximum evaluated pore radius of 2.8 nm would have been based on assumptions concerning the behaviour of the pore size distribution. If information about the regime of larger pore radii would be needed, a gaussian behaviour of the pore size distribution would be the best fit. Based on the nearly symmetric-shaped PSD curves of the samples heated up to 500 °C and 600 °C, a gaussian fit seems justified and would probably not overestimate the fraction of wider pores.

The PSDs shown in figure 4.7 indicate, that with higher annealing temperatures (compare table 4.2), the average pore size becomes smaller. For the thin films ABC₁, ABC₂ and ABC₃ the PSDs reveal an expectation value of the pore radius of approximately 2.8 nm, 1.9 nm and 1.8 nm. The results obtained for the three samples of the ABC-batch are presented in table 4.8.

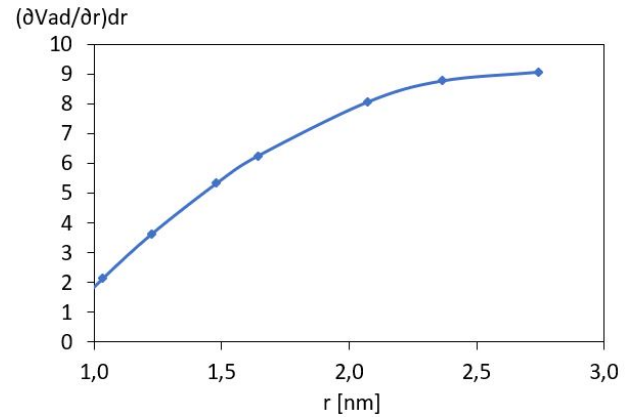
Table 4.8: Porosity details of the ABC-batch samples

Sample	Open porosity [%]	Expected pore radius [nm]
ABC ₁	24	2.8
ABC ₂	10	1.9
ABC ₃	4	1.8

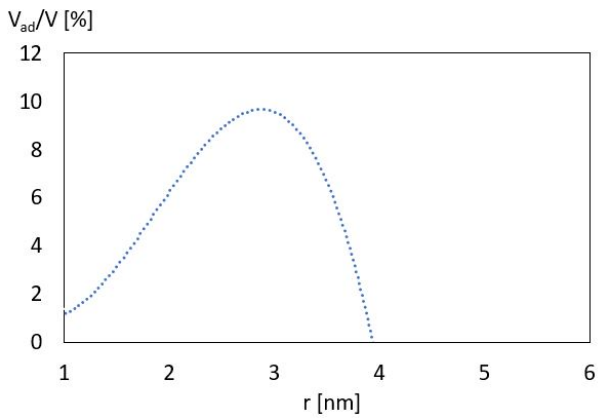
The zinc-oxide film, which was annealed only up to 400 °C, exhibits the highest expectation value of the pore radius with 2.8 nm, which is about one third larger than ABC₂ and ABC₃. It also presents a mesoporosity of about 24%, which is more than twice as much than ABC₂ and even six times as much as ABC₃. This leads to the assumption that the crystallites grow at the cost of the mesopores in the regime between 400°C and 600°C.



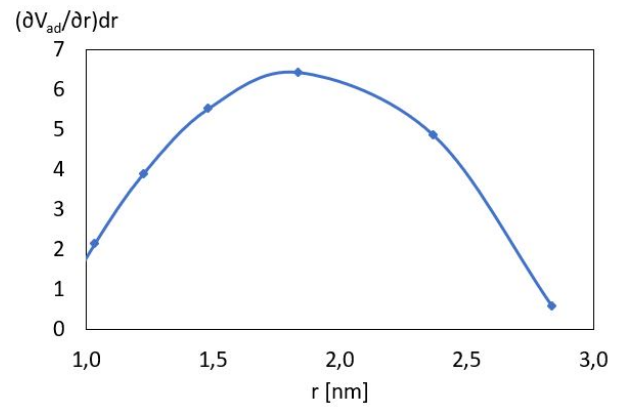
(a) ABC₁: $\frac{V_{ad}}{V}(r)$



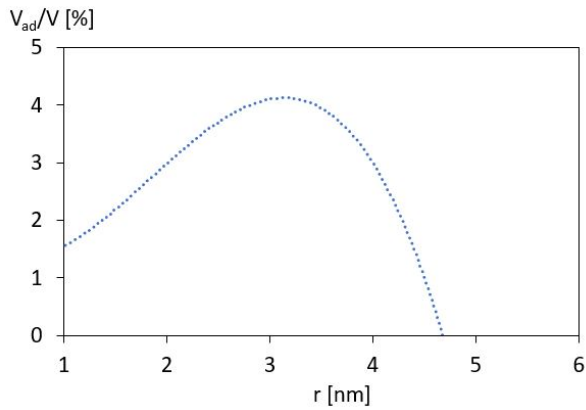
(b) ABC₁: Pore size distribution



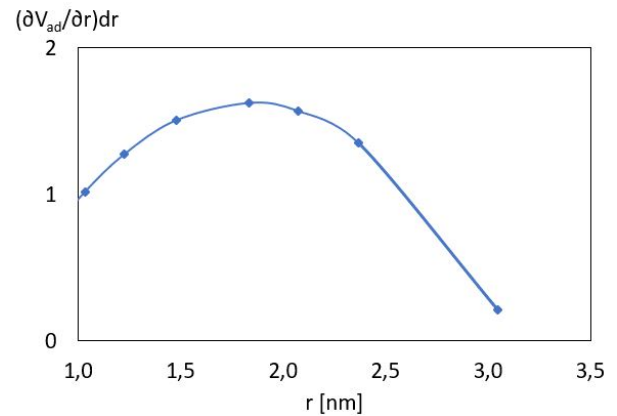
(c) ABC₂: $\frac{V_{ad}}{V}(r)$



(d) ABC₂: Pore size distribution



(e) ABC₃: $\frac{V_{ad}}{V}(r)$



(f) ABC₃: Pore size distribution

Figure 4.7: Evaluation of the EP measurement data of all three samples:

The interpolated volume fraction of the adsorbate within the pore system ($\frac{V_{ad}}{V}$) over the maximum radius of the pores, which are already filled, and the pore size distribution $\frac{\partial V_{ad}(r_{pore})}{\partial r_{pore}} dr_{pore}$.

Second Measurement Loop

After the Covid-19 induced quarantine, which stopped the laboratory work all together for several months, the samples of the ABC-batch were measured once again on the old set-up to reach higher values of relative humidity through heating the adsorbate liquid before vaporisation. During the initial SE measurements of all three samples a possible degradation became apparent. A comparison between the ABC₁ thin film's properties before and after the quarantine is shown in table 4.9.

The ellipsometer software could only fit the data properly, if a certain surface roughness was taken into account. Unfortunately the surface roughness was calculated to be of a similar size as the film thickness, which more or less hindered any further porosimetric analyses completely. Additionally, the laser exhibited a certain adsorption by the thin film, which was not pre-existing. This is indicated by the k-value included by the fitting model, which would be zero, if the sample was transparent. The changes within the model lead to the assumption of an unfortunate structural reconstruction of the zinc-oxide thin film.

Table 4.9: Model details of sample ABC₁ before and after the quarantine

Period	t [nm]	r [nm]	n [-]	k [-]
February 2020	21.1	0.0	1.69	0.00
July 2020	27.5	23.7	1.63	0.13

The other two thin films of the ABC-batch presented similar changes. Even though the SE results did not seem very promising, EP measurements of the samples were attempted. Each of them had to be aborted soon after the beginning due to the formation of a water layer on the samples' surface at rather low RH values. The formation of the water layer was indicated by a rapid drop of the refractive index and a significant increase in film thickness.

Subsequently, the samples were also tested using the new porosimeter set-up, but, as expected, the same results were obtained. As an example the EP measurement of the ABC₁ sample after the quarantine on the new set-up is shown in figure 4.8.

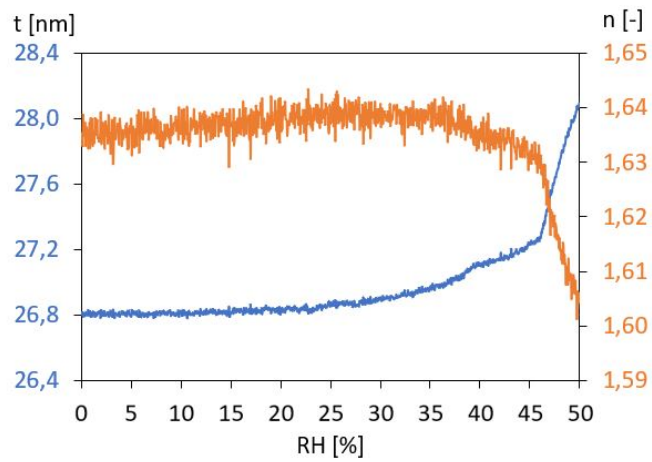


Figure 4.8: EP measurement of the sample ABC_1 at ambient pressure after degradation.

As already suggested by the SE analysis, the sample ABC_1 had an increased film thickness and a lower refractive index compared to the EP initial measurements. The film showed little to no changes until 45% RH. At that point, the refractive index experienced a sudden drop and the thickness abruptly rose, which indicated the formation of a water layer on top of the sample.

The plans of the ellipsometric porosimeter were finalised, all parts were assembled and the set-up was established. The components were checked concerning their compatibility and their functionality.

Subsequently a GUI was scripted to automate the measurement procedure using the Python binding Tkinter. The GUI calculates the flow setpoints forming an adsorption curve based on the working pressure and temperature and the probing fluid and inert gas in use and sends them one at a time to both flowmeters to control their valve opening.

A second GUI was coded to accelerate the post-processing of the obtained data. This is done by applying the EMA and the Kelvin equation to the estimated refractive index at each setpoint during the EP measurement. The volume fraction of the condensate-filled open pores and the PSD are calculated and saved within a .txt-document and as graphs to the measurement folder.

Additionally, a library document was created. It contains the material data of different carrier gases and probing liquids, which can be used during an EP measurement. Both GUIs resort to the library to carry out their calculations.

To check the operational reliability of the set-up, ZnO samples, produced by two different MLD processes and subsequently annealed, were analysed using the spectroscopic ellipsometer set-up and the new ellipsometric porosimeter.

The pre-existing sample AB had been deposited using DEZ and EG in 2018 and later annealed up to 600 °C. It was analysed at 650 mbar and at ambient pressure using the new EP set-up.

The SE measurement showed a slight increase in film thickness and a decrease of the refractive index compared to the original analysis. During both EP measurements the step-wise increase of the film thickness confirmed the functionality of the new set-up for both working pressures. The refractive index stayed constant throughout both adsorption-desorption cycles, what indicated the disappearance of open mesoporosity. This led to the assumption, that the ZnO thin film had degraded over the last 1.5 years.

The ABC-batch thin films were created using DEZ and two organic precursors, MA and EA, during the MLD process. The in-situ SE measurement during the annealing process of one of these samples showed the structural changes within the zincone film. The thin film collapsed starting at 300 °C until 380 °C upon removal of the organic parts. This was followed by a structural reorganisation and crystallisation, which ended at approximately 430 °C.

The three thin films of the second batch, ABC₁, ABC₂ and ABC₃, were heated to 400 °C, 500 °C and 600 °C, respectively. While they all lost approximately the same percentage of thickness (75%) during the annealing process and ended up with similar refractive indices (1.69, 1.72 and 1.68), different mesoporosities were expected based on the maximum annealing temperatures and heating rates.

The first EP analysis were done up to 83% relative humidity on the older set-up. The measurement showed, that the reduced maximum temperture, led to a higher mesoporosity and expectation value of the pore radius. While samples ABC₂ and ABC₃ exhibit an open porosity of 10% and 4% and a mean open pore radius of 1.9 nm and 1.8 nm, the thin film ABC₁ presents with a mesoporosity of 24% and an expected mean open pore radius of 2.8 nm. Based on these results, it is assumed, that after 400 °C the crystallites grow at the cost of the mesopores during the annealing process.

During the measurements done on both set-ups after the Covid-19 induced quarantine, it became apparent, that the samples of the ABC-batch also degraded. A severe surface roughness had developed, which the ellipsometer software estimated to be about the same thickness as the thin films. This structural change hindered proper additional EP measurements on both set-ups, as it led to the early on formation of water layers on top of the film surface.

Unfortunately, due to the pandemic no further porous samples could be produced in time for this thesis. For future use, the set-up should be tested with new mesoporous thin films using water and other probing liquids at various working pressures.

CHAPTER 6

BIBLIOGRAPHY

- [1] *Hierarchically Structured Porous Materials: From Nanoscience to Catalysis, Separation, Optics, Energy, and Life Science*, B.-L.Su, C. Sanchez and X.-Y. Yang, Wiley-VCH Verlag GmbH & Co. KGaA, 2011.
- [2] *Recommendations for the characterization of porous solids*, International Union of pure and applied chemistry, Pure & Appl. Chem., Vol. 66, No. 8, pp. 1739-1758, 1994.
- [3] *Anatomie*, Chapter: Allgemeine Gewebelehre, Benninghoff and Drenckhahn, Urban & Fischer Verlag/Elsevier GmbH, 2008.
- [4] *Porosity and pore size distribution of different wood types as determined by mercury intrusion porosimetry*, M. Plötze and P. Niemz, European Journal of Wood and Wood Products, Vol. 69, pp. 649–657, 2011.
- [5] *Porous materials: Process technology and applications*, Chapter: Applications of porous materials, K. Ishizaki, S. Komarneni and M. Nanko, Springer Verlag, 1998.
- [6] *Porous materials: Process technology and applications*, Chapter: Introduction , K. Ishizaki, S. Komarneni and M. Nanko, Springer Verlag, 1998.
- [7] *Looking down the rabbit hole : nano-porosity in thin films*, Chapter: Introduction, A. Perrotta, Technische Universiteit Eindhoven, 2016.
- [8] *Molecular Sieving Using Nanofilters: Past, Present and Future*, J. Han, J. Fu and R.B. Schoch, Lab Chip, Vol. 8, pp. 23-33, 2008.
- [9] *Electrospinning of Nanofibers: Reinventing the Wheel?*, D. Li and Y. Xia, Advanced Materials, Vol. 16, No. 14, pp. 1151-1170, 2004.

- [10] *Electrospinning: a fascinating method for the preparation of ultrathin fibers*, A. Greiner and J. H. Wendorff, *Angew. Chem. Int. Ed. Engl.*, Vol. 46, No. 30, pp. 5670-5703, 2007.
- [11] *Micro-Mesoporous Materials Obtained by Zeolite Recrystallization: Synthesis, Characterization and Catalytic Applications*, I. I. Ivanova and E. E. Knyazeva, *Chem. Soc. Rev.*, Vol. 42, No. 9, pp. 3671-3688, 2013.
- [12] *Determination of pore size distribution in thin films by ellipsometric porosimetry*, M. R. Baklanov, K. P. Mogilnikov, V. G. Polovinkin and F. N. Dultsev, *J. Vac. Sci. Technol. B*, No. 18, pp. 1385, 2000.
- [13] *Ordered Porous Materials for Emerging Applications*, M. E. Davis, *Nature*, Vol. 417, pp. 813-821, 2002.
- [14] *Handbook of Thin-Film Technology*, Chapter: Chemical Vapor Deposition, H. Frey and H. R. Khan, Springer Verlag, 2015.
- [15] *The Materials Science of Semiconductors*, Chapter: CVD, A. Rockett, Springer Verlag, 2008.
- [16] *25th Anniversary Article: CVD Polymers: A New Paradigm for Surface Modification and Device Fabrication*, A. M. Coclite, R. M. Howden, D. C. Borelli et al., *Advanced Materials*, Vol. 25, No. 38, pp. 5392-5423, 2013.
- [17] *Initiated chemical vapor deposition of polyvinylpyrrolidone-based thin films*, K. Chan, L.E. Kostun, W.E. Tenhaeff and K.K. Gleason, *Polymer*, Vol. 47, p. 6941, 2006.
- [18] *Initiated chemical vapor deposition of trivinyltrimethylcyclotrisiloxane for biomaterial coatings*, W. S. O'shaughnessy, M. Gao and K. K. Gleason, *Langmuir*, Vol. 22, No. 16, pp. 7021-7026, 2006.
- [19] *Initiated chemical vapor deposition of poly(1H,1H,2H,2H-perfluorodecyl acrylate) thin films*, M. Gupta and K. K. Gleason, *Langmuir*, Vol. 22, No. 24, pp. 10047-10052, 2006.
- [20] *Perfluorooctane sulfonyl fluoride as an initiator in hot-filament chemical vapor deposition of fluorocarbon thin films*, H. G. P. Lewis, J. A. Caulfield and K. K. Gleason, *Langmuir*, Vol. 17, No. 24, pp. 7652-7655, 2001.
- [21] *Porous Polymer by Vapor Deposition Polymerization*, Chapter: Porous Polymers by Controlling Phase Separation during Vapor Deposition Polymerization, R. Tao, University of Rochester, 2015.

- [22] *In Situ Monitoring of Atomic Layer Deposition in Nanoporous Thin Films Using Ellipsometric Porosimetry*, J. Dendooven, K. Devloo-Casier, E. Levrau et al., *Langmuir*, Vol. 28, pp. 3852-3859, 2012.
- [23] *Tailoring nanopore formation in atomic layer deposited ultrathin films [Nanopore formation in atomic layer deposited ultrathin films]*, S. Krawal, T. Li, A. Yanguas-Gil et al., *Journal of Vacuum Science and Technology*, Vol. 36, No. 1, 2017.
- [24] *New development of atomic layer deposition: processes, methods and applications*, P. O. Oviroh, R. Akbarzadeh et al., *Sci. Technol. Adv. Mater.*, Vol. 20, No. 1, pp. 465-496, 2019.
- [25] *Surface Chemistry for Molecular Layer Deposition of Organic and Hybrid Organic-Inorganic Polymers*, S. M. George, B. Yoon and A. A. Dameron, *Accounts of chemical research*, Vol. 42, No. 4, pp. 498-508, 2009.
- [26] *Organic and inorganic-organic thin film structures by molecular layer deposition: A review*, P. Sundberg and M. Karppinen, *Beilstein J. Nanotechnol.*, Vol. 5, pp. 1104-1136, 2014.
- [27] *Organic-inorganic hybrid nanocomposite-based gas sensors for environmental monitoring*, A. Kaushik, R. Kumar, S. Arya et al., *S. Chem. Rev.*, Vol. 115, pp. 4571-4606, 2015.
- [28] *Vapor phase infiltration (VPI) for transforming polymers into organic-inorganic hybrid materials: a critical review of current progress and future challenges*, C. Z. Leng and M. D. Losego, *Mater. Horiz.*, Vol. 4, pp. 747-771, 2017.
- [29] *Embedded metalelectrode for organic-inorganic hybrid nanowire solar cells*, H. D. Um, D. Choi, A. Choi et al., *ACS Nano*, Vol. 11, pp. 6218-6224, 2017.
- [30] *Molecular Layer Deposition for Energy Conservation and Storage*, Y. Zhao and X. Sun, *ACS Energy Letters*, Vol. 3, pp. 899-914, 2018.
- [31] *Mesoporous ZnO thin films obtained from molecular layer deposited "zincones"*, A. Perotta, R. Berger, F. Muralter and A. M. Coclite, *Dalt. Trans.*, Vol. 48, No. 37, pp. 14178-14188, 2019.
- [32] *Nano-Porous Zinc Oxide via Molecular Layer Deposition*, Chapter: Introduction, R. Berger, Technische Universität Graz, 2019.
- [33] *Effects of Annealing on the Morphology and Porosity of Porous TiO₂ Films Fabricated by Deposition of Aerosol Nanoparticles*, M. Kubo, Y. Mantani and M. Shimada, *Journal of Chemical Engineering of Japan*, Vol. 48, No. 4, pp. 292-299, 2015.

- [34] *Long-term Performance and Durability of Masonry Structures*, Chapter: Stone, A. Zornoza-Indart and P. Lopez-Arce, Woodhead Publishing, 2019.
- [35] *Applications of the standard porosimetry method for nanomaterials*, Y. M. Volkovich, A. V. Sakars and A. A. Volinsky, *Int. J. Nanotechnology*, Vol. 2, No. 3, pp. 292–302, 2005.
- [36] *Complete EASE Software Manual: Data Acquisition and Analysis Software for J.A. Woollam Co. spectroscopic Ellipsometer*, J.A. Woollam Co. Inc., 2004.
- [37] *Handbook of Ellipsometry*, H. G. Tompkins and E. A. Irene, William Andrew Inc., 2005.
- [38] *In situ spectroscopic ellipsometry as a versatile tool for studying atomic layer deposition*, E. Langereis, S. B. S. Heil, H. C. M. Knoop et al., *Journal of Physics D: Applied Physics*, Vol. 42, No. 7, pp. 1–19, 2009.
- [39] *Looking down the rabbit hole : nano-porosity in thin films*, Chapter: Detection and characterization of (nano-) porosity in inorganic thin films, p. 58, A. Perrotta, Technische Universiteit Eindhoven, 2016.
- [40] *Characterization of Nanoporous Polystyrene Thin Films by Environmental Ellipsometric Porosimetry*, M. Vayer, T. H. Nguyen, D. Grosso et al., *Macromolecules*, Vol. 44, pp. 8892-8897, 2011.
- [41] *Porosity and Mechanical Properties of Mesoporous Thin Films Assessed by Environmental Ellipsometric Porosimetry*, C. Boissiere, D. Grosso, S. Lepoutre et al., *Langmuir*, Vol. 21, pp. 12362-12371, 2005.
- [42] *Nano-Porous Zinc Oxide via Molecular Layer Deposition*, Chapter: Fundamentals, R. Berger, Technische Universität Graz, 2019.
- [43] *Dispersion measurement of inert gases and gas mixtures at 800 nm*, A. Börzsönyi, Z. Heiner, M. P. Kalashnikov et al., *Applied Optics*, Vol. 47, No. 27, pp. 4856-4863, 2008.
- [44] *The Vacuum Technology Book*, Chapter: Einführung in die Vakuumtechnik, Pfeifer Vacuum, 2013.
- [45] [https://www.bronkhorst.com/en-us/service-support/technologies/coriolis-mass-flow-measuring-principle/\(24.06.2020\)](https://www.bronkhorst.com/en-us/service-support/technologies/coriolis-mass-flow-measuring-principle/(24.06.2020)).
- [46] *Instruction Manual of the Controlled Evaporator Mixer*, Bronkhorst (2018).
- [47] <https://www.bronkhorst.com/int/service-support-1/technologies/theory-and-advantages-of-cem-vapour-control> (24.06.2020).

- [48] *Instruction Manual mini CORI-FLOW M1x*, Chapter: Digital Parameters, Bronkhorst (2018).
- [49] *Instruction Manual RS232 Interface*, Chapter: FProPar Protocol Description, Bronkhorst (2018)
- [50] <https://www.nist.gov/srd> (23.06.2020).
- [51] <https://www.mksinst.com/n/gas-correction-factors-for-thermal-based-mass-flow-controllers> (23.06.2020).
- [52] *Nano-Porous Zinc Oxide via Molecular Layer Deposition*, Chapter: Experiments & results, R. Berger, Technische Universität Graz, 2019.
- [53] *Deposition and characterization of coatings by Molecular Layer Deposition*, M. Seiler, Technische Universität Graz, 2020.

CHAPTER 7

LIST OF DEVICES

Dev. no.	Device	Brand	Type
1	Reactor	costum-built by Vacom	-
2	Bubbler	made by TU Graz	-
3	Flowmeter	Bronkhorst	F-201CV-10K-AAD-33-V
4	Flowmeter	Bronkhorst	M13-AAD-33-0-S
5	CEM	Bronkhorst	W-202A-333-K
6	Needle valve	balzers	EVA 025 SX
7	Pressure sensor	MKS Instruments	626C13TDE
8	Pressure control valve	MKS Instruments	253B-2-50-1
9	PID valve controller	MKS Instruments	651CD2S1N
10	Rotary vane pump	Pfeiffer vacuum	DUO 20 M
11	Ellisometer	J. A. Woolam Co.	M-2000V
12	Ellipsometer heating stage	Linkam	THMS600
13	Link Pad System Controller	Linkam	T95-PE
14	Liquid nitrogen cooling pump	Linkam	LNP95

Dev. no.	Device	Brand	Type
15	Microcontroller	Arduino	Uno
16	Humidity sensor	Sparkfun	SHT15
17	Thermofilter	Eheim	Professional 3
18	Adapter	DIGITUS	DA-70156

CHAPTER 8

LIST OF SOFTWARES

Software no.	Application	Software	Company
1	Ellipsometer software	CompleteEASE	J.A. Woollam Co. Inc.
2	Leak rate estimation	LabView v14	National Instruments
3	Humidity sensor control	Matlab R2018a	MathWorks

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CHAPTER 11

ACRONYMS

ALD Atomic Layer Deposition

CEM Controlled Evaporator Mixer

CVD Chemical Vapour Deposition

DEZ Diethyl Zinc

EA Ethanolamine

EG Ethylene Glycol

EMA Effective Medium Approximation

EP Ellispometric Porosimetry

GUI Graphical User Interfaces

ICVD Initiated Chemical Vapour Deposition

IUPAC International Union Of Pure And Applied Chemistry

MA Maleic Anhydrate

MLD Molecular Layer Deposition

PSD Pore Size Distribution

PVD Physical Vapour Deposition

RH Relative Humidity

SE Spectroscopic Ellipsometry

GUI Codes

The following pages contain the codes of both GUIs. The codes were included within the thesis on 17.08.2020. It is possible, that one or both of them have been altered since then to ensure proper calculations and the best possible mode of operation in combination with the EP set-up.

Set-up and Measurement control

```
print('')
print('Opening the porosimeter control tool')
print('Loading required packages...')

from tkinter import *
from tkinter import ttk
import tkinter as tk
import numpy as np
import sys
import time
import os
import propar
import python2_3
import serial
from serial import Serial

#might be necessary later on:
#import cmath as math
#import matplotlib.pyplot as plt

print('done')

print('Starting the GUI.')

Large_Font = ("Verdana", 12)

class PorosimeterGui(tk.Tk):

    #init function is initialized right upon calling the class
    #this might be useful for connecting the flowmeter and so on

    #self is not necessary, but convention
    #*args is short for arguments (=variables passed through)
    #**kwargs is keyword arguments (=passing through dictionaries)

    def __init__(self, *args, **kwargs):
        tk.Tk.__init__(self, *args, **kwargs)
        container = tk.Frame(self)

        container.pack(side="top", fill="both", expand = True)

        container.grid_rowconfigure(0, weight=1)
        container.grid_columnconfigure(0, weight=1)

        self.frames = {}

        for F in (StartPage, PageZero, PageOne, PageTwo, Page3, Page3_a, Page4, Page4_a,
                 Page5, Page6):

            frame = F(container,self)

            self.frames[F] = frame

            frame.grid(row = 0, column = 0, sticky = "nsew")

        self.show_frame(StartPage)
```



```

def show_frame(self, cont):
    frame = self.frames[cont]
    frame.tkraise()

# Import the dictionary (Environmental list)
import ast
with open('dict.py') as f:
    material=ast.literal_eval(f.read())

#Make a list of all pre-defined environments and rewrite it as dictionary
Environments = [d['name'] for d in material if 'name' in d]
choices = {k for k in Environments}
Setpoints_g = []
Setpoints_l = []

#Open, write and close output file - Setpoints
fidn = open("Setpoints.txt","w+")
fidn.write("Setpointlist")
fidn.close()

#Open, write and close output file - Refractive index and thickness of film
fidn = open("thick_and_refractive.txt","w+")
fidn.write("Film thickness /nm \t \t Refractive index")
fidn.close()

#-----
#Here the chamber's volume will be announced or calculated!
#-----

Volume = 6.9 #liter

#-----
#Here the maximal flow rate of the flowmeters is announced!
#-----

#NAME: M13 AAD 33 0 S
maxflow_cori = 50 #g/h

#NAME: F201 CV 10K
maxflow_el = 10 #l/min normed for air
texti= ["The maximum flow of the EL-FLOW is ", maxflow_el, "l/min."]

print('Connecting instruments...')

class Bronkhorst(object):

```

```

#Connecting the Flowmeters via Comports
el_flow = Bronkhorst('COM8', maxflow_el)
cori_flow = Bronkhorst('COM9', maxflow_cori)

#Test run EL-FLOW
print(el_flow.read_serial())
print(el_flow.read_flow('80', maxflow_el))
print(el_flow.read_unit())
print(el_flow.set_control_mode())
print(el_flow.close_valve())
print(el_flow.read_setpoint('80', maxflow_el))
print(el_flow.set_flow('0', '80', maxflow_el))

#Test run Cori-FLOW
print(cori_flow.read_serial())
print(cori_flow.read_flow('80', maxflow_cori))
print(cori_flow.read_unit())
print(cori_flow.set_control_mode())
print(cori_flow.close_valve())
print(cori_flow.read_setpoint('80', maxflow_cori))
print(cori_flow.set_flow('0', '80', maxflow_cori))

print('done')

class StartPage(tk.Frame):

    def __init__(self, parent, controller):
        tk.Frame.__init__(self, parent)
        label = tk.Label(self, text = "Welcome to the Ellipsometric Porosimetry GUI", font
        Large_Font)
        label.pack(pady=10, padx=10)
        self.controller=controller

        button1 = tk.Button(self, text = "Start", command = lambda:
        controller.show_frame(PageZero))
        button1.pack()

#to start CompleteEASE
#os.startfile('C://CompleteEASE/CompleteEASE.exe');

#-----
#Here the chamber is evacuated and the sample will be degassed at a high temperature. This
will take several minutes (15 to 30).
#Meanwhile the first (dynamic) ellipsometric measurement will be done to monitor the
degassing process.

```

```

#When the ellipsometric angles show a constant value an accurate SE scan is taken to obtain
the refractive index!
#The chamber's temperature is set to a certain value (controllable (colder and warmer?), or
just the surrounding temp?).
#Meanwhile the second dynamic ellipsometric measurement will be done to monitor the
temperature setting process.
#-----

```

```

class PageZero(tk.Frame):
    def __init__(self, parent, controller):

        tk.Frame.__init__(self, parent)
        label = tk.Label(self, text = "First ellipsometric measurement", font = Large_Font)
        label.pack(pady=10, padx=10)
        self.controller=controller

        #input refractive index
        label1 = tk.Label(self, text = "Please enter the refractive index measured within
the degassed environment: ")
        label1.pack(pady=10, padx=10)
        PageZero.ref_index0 = tk.Entry(self)
        PageZero.ref_index0.pack(pady=10, padx=10)
        self.controller=controller

        #input film thickness
        label2 = tk.Label(self, text="Please enter the film thickness measured within the
degassed environment in nm: ")
        label2.pack(pady=10, padx=10)
        PageZero.thick0 = tk.Entry(self)
        PageZero.thick0.pack(pady=10, padx=10)

        button1 = tk.Button(self, text = "Continue", command = lambda:
[self.savechoice(PageZero),controller.show_frame(PageOne)])
        button1.pack()

    def savechoice(self, *args):
        if len(PageZero.ref_index0.get()) == 0:
            print("ERROR: Please enter the refractive index within the degassed environmen
Return!")
        elif len(PageZero.thick0.get()) == 0:
            print("ERROR: Please enter the film thickness within the degassed environment
Return!")
        else:
            PageZero.index = PageZero.ref_index0.get()
            print("The measured refractive index is " + PageZero.index + ".")
            PageZero.thick = PageZero.thick0.get()
            print("The measured film thickness is " + PageZero.thick + "nm.")

            fidn = open("thick_and_refractive.txt","a")
            fidn.write("\n" + PageZero.thick + "\t\t" + PageZero.index)
            fidn.close()

```

```

class PageOne(tk.Frame):
    def __init__(self, parent, controller):

        tk.Frame.__init__(self, parent)
        label = tk.Label(self, text = "Choice of environment", font = Large_Font)

```

```

label.pack(pady=10, padx=10)
self.controller=controller

# Create a Tkinter variable
PageOne.tkvar1 = StringVar(self)
PageOne.tkvar2 = StringVar(self)
PageOne.gas = StringVar(parent)
PageOne.liquid = StringVar(parent)

# set the default option for carrier gas and vapor
PageOne.tkvar1.set('Argon')
PageOne.tkvar2.set('Argon')

#Dropdown menu gas
popupMenu1 = OptionMenu(self, PageOne.tkvar1, *choices)
Label(self, text="Choose a gas").pack()
popupMenu1.pack()

#Dropdown menu liquid
popupMenu2 = OptionMenu(self, PageOne.tkvar2, *choices)#, command=grab_and_assign:
Label(self, text="Choose a liquid").pack()
popupMenu2.pack()

button1 = tk.Button(self, text = "Back to the Start", command = lambda:
controller.show_frame(PageZero))
button1.pack()

button2 = tk.Button(self, text = "Continue", command = lambda:
[self.savechoice(PageOne),controller.show_frame(PageTwo)])
button2.pack()

def savechoice(self, *args):
PageOne.gas = PageOne.tkvar1.get()
PageOne.liquid = PageOne.tkvar2.get()
print(PageOne.gas)
print(PageOne.liquid)
fidn = open("Setpoints.txt","a")
fidn.write(("Flow of " + PageOne.gas + " \t \tFlow of " + PageOne.liquid + " \t
\tPartial pressure of " + PageOne.liquid+ " \t \tPercentage of saturation pressure
" + PageOne.liquid))
fidn.close()

class PageTwo(tk.Frame):
def __init__(self, parent, controller):
tk.Frame.__init__(self, parent)
label = tk.Label(self, text = "Temperature evaluation", font = Large_Font)
label.pack(pady=10, padx=10)
self.controller=controller

#input chamber temperature
label2 = tk.Label(self, text="Enter the chamber temperature in °C")
label2.pack(pady=10, padx=10)
PageTwo.Temp_chamber = tk.Entry(self)
PageTwo.Temp_chamber.pack(pady=10, padx=10)

button1 = tk.Button(self, text = "Back to the Start", command = lambda:
controller.show_frame(PageZero))

```

```

button1.pack()

button2 = tk.Button(self, text = "Back to the environment choice", command = lambda
controller.show_frame(PageOne))
button2.pack()

button3 = tk.Button(self, text = "Continue", command = lambda:
[self.savechoice(PageTwo),controller.show_frame(Page3)])
button3.pack()

def savechoice(self, *args):
    if len(PageTwo.Temp_chamber.get()) == 0:
        print("ERROR: Please enter the temperature within the chamber. Return!")
    else:
        PageTwo.Temp = PageTwo.Temp_chamber.get()
        print(PageTwo.Temp + "°C")

class Page3(tk.Frame):
    def __init__(self, parent, controller):
        tk.Frame.__init__(self, parent)
        label = tk.Label(self, text = "Saturation Pressure", font = Large_Font)
        label.pack(pady=10, padx=10)
        self.controller=controller

        #Button to start saturation pressure of both materials
        button0 = tk.Button(self, text = "Calculate Saturation Pressures", command = lambda
[self.SatPressure(Page3), self.ShowSatPressure(Page3)])
        button0.pack()

        #input total pressure
        labell1 = tk.Label(self, text="Please enter the total pressure in the chamber in
mbar:")
        labell1.pack(pady=10, padx=10)
        Page3.p_tot = tk.Entry(self)
        Page3.p_tot.pack(pady=10, padx=10)

        button1 = tk.Button(self, text = "Back to the Start", command = lambda:
controller.show_frame(PageOne))
        button1.pack()

        button2 = tk.Button(self, text = "Back to Temperature evaluation", command = lambda
controller.show_frame(PageTwo))
        button2.pack()

        button3 = tk.Button(self, text = "Continue", command = lambda:
[self.SatPressure(Page3), self.savechoice(Page3), controller.show_frame(Page3_a)])
        button3.pack()

        #Save the input of the total pressure within the chamber
        #and the saturation pressure of the liquid in mbar
        def savechoice(self, *args):
            if len(PageZero.ref_index0.get()) == 0:
                print("ERROR: Please enter the total pressure within the chamber. Return!")
            else:
                Page3.P_tot = Page3.p_tot.get()
                print("The total pressure within the chamber is " + Page3.P_tot + " mbar.")
                Page3.p_s_l = Page3.P_sat_l*1.33322387415

```

```

#Calculation of Antoine equation
def SatPressure(self, *args):
    gas_dic = next((item for item in material if item["name"] == PageOne.gas), None)
    liquid_dic = next((item for item in material if item["name"] == PageOne.liquid), None)

    A_gas1 = float(gas_dic.get("A1"))
    B_gas1 = float(gas_dic.get("B1"))
    C_gas1 = float(gas_dic.get("C1"))
    A_liquid1 = float(liquid_dic.get("A1"))
    B_liquid1 = float(liquid_dic.get("B1"))
    C_liquid1 = float(liquid_dic.get("C1"))
    A_gas2 = float(gas_dic.get("A2"))
    B_gas2 = float(gas_dic.get("B2"))
    C_gas2 = float(gas_dic.get("C2"))
    A_liquid2 = float(liquid_dic.get("A2"))
    B_liquid2 = float(liquid_dic.get("B2"))
    C_liquid2 = float(liquid_dic.get("C2"))

    Gas = PageOne.gas
    Liquid = PageOne.liquid
    Temperature = PageTwo.Temp

    #interval choice for Antoine parameters
    while True:
        if (float(Temperature) <= float(gas_dic.get("T_max1")) and float(Temperature)
            float(gas_dic.get("T_min1"))):
            P_sat_gas = 10**(A_gas1 - B_gas1/(float(PageTwo.Temp) + C_gas1))
            break
        elif (float(Temperature) <= float(gas_dic.get("T_max2")) and float(Temperature)
            >= float(gas_dic.get("T_min2"))):
            P_sat_gas = 10**(A_gas2 - B_gas2/(float(PageTwo.Temp) + C_gas2))
            break
        else:
            P_sat_gas = (10**(A_gas1 - B_gas1/(float(PageTwo.Temp) +
                C_gas1))+10**(A_gas2 - B_gas2/(float(PageTwo.Temp) + C_gas2)))/2
            break

    while True:
        if (float(Temperature) <= float(liquid_dic.get("T_max1")) and float(Temperature)
            >= float(liquid_dic.get("T_min1"))):
            P_sat_liquid = 10**(A_liquid1 - B_liquid1/(float(PageTwo.Temp) + C_liquid1))
            break
        elif (float(Temperature) <= float(liquid_dic.get("T_max2")) and
            float(Temperature) >= float(liquid_dic.get("T_min2"))):
            P_sat_liquid = 10**(A_liquid2 - B_liquid2/(float(PageTwo.Temp) + C_liquid2))
            break
        else:
            P_sat_liquid = (10**(A_liquid1 - B_liquid1/(float(PageTwo.Temp) +
                C_liquid1))+10**(A_liquid2 - B_liquid2/(float(PageTwo.Temp) + C_liquid2)))/2
            break

    #Both values are given in mmHg
    Page3.P_sat_g = P_sat_gas
    Page3.P_sat_l = P_sat_liquid

#Printing of the saturation pressures on the Gui interface

```

```

def ShowSatPressure(self, *args):
    label1 = tk.Label(self, text = "The Saturation Pressure of " + PageOne.gas + " at
+ PageTwo.Temp + "°C is " + str(round(Page3.P_sat_g*1.33322387415,2)) + "mbar.")
    label1.pack(pady=10, padx=10)
    label2 = tk.Label(self, text = "The Saturation Pressure of " + PageOne.liquid + "
" + PageTwo.Temp + "°C is " + str(round(Page3.P_sat_l*1.33322387415,2)) + "mbar.")
    label2.pack(pady=10, padx=10)

#-----
#Here the chamber is flooded with the carrier gas (Helium, Argon, N2, etc.) until a
continuous flow is reached.
#-----

class Page3_a(tk.Frame):
    def __init__(self, parent, controller):
        tk.Frame.__init__(self, parent)
        label = tk.Label(self, text = "Check of the flowmeters", font = Large_Font)
        label.pack(pady=10, padx=10)
        self.controller=controller
        Page3_a.El_opening = 0

        button1 = tk.Button(self, text = "Back to choice of environment", command = lambda:
controller.show_frame(PageOne))
        button1.pack()

        button2 = tk.Button(self, text = "Check flows", command = lambda:
[self.check_gas(Page3_a)])
        button2.pack()

        button3 = tk.Button(self, text = "Close both valves", command = lambda:
[self.close_valves(Page3_a)])
        button3.pack()

        label1 = tk.Label(self, text=texti)
        label1.pack(pady=10, padx=10)

        label2 = tk.Label(self, text="Adjust the valve opening of the EL-FLOW to: %")
        label2.pack(pady=10, padx=10)
        Page3_a.per_el = tk.Entry(self)
        Page3_a.per_el.pack(pady=10, padx=10)

        #button4 = tk.Button(self, text = "Introduce Carrier Gas", command = lambda:
[self.check_gas(Page3_a),self.introduce_carriergas(Page3_a)])
        button4 = tk.Button(self, text = "Introduce Carrier Gas", command = lambda:
[self.introduce_carriergas(Page3_a)])
        button4.pack()

        button5 = tk.Button(self, text = "Continue", command = lambda:
controller.show_frame(Page4))
        button5.pack()

    def check_gas(self, *args):
        #Check whether both flowmeters are set to 0
        #If so: set 100% el_flow for a sufficiently long time

        flow_el = el_flow.read_flow('80', maxflow_el)
        flow_cori = cori_flow.read_flow('80', maxflow_cori)

```

```

if flow_el ==0 and flow_cori == 0:
    print('Everything is ready!')
elif flow_el == 0 and flow_cori >= 50:
    print('Everything is ready!')
elif flow_el != 0:
    print('The EL-FLOW is not switched off!')
    print('Please check it.')
    print('Its current flow is ' + str(flow_el) + '.')
else:
    print('The mini Cori-FLOW is not switched off!')
    print('Please check it.')
    print('Its current flow is ' + str(flow_cori) + '.')

def introduce_carriergas(self, *args):
    gas_dic = next((item for item in material if item["name"] == PageOne.gas), None)
    liquid_dic = next((item for item in material if item["name"] == PageOne.liquid), None)

    factor_liq = float(liquid_dic.get("factor"))
    factor_gas = float(gas_dic.get("factor"))
    rho_liq = float(gas_dic.get("density"))
    rho_gas = float(gas_dic.get("density"))

    if len(Page3_a.per_el.get()) == 0:
        print("ERROR: Please enter the valve opening setpoint!")
    elif Page3_a.El_opening == Page3_a.per_el.get():
        print("ERROR: Please enter another opening setpoint!")
    else:
        Page3_a.El_opening = Page3_a.per_el.get()
        el_flow.set_control_mode()
        el_flow.set_flow(str(float(Page3_a.El_opening)/100*32000), '80', maxflow_el)
        print("The valve opening is set to " + Page3_a.El_opening + "%.")
        print('The flow of the carrier gas should be around ' +
              str(float(Page3_a.El_opening)*maxflow_el/100*factor_gas/1.4) + 'l/min.')

```



```

label2.pack(pady=4, padx=10)
Page4.pp_max = tk.Entry(self)
Page4.pp_max.pack(pady=5, padx=10)

#Entry menu partial pressure step size
label2 = tk.Label(self, text="Enter the number of steps from minimum to maximum:")
label2.pack(pady=4, padx=10)
Page4.pp_step = tk.Entry(self)
Page4.pp_step.pack(pady=5, padx=10)

Page4.Setpointlist_g = []
Page4.Setpointlist_l = []
Page4.fl = []

button0 = tk.Button(self, text = "Show Setpoint", command = lambda:
self.showsetpoint(Page4))
button0.pack()

button = tk.Button(self, text = "Calculate Setpoint", command = lambda:
[self.showsetpoint(Page4), self.calculatesetpoint(Page4)])
button.pack()

button1 = tk.Button(self, text = "Save Setpoint", command = lambda:
[self.showsetpoint(Page4), self.calculatesetpoint(Page4), self.savesetpoint(Page4)])
button1.pack()

button2 = tk.Button(self, text = "Back to the Start", command = lambda:
controller.show_frame(PageZero))
button2.pack()

button3 = tk.Button(self, text = "Back to saturation pressure calculation", commar
= lambda: controller.show_frame(Page3))
button3.pack()

button4 = tk.Button(self, text = "Continue", command = lambda:
[self.reverse_sp(Page4), controller.show_frame(Page4_a)])
button4.pack()

#Here the flow of the adsorptant is calculated based on the wanted partial pressure and the
user is notified.
#In case of approval the values are saved to a list if not an other set of values needs to
be chosen.

def showsetpoint(self, *args):

Page4.PP_max = float(Page4.pp_max.get())
Page4.PP_min = float(Page4.pp_min.get())
Page4.PP_step = float(Page4.pp_step.get())

Page4.Setpoints_pp = []
Page4.Setpoints_pp = Page4.Setpoints_pp + [Page4.PP_min]

for i in range(1, int(Page4.PP_step)+1):
Page4.Setpoints_pp = Page4.Setpoints_pp + [Page4.PP_min +
i*(Page4.PP_max-Page4.PP_min)/Page4.PP_step]

print(Page4.Setpoints_pp)

```

```

def calculatsetpoint(self, *args):
    Page4.PP_max = Page4.pp_max.get()
    Page4.PP_min = Page4.pp_min.get()
    Page4.PP_step = Page4.pp_step.get()

    Liquid = PageOne.liquid
    gas_dic = next((item for item in material if item["name"] == PageOne.gas), None)
    liquid_dic = next((item for item in material if item["name"] == PageOne.liquid), None)
    rho_gas = float(gas_dic.get("density"))
    Page4.rho_liquid = float(liquid_dic.get("density"))
    factor_gas = float(gas_dic.get("factor"))
    factor_liquid = float(liquid_dic.get("factor"))
    molv_gas = float(gas_dic.get("molvol"))
    molm_liquid = float(liquid_dic.get("molmass"))

    Page4.flow_el_max = maxflow_el*factor_gas/1.4 #l/min

#Following the calculation from factorial partial pressure to flow of the vapor
#p_f_l = known [% of the p_sat_l]
#p_p_l = p_f_l/100*p_sat_l [mbar]
#v_p_l = p_p_l/p_tot*100 [%]
#flow_l * corr_l = v_p_l*flow_g*corr_g/(100-v_p_l) [l/min] --> material specific

#Setpoint list of vapor pressure in %
pp_list = Page4.Setpoints_pp

#Setpoint list of vapor pressure in mbar
Page4.PP_list = [u * 0.01*Page3.p_s_l for u in pp_list]

#Setpoint list of volume fraction of the vapor in %
Page4.cv_list = [i / float(Page3.P_tot) for i in Page4.PP_list]

#Setpoint list of the material specific flow of the vapor in g/h
Page4.flow_vapor = []
Page4.flow_gas = float(Page3_a.El_opening)*maxflow_el/100*factor_gas/1.4
for i2 in range(0,len(Page4.cv_list)):
    Page4.flow_vapor = Page4.flow_vapor
    +[Page4.cv_list[i2]*molm_liquid*Page4.flow_gas*60/molv_gas/((float(PageTwo.Ter
73.15)/273.15)/(float(Page3.P_tot)/1000)]

#Open, write and close output file
def savesetpoint(self, *args):
    gas_dic = next((item for item in material if item["name"] == PageOne.gas), None)
    liquid_dic = next((item for item in material if item["name"] == PageOne.liquid), None)
    factor_gas = float(gas_dic.get("factor"))
    factor_liquid = float(liquid_dic.get("factor"))

    fg = float(Page3_a.El_opening)*maxflow_el/100*factor_gas/1.4
    pp = Page4.PP_list
    pf = Page4.Setpoints_pp

    fidn = open("Setpoints.txt","a")
    for i3 in range(0,len(Page4.flow_vapor)):
        fidn.write(("\\n" + str(round(fg,3)) + " l/min \\t \\t" +
str(round(float(Page4.flow_vapor[i3]),3)) + " g/h \\t \\t" + str(round(pp[i3],3)

```

```

    + " mbar \t \t" + str(round(pf[i3],1)) + " %")

fidn.close()

Liquid = PageOne.liquid
liquid_dic = next((item for item in material if item["name"] == PageOne.liquid), 1)
factor_liquid = float(liquid_dic.get("factor"))

#Create list for flowmeters
for i4 in range(0,len(Page4.flow_vapor)):
    Page4.Setpointlist_g = Page4.Setpointlist_g + [Page4.flow_gas]
    Page4.Setpointlist_l = Page4.Setpointlist_l + [Page4.flow_vapor[i4]]
# for i5 in range(0,len(Page4.Setpointlist_l)):

def reverse_sp(self, *args):
    f = open("Setpoints.txt", "r")
    lines = f.readlines()
    f.close()
    f = open("Setpoints.txt", "a")
    f.write("\n")
    lines.reverse()
    f.writelines([item for item in lines[1:-2]])
    f.close()

#List for flowmeters
rev_g = list(reversed(Page4.Setpointlist_g))
Page4.Setpointlist_g = Page4.Setpointlist_g + rev_g[1:]
#Page4.Setpointlist_g = Page4.Setpointlist_g[1:-1]
rev_l = list(reversed(Page4.Setpointlist_l))
Page4.Setpointlist_l = Page4.Setpointlist_l + rev_l[1:]
#Page4.Setpointlist_l = Page4.Setpointlist_l[1:-1]

class Page4_a(tk.Frame):
    def __init__(self, parent, controller):
        tk.Frame.__init__(self, parent)
        label = tk.Label(self, text = "Number of Cycles", font = Large_Font)
        label.pack(pady=1, padx=10)
        self.controller=controller

        #Entry menu partial pressure min
        labell = tk.Label(self, text="How many cycles should be done of the Setpoint list")
        labell.pack(pady=2, padx=10)
        Page4_a.cycle = tk.Entry(self)
        Page4_a.cycle.pack(pady=3, padx=10)

        button1 = tk.Button(self, text = "Back to the Start", command = lambda:
        controller.show_frame(PageZero))
        button1.pack()

        button2 = tk.Button(self, text = "Back to saturation pressure calculation", commar
        = lambda: controller.show_frame(Page3))
        button2.pack()

        button3 = tk.Button(self, text = "Continue", command = lambda:
        [self.cycles(Page4_a), controller.show_frame(Page5)])
        button3.pack()

```

```

def cycles(self, *args):

    Page4_a.Cycle = int(Page4_a.cycle.get())

    #List for flowmeters
    Page4.Setpointlist_g = Page4.Setpointlist_g*Page4_a.Cycle
    Page4.Setpointlist_l = Page4.Setpointlist_l*Page4_a.Cycle

#-----
#Here the proper script is opened to set the flow rate setpoints.
#Besides the time span (?) inbetween the setpoints needs to be included here.
#-----

#-----
#Then it will be sent to the flowmeters one by one and right after each change a dynamic
ellipsometric scan is done.
#After the ellipsometric angles stabilize following the change of composition, a SE scan :
done to evaluate the refractive index and thickness of the film.
#Then the next setpoint will be sent to the flowmeters.
#After reaching the saturation pressure, desorption starts by applying the setpoints in
reverse order.
#-----

class Page5(tk.Frame):
    def __init__(self, parent, controller):
        tk.Frame.__init__(self, parent)
        label = tk.Label(self, text = "Setting the setpoints", font = Large_Font)
        label.pack(pady=10, padx=10)
        self.controller=controller

        Page5.ref_index = StringVar(self)
        Page5.thickness = StringVar(self)
        Page5.list_index = 0

        button = tk.Button(self, text = "Check the current Setpoint", command = lambda:
[self.checksetpoint(Page5)])
        button.pack()

        button1 = tk.Button(self, text = "Set next Setpoint", command = lambda:
[self.setsetpoint(Page5)])
        button1.pack()

        #Entry menu refractive index
        label1 = tk.Label(self, text="Enter the refractive index of the film:")
        label1.pack(pady=2, padx=10)
        Page5.ref_index = tk.Entry(self)
        Page5.ref_index.pack(pady=3, padx=10)

        #Entry menu film thickness
        label2 = tk.Label(self, text="Enter the film thickness in nm:")
        label2.pack(pady=4, padx=10)
        Page5.thickness = tk.Entry(self)
        Page5.thickness.pack(pady=5, padx=10)

        button2 = tk.Button(self, text = "Save refractive index and thickness", command =
lambda: [self.savesetpoint(Page5)])

```

```

button2.pack()

button3 = tk.Button(self, text = "Back to the Start", command = lambda:
controller.show_frame(PageZero))
button3.pack()

button4 = tk.Button(self, text = "Continue", command = lambda:
[controller.show_frame(Page6)])
button4.pack()

#Open, write and close output file
def savesetpoint(self, *args):
    Page5.ref = Page5.ref_index.get()
    Page5.thick = Page5.thickness.get()

    fidn = open("thick_and_refractive.txt","a")
    fidn.write("\n" + Page5.thick + "\t\t" + Page5.ref)
    fidn.close()

#Check the flow rate of both flowmeters
#Print them in the console
def checksetpoint(self, *args):
    flow_el = el_flow.read_flow('80', maxflow_el)
    flow_cori = cori_flow.read_flow('80', maxflow_cori)
    setp_el = el_flow.read_setpoint('80', maxflow_el)
    setp_cori = cori_flow.read_setpoint('80', maxflow_cori)
    print('The current flow of the EL-FLOW is ' + str(flow_el) + '.')
    print('Its current flow of the mini Cori-FLOW is ' + str(flow_cori) + '.')
    print('The latest setpoint sent to the EL-FLOW is ' + str(setp_el) + '.')
    print('Its latest setpoint sent to the mini Cori-FLOW is ' + str(setp_cori) + '.')

#Select new setpoint and set to flowmeters to it
#if the last set setpoint is reached, the vapor input is set to 0
#and the carrier gas flow to 100% for the last measurement
def setsetpoint(self, *args):

    if Page5.list_index <= ((len(Page4.Setpointlist_g))-1):
        fl_el = str(float(Page3_a.El_opening)/100*32000)
        fl_cori =
        str(round(float(Page4.Setpointlist_l[Page5.list_index])/maxflow_cori*32000))
        el_flow.set_flow(fl_el, '80', maxflow_el)
        cori_flow.set_control_mode()
        cori_flow.set_flow(fl_cori, '80', maxflow_cori)
        print('The flow of the vapor is now set to ' +
        str(Page4.Setpointlist_l[Page5.list_index]) + 'g/h.')
        Page5.list_index += 1
    else:
        cori_flow.set_flow(0, '80', maxflow_cori)
        print('The flow of the vapor is now set to 0%.')
        el_flow.set_flow(32000, '80', maxflow_el)
        print('The flow of the carrier gas is now set to 100%.')
        print('End of setpoints is reached. Have fun postprocessing the data!')

#The following page does nothing for now.
#It might be used to plot the refractive index and thickness datapoints!
class Page6(tk.Frame):
    def __init__(self, parent, controller):

```

```
tk.Frame.__init__(self, parent)
label = tk.Label(self, text = "Nothing to see here - go back or do the
postprocessing!", font = Large_Font)
label.pack(pady=10, padx=10)
self.controller=controller

app = PorosimeterGui()
app.title("Porosimeter Gui")
app.mainloop()
```

Calculation and evaluation

```
print('')
print('Opening the porosimeter control tool')
print('Loading required packages...')

from tkinter import *
from tkinter import ttk
import tkinter as tk
import numpy as np
import sys
import time
import os
import propar
import python2_3

#might be necessary later on:
import cmath as math
import matplotlib.pyplot as plt

print('done')
print('Starting the GUI.')

Large_Font = ("Verdana", 12)

class PorosimeterEvalGui(tk.Tk):

    #init function is initialized right upon calling the class
    #this might be useful for connecting the flowmeter and so on

    #self is not necessary, but convention
    #*args is short for arguments (=variables passed through)
    #**kwargs is keyword arguments (=passing through dictionaries)

    def __init__(self, *args, **kwargs):
        tk.Tk.__init__(self, *args, **kwargs)
        container = tk.Frame(self)
        container.pack(side="top", fill="both", expand = True)
        container.grid_rowconfigure(0, weight=1)
        container.grid_columnconfigure(0, weight=1)

        self.frames = {}

        for F in (P0, P1, P2, P3, P4, P5, P2a, P2b):#, P6, P7, P8, P9, P10):
            frame = F(container,self)
            self.frames[F] = frame
            frame.grid(row = 0, column = 0, sticky = "nsew")

        self.show_frame(P0)

    def show_frame(self, cont):
        frame = self.frames[cont]
        frame.tkraise()

choices = {'t', 'n', 'P', 'r', 'p_{par}/p_{sat}', 'V_{ads}/V', 'dV_{ads}/dr'}

#Open, write and close output file - Setpoints
fidn = open("Setpoints_n_t.txt","w+")
```

```
fidn.write("Setpointlist")
fidn.close()
```

```
class P0(tk.Frame):
```

```
    def __init__(self, parent, controller):
```

```
        tk.Frame.__init__(self, parent)
```

```
        label = tk.Label(self, text = "Welcome to the Ellipsometric Porosimetry Result  
Evaluation", font = Large_Font)
```

```
        label.pack(pady=10, padx=10)
```

```
        self.controller=controller
```

```
        button1 = tk.Button(self, text = "Start", command = lambda: controller.show_frame(P1))
        button1.pack()
```

```
#-----
```

```
#Here the setpoints p/p_sat (%), the thickness t(nm) and the refractive index n (-) are  
entered one after another.
```

```
#-----
```

```
class P1(tk.Frame):
```

```
    def __init__(self, parent, controller):
```

```
        tk.Frame.__init__(self, parent)
```

```
        label = tk.Label(self, text = "The measured data at every setpoint", font =  
Large_Font)
```

```
        label.pack(pady=10, padx=10)
```

```
        self.controller=controller
```

```
        P1.Setpoints_1 = []
```

```
        P1.Setpoints_2 = []
```

```
        P1.Setpoints_3 = []
```

```
        #input refractive index
```

```
        label1 = tk.Label(self, text = "Please enter the setpoint p/p_sat in %: ")
```

```
        label1.pack(pady=10, padx=10)
```

```
        P1.SP = tk.Entry(self)
```

```
        P1.SP.pack(pady=1, padx=10)
```

```
        #input film thickness
```

```
        label2 = tk.Label(self, text="Please enter the film thickness in nm: ")
```

```
        label2.pack(pady=10, padx=10)
```

```
        P1.t = tk.Entry(self)
```

```
        P1.t.pack(pady=1, padx=10)
```

```
        #input refractive index
```

```
        label3 = tk.Label(self, text = "Please enter the refractive index: ")
```

```
        label3.pack(pady=10, padx=10)
```

```
        P1.n = tk.Entry(self)
```

```
        P1.n.pack(pady=1, padx=10)
```

```
        button1 = tk.Button(self, text = "Add new setpoint", command = lambda:
```

```
        [self.savechoice(P1)])
```

```
        button1.pack(pady=2, padx=5)
```

```
        button2 = tk.Button(self, text = "Saved last setpoint", command = lambda:
```

```
        [controller.show_frame(P2)])
```



```

button2.pack(pady=2, padx=15)

def savechoice(self, *args):
    if len(P1.n.get()) == 0:
        print("ERROR: Please enter a new refractive index. Return!")
    elif len(P1.SP.get()) == 0:
        print("ERROR: Please enter a new Setpoint. Return!")
    elif len(P1.t.get()) == 0:
        print("ERROR: Please enter a new film thickness Return!")
    else:
        P1.setpoint = float(P1.SP.get())
        P1.thickness = float(P1.t.get())
        P1.index = float(P1.n.get())
        print(str(P1.setpoint) + "% \t" + str(P1.thickness) + "nm \t" + str(P1.index))
        P1.Setpoints_1 = P1.Setpoints_1 + [P1.setpoint]
        P1.Setpoints_2 = P1.Setpoints_2 + [P1.thickness]
        P1.Setpoints_3 = P1.Setpoints_3 + [P1.index]

fidn = open("Setpoints_n_t.txt","a")
fidn.write("\n" + str(P1.setpoint) + "% \t" + str(P1.thickness) + "nm \t" +
str(P1.index))
fidn.close()

#-----
#Here the setpoints are checked and can be adjusted if necessary. Additionally t and n are
plotted vs. p/p_sat.
#-----

class P2(tk.Frame):
    def __init__(self, parent, controller):

        tk.Frame.__init__(self, parent)
        label = tk.Label(self, text = "Please check the list of setpoint you've just
entered.", font = Large_Font)
        label.pack(pady=10, padx=10)
        self.controller=controller

        P2.lists=[]

        button0 = tk.Button(self, text = "Show the list", command = lambda:
[self.show_list(P2)])
        button0.pack()

        button1 = tk.Button(self, text = "Change an entry line", command = lambda:
[controller.show_frame(P2a)])
        button1.pack()

        button2 = tk.Button(self, text = "Add an entry line", command = lambda:
[controller.show_frame(P2b)])
        button2.pack()

        button3 = tk.Button(self, text = "Plot t vs. p/p_sat", command = lambda:
[self.plot_t_vs_p(P2)])
        button3.pack()

        button4 = tk.Button(self, text = "Plot n vs. p/p_sat", command = lambda:
[self.plot_n_vs_p(P2)])

```

```

button4.pack()

button5 = tk.Button(self, text = "Everything is correct and done.", command =
lambda: [controller.show_frame(P3)])
button5.pack()

def show_list(self, *args):
    window = tk.Toplevel()
    label = tk.Label(window, text="List of Setpoints")
    label.pack()
    P2.lists=[]
    for i in range(0,len(P1.Setpoints_1)):
        P2.lists = P2.lists +[(str(i)+' '+str(P1.Setpoints_1[i])+"%
"+str(P1.Setpoints_2[i])+"nm "+str(P1.Setpoints_3[i]))]
    lb=Listbox(window, selectmode='multiple')
    lb.delete(0,END)
    for num in P2.lists:
        lb.insert(END,num)
    lb.pack()

def plot_t_vs_p(self, *args):
    plt.figure(1)
    plt.plot(P1.Setpoints_1,P1.Setpoints_2)
    plt.xlabel('$p_{par}/p_{sat}$ [%]')
    plt.ylabel('film thickness t [nm]')
    plt.grid(True)
    plt.savefig('t_vs_pp.png')

def plot_n_vs_p(self, *args):
    plt.figure(2)
    plt.plot(P1.Setpoints_1,P1.Setpoints_3)
    plt.xlabel('$p_{par}/p_{sat}$ [%]')
    plt.ylabel('refractive index n [-]')
    plt.grid(True)
    plt.savefig('n_vs_pp.png')

#-----
#Here the porosity is calculated for each setpoint and plotted vs. p/p_sat.
#-----

class P3(tk.Frame):
    def __init__(self, parent, controller):

        tk.Frame.__init__(self, parent)
        label = tk.Label(self, text = "Calculation of the films porosity.", font = Large_I
label.pack(pady=10, padx=10)
        self.controller=controller

        P3.Por=[]
        P3.printpor=[]

        #input n_0
        label1 = tk.Label(self, text="Please enter the refractive index of the sample
measured within the degassed environment: ")
        label1.pack(pady=10, padx=10)
        P3.n0 = tk.Entry(self)
        P3.n0.pack(pady=10, padx=10)

```

```


label2 = tk.Label(self, text = "Please enter the 'normal' refractive index of your adsorbate: ")
label2.pack(pady=10, padx=10)
P3.n_ads = tk.Entry(self)
P3.n_ads.pack(pady=10, padx=10)

button1 = tk.Button(self, text = "Calculate and plot the film's porosity.", command = lambda: [self.calculate_and_plot_Porosity(P3)])
button1.pack()

button2 = tk.Button(self, text = "Continue.", command = lambda: [controller.show_frame(P4)])
button2.pack()

def calculate_and_plot_Porosity(self, *args):

    for i in range(0, len(P1.Setpoints_3)):
        Por =
            (((float(P1.Setpoints_3[i])**2-1)/(float(P1.Setpoints_3[i])**2+2))-((float(P3.setpoint.get())**2-1)/(float(P3.n0.get())**2+2)))/((float(P3.n_ads.get())**2-1)/(float(P3.n0.get())**2+2))
        P3.printpor= P3.printpor + [Por*100]
        P3.Por= P3.Por + [Por]

    plt.figure(3)
    plt.plot(P1.Setpoints_1, P3.printpor)
    plt.xlabel('$p_{par}/p_{sat}$ [%]')
    plt.ylabel('$V_{ads}/V_{sat}$ [%]')
    plt.grid(True)
    plt.savefig('Por_vs_pp.png')

#-----
#Here the pore size distribution for each setpoint is calculated and plotted vs. p/p_sat.
#Additionally the porosity is plotted over the pore size distribution.
#-----

class P4(tk.Frame):
    def __init__(self, parent, controller):

        tk.Frame.__init__(self, parent)
        label = tk.Label(self, text = "Calculation of the pore size distribution.", font = Large_Font)
        label.pack(pady=10, padx=10)
        self.controller=controller

        P4.radii=[]
        P4.dVdr=[]


label1 = tk.Label(self, text="Please enter the surface tension of the adsorbate in N/m: ")
label1.pack(pady=10, padx=10)
P4.gamma = tk.Entry(self)
P4.gamma.pack(pady=10, padx=10)

```

```


label2 = tk.Label(self, text = "Please enter the molar volume of your adsorbate in
m^3/mol: ")
label2.pack(pady=10, padx=10)
P4.Vm = tk.Entry(self)
P4.Vm.pack(pady=10, padx=10)


label3 = tk.Label(self, text = "Please enter the temperature, at which your
measurement took place in K: ")
label3.pack(pady=10, padx=10)
P4.Tm = tk.Entry(self)
P4.Tm.pack(pady=10, padx=10)

button1 = tk.Button(self, text = "Calculate and plot the film's pore size
distribution.", command = lambda: [self.calculate_and_plot_radII(P4)])
button1.pack()

button2 = tk.Button(self, text = "Continue.", command = lambda:
[controller.show_frame(P5)])
button2.pack()

def calculate_and_plot_radII(self, *args):

for i in range(0, len(P1.Setpoints_3)):
if float(P1.Setpoints_1[i]) > 0:
r =
float(P4.gamma.get())*float(P4.Vm.get())/(8.314)/float(P4.Tm.get())/math.l
float(P1.Setpoints_1[i])/100)
r=abs(r.real)*1000000000
P4.radII= P4.radII + [r]
else:
r = 0
P4.radII= P4.radII + [r]

P4.dVdr = P4.dVdr + [float(P3.Por[0])/float(P3.Por[len(P3.Por)-1])]
for i2 in range(1, len(P3.Por)):
l2 = abs((float(P3.Por[i2])-float(P3.Por[i2-1]))/float(P3.Por[len(P3.Por)-1]))
P4.dVdr= P4.dVdr + [l2]

plt.figure(4)
plt.plot(P1.Setpoints_1, P4.radII)
plt.xlabel('$p_{par}/p_{sat}$ [%]')
#plt.xlim(0, len(P1.Setpoints_1))
plt.ylabel('pore size distribution r [nm]')
plt.grid(True)
plt.savefig('radII_vs_pp.png')
print('setpoint')
print(P1.Setpoints_1)
print('radII')
print(P4.radII)

#-----
#Here additional plots can be done and saved.
#-----

class P5(tk.Frame):

```

```

def __init__(self, parent, controller):

    tk.Frame.__init__(self, parent)
    label = tk.Label(self, text = "Creation of additional plots.", font = Large_Font)
    label.pack(pady=10, padx=10)
    self.controller=controller

    # Create a Tkinter variable
    P5.x = StringVar(self)
    P5.y = StringVar(self)
    P5.X = []
    P5.Y = []
    P5.Xlabel = []
    P5.Ylabel = []
    P5.count = 5

    # set the default option for carrier gas and vapor
    P5.x.set('$p_{par}/p_{sat}$')
    P5.y.set('t')

    #Dropdown menu x-axis
    popupMenu1 = OptionMenu(self, P5.x, *choices)
    Label(self, text="x= ").pack()
    popupMenu1.pack()

    #Dropdown menu y-axis
    popupMenu2 = OptionMenu(self, P5.y, *choices)
    Label(self, text="y= ").pack()
    popupMenu2.pack()

    #x-axis in log?
    P5.xlog = IntVar()
    cb = Checkbutton(self, text="X-axis in log", variable=P5.xlog)
    cb.pack()

    #y-axis in log?
    P5.ylog = IntVar()
    cb2 = Checkbutton(self, text="Y-axis in log", variable=P5.ylog)
    cb2.pack()

    button1 = tk.Button(self, text = "Plot it.", command = lambda: [self.plotting(P5)])
    button1.pack()
    label2 = tk.Label(self, text = "Please rename your plots right away. Otherwise the
will be overwritten.", font = Large_Font)
    label2.pack(pady=10, padx=10)

def plotting(self, *args):
    P5.xvar = P5.x.get()
    P5.yvar = P5.y.get()
    P5.xlog_yes = P5.xlog.get()
    P5.ylog_yes = P5.ylog.get()
    print(P5.xlog_yes)
    print(P5.ylog_yes)

    if P5.xvar == 'r':
        P5.X = P4.radii

```

```

    P5.Xlabel = 'maximum radius of water adsorbing pores r [nm]'
elif P5.xvar == 't':
    P5.X = P1.Setpoints_2
    P5.Xlabel = 'thickness t [nm]'
elif P5.xvar == 'dV_{ads}/dr':
    P5.X = P4.dVdr
    P5.Xlabel = 'pore size distribution $dV_{ads}/dr$ [%]'
elif P5.xvar == 'n':
    P5.X = P1.Setpoints_3
    P5.Xlabel = 'refractive index n [-]'
elif P5.xvar == 'V_{ads}/V':
    P5.X = P3.printpor
    P5.Xlabel = 'Volume of water within the sample $V_{ads}/V$ [%]'
else:
    P5.X = P1.Setpoints_1
    P5.Xlabel = '$p_{par}/p_{sat}$ [%]'

if P5.yvar == 'r':
    P5.Y = P4.radii
    P5.Ylabel = 'maximum radius of water adsorbing pores r [nm]'
elif P5.yvar == 't':
    P5.Y = P1.Setpoints_2
    P5.Ylabel = 'thickness t [nm]'
elif P5.yvar == 'dV_{ads}/dr':
    P5.Y = P4.dVdr
    P5.Ylabel = 'pore size distribution $dV_{ads}/dr$ [%]'
elif P5.yvar == 'n':
    P5.Y = P1.Setpoints_3
    P5.Ylabel = 'refractive index n [-]'
elif P5.yvar == 'V_{ads}/V':
    P5.Y = P3.printpor
    P5.Ylabel = 'Volume of water within the sample $V_{ads}/V$ [%]'
else:
    P5.Y = P1.Setpoints_1
    P5.Ylabel = '$p_{par}/p_{sat}$ [%]'

plt.figure(P5.count)
plt.plot(P5.X,P5.Y)
plt.xlabel(P5.Xlabel)
plt.ylabel(P5.Ylabel)
plt.grid(True)
plt.savefig('Please_rename')
if P5.xlog_yes != 0:
    plt.semilogx()
if P5.ylog_yes != 0:
    plt.semilogy()

P5.count += 1

#-----
#Here certain setpoints can be changed.
#-----

class P2a(tk.Frame):
    def __init__(self, parent, controller):
        tk.Frame.__init__(self, parent)
        label = tk.Label(self, text = "Change of lines.", font = Large_Font)

```

```

label.pack(pady=10, padx=10)
self.controller=controller

#input line number
label1 = tk.Label(self, text = "Which line of the setpoint list should be changed")
label1.pack(pady=10, padx=10)
P2a.line = tk.Entry(self)
P2a.line.pack(pady=10, padx=10)

#input p/p_sat
label2 = tk.Label(self, text = "Please re-enter the setpoint p/p_sat in %: ")
label2.pack(pady=10, padx=10)
P2a.p_psat = tk.Entry(self)
P2a.p_psat.pack(pady=10, padx=10)

#input n_ads
label3 = tk.Label(self, text = "Please re-enter the film thickness in nm: ")
label3.pack(pady=10, padx=10)
P2a.t = tk.Entry(self)
P2a.t.pack(pady=10, padx=10)

#input n_ads
label4 = tk.Label(self, text = "Please re-enter the refractive index: ")
label4.pack(pady=10, padx=10)
P2a.n = tk.Entry(self)
P2a.n.pack(pady=10, padx=10)

button1 = tk.Button(self, text = "Change the entry line.", command = lambda:
[self.yes_change(P2a)])
button1.pack()

button2 = tk.Button(self, text = "All wrong entries have been corrected.", command =
lambda: [controller.show_frame(P2)])
button2.pack()

def yes_change(self, *args):
    P2a.setpoint = float(P2a.p_psat.get())
    P2a.thickness = float(P2a.t.get())
    P2a.index = float(P2a.n.get())

    P1.Setpoints_1[int(P2a.line.get())] = P2a.setpoint
    P1.Setpoints_2[int(P2a.line.get())] = P2a.thickness
    P1.Setpoints_3[int(P2a.line.get())] = P2a.index

#-----
#Here setpoints can be added to the list.
#-----

class P2b(tk.Frame):
    def __init__(self, parent, controller):
        tk.Frame.__init__(self, parent)
        label = tk.Label(self, text = "Additional lines.", font = Large_Font)
        label.pack(pady=10, padx=10)
        self.controller=controller

        P2b.SP1=[]
        P2b.SP2=[]

```

```

P2b.SP3=[]

label1 = tk.Label(self, text = "Between which lines of the setpoint list is a
setpoint missing?")
label1.pack(pady=10, padx=10)
P2b.line1 = tk.Entry(self)
P2b.line1.pack(pady=10, padx=10)
P2b.line2 = tk.Entry(self)
P2b.line2.pack(pady=10, padx=20)

#input p/p_sat
label2 = tk.Label(self, text = "Please enter the setpoint p/p_sat in %: ")
label2.pack(pady=10, padx=10)
P2b.p_psat = tk.Entry(self)
P2b.p_psat.pack(pady=10, padx=10)

#input n_ads
label3 = tk.Label(self, text = "Please enter the film thickness in nm: ")
label3.pack(pady=10, padx=10)
P2b.t = tk.Entry(self)
P2b.t.pack(pady=10, padx=10)

#input n_ads
label4 = tk.Label(self, text = "Please enter the refractive index: ")
label4.pack(pady=10, padx=10)
P2b.n = tk.Entry(self)
P2b.n.pack(pady=10, padx=10)

button1 = tk.Button(self, text = "Add an entry line", command = lambda:
[self.yes_add(P2b)])
button1.pack()

button2 = tk.Button(self, text = "All missing entries have been added.", command =
lambda: [controller.show_frame(P2)])
button2.pack()

def yes_add(self, *args):

    P2b.SP1=P1.Setpoints_1
    P2b.SP2=P1.Setpoints_2
    P2b.SP3=P1.Setpoints_3
    P2b.SP1=P2b.SP1+[0]
    P2b.SP2=P2b.SP2+[0]
    P2b.SP3=P2b.SP3+[0]

    for i in range(int(P2b.line2.get()),len(P1.Setpoints_3)):
        P2b.SP1[i+1]=P1.Setpoints_1[i]
        P2b.SP2[i+1]=P1.Setpoints_2[i]
        P2b.SP3[i+1]=P1.Setpoints_3[i]

    P2b.setpoint = float(P2b.p_psat.get())
    P2b.thickness = float(P2b.t.get())
    P2b.index = float(P2b.n.get())
    P1.Setpoints_1 = P2b.SP1
    P1.Setpoints_2 = P2b.SP2
    P1.Setpoints_3 = P2b.SP3
    P1.Setpoints_1[int(P2b.line2.get())] = P2b.setpoint

```



```
P1.Setpoints_2[int(P2b.line2.get())] = P2b.thickness
P1.Setpoints_3[int(P2b.line2.get())] = P2b.index

app = PorosimeterEvalGui()
app.title("Porosimeter Evaluation Gui")
app.mainloop()
```